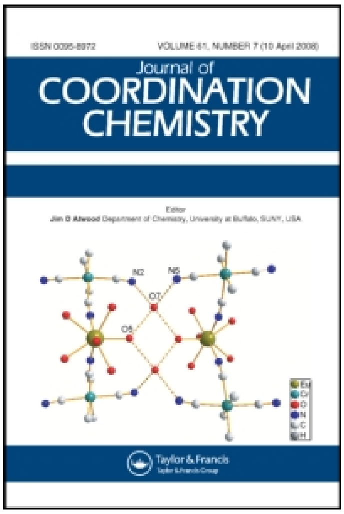

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Synthesis, spectroscopic characterization and x-ray studies of new complexes of organotin(IV) chlorides with N-alkylated 2-amino-1-cyclopentene-1-carbodithioic acids

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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND X-RAY STUDIES OF NEW COMPLEXES OF ORGANOTIN(IV) CHLORIDES WITH N-ALKYLATED 2-AMINO-1-CYCLOPENTENE-1-CARBODITHIOIC ACIDS

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The new complexes [$Ph_2SnCl(BuACDA)$] (**1**), [$Ph_3Sn(BuACDA)$] (**2**), [$Bu_2Sn(BuACDA)_2$] (**3**), [$Ph_2SnCl(EtACDA)$] (**4**), [$Ph_3Sn(EtACDA)$] (**5**) and [$Bu_2Sn(EtACDA)_2$] (**6**) have been prepared from reactions between 2-*N*-butylamino-1-cyclopentene-1-carbodithioic acid (BuACDA) or 2-*N*-ethylamino-1-cyclopentene-1-carbodithioic acid (EtACDA) and Ph_2SnCl_2, Ph_3SnCl or Bu_2SnCl_2. The ^{1}H NMR, ^{119}Sn NMR, UV-Vis and IR data and the elemental analyses support the structures of these organotin compounds. In all these complexes, the S–H proton has been removed and coordination takes place through the carbodithioate group. The ^{119}Sn NMR data are consistent with the presence of five-coordinated tin(IV) in solution. Structures of **1** and **3** have also been confirmed by single crystal X-ray crystallography.The crystals of both are triclinic with space group $P\bar{1}$. In the structure of **1**, the tin environment is distorted trigonal bipyramidal with the Cl and one of the sulfur atoms in apical positions. In the structure of **3** the overall geometry at tin is highly distorted trans octahedral with the four S atoms on the equatorial plane. In both complexes, the ligand is asymmetrically chelated to the tin and there is an intramolecular hydrogen bond between the sulfur and the proton of the amine group.

Keywords: Organotin; Carbodithioate complexes; X-ray crystallography

INTRODUCTION

Owing to the widespread applications of organotin(IV) complexes, the synthesis, characterization and biological properties of many of these compounds have been investigated in recent years [1–4]. Since organotin compounds have antifungal activity, recent interesting work has introduced variations in the ligand groups which are themselves bioactive. Of particular interest among these are certain complexes

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of potentially chelating dithioanionic ligands. Increasing industrial use of organotin compounds containing an Sn–S bond, especially as stabilizers of polyvinyl chlorides, and recognition of the importance of this bond for the biological properties of organotin compounds [5–7], have together spurred study of thiolates of tin [8–15]. The antifungal activity of 2-amino-1-cyclopentene-1-carbodithioic acid (ACDA) and its derivatives [16], provided impetus to synthesize organotin(IV) complexes of *N*-alkylated ACDA (RACDA) and investigate the structural features and bonding with tin. This work is a further step toward the design of a sulfur–nitrogen ligand with suitable competing reactive centers. The results of these studies are reported herein.

EXPERIMENTAL

Materials and Methods

All chemicals and solvents were purchased from Merck Chemical Company. 2-*N*-Butylamino-1-cyclopentene-1-carbodithioic acid (BuACDA) and 2-*N*-ethylamino-1-cyclopentene-1-carbodithioic acid (EtACDA) were prepared by literature methods [17,18]. UV-Vis spectra of the ligands and complexes were recorded on a Jasco model 7850 spectrophotometer. IR spectra were obtained using a Shimadzu 470 spectrophotometer in the 4000–400 cm^{-1} and KBr discs. ^1H NMR spectra were recorded on a Bruker Advance DPX-250 (250.130 MHz) spectrometer and a Varian VXR-300 (299.948 MHz) spectrometer. The proton decoupled ^{119}Sn NMR spectra were obtained on Bruker Advance DPX-500 (186.496 MHz) spectrometer and a Varian VXR-300 (111.854 MHz) spectrometer. Mass spectra were obtained on a HP59-89A spectrometer equipped for electrospray ionization. The C, H and N analyses were performed by the microanalytical service of N.I.O.C Research Institute of Petroleum Industry. Melting points were measured on a Mettler FP5 apparatus.

Syntheses of Complexes

[$Ph_2SnCl(BuACDA)$] (***1***) BuACDA (1.08 g, 5 mmol) was dissolved in warm methanol and slowly added to a methanolic solution of Ph_2SnCl_2 (1.72 g, 5 mmol). A yellow crystalline precipitate was formed gradually. The product was isolated and washed with methanol. Yield 60%, M.p. 170°C (dec.). λ_{max}(nm) (CH_2Cl_2): 325, 396 (log ε 3.77, 4.54). *Anal.* Calcd. for $C_{22}H_{26}ClNS_2Sn$(%): C, 50.5; H, 5.0; N, 2.7. Found: C, 51.0; H, 4.9; N, 3.0.

[$Ph_3Sn(BuACDA)$] (***2***) Complex **2** was prepared as **1** with Ph_3SnCl (1.93 g, 5 mmol) and BuACDA (1.08 g, 5 mmol). Yield 50%, M.p. 152°C (dec.). λ_{max}(nm) (CH_2Cl_2): 324, 400 (log ε 3.97, 4.52). *Anal.* Calcd. for $C_{28}H_{31}NS_2Sn$(%): C, 59.5; H, 5.5; N, 2.5. Found: C, 59.5; H, 5.6; N, 2.5.

[$Bu_2Sn(BuACDA)_2$] (***3***) To a methanolic solution of Bu_2SnCl_2 (1.52 g, 5 mmol) was added $AgNO_3$ (1.70 g, 10 mmol). The mixture was stirred for 1 h at room temperature and then AgCl was filtered. To the filtrate, a solution of BuACDA (2.16 g, 10 mmol) in methanol was added dropwise. A yellow precipitate formed immediately, was isolated and washed with methanol. Yield 55%, M.p. 220°C (dec.). λ_{max}(nm) (CH_2Cl_2): 335, 405

(log ε 4.20, 4.89). *Anal.* Calcd. for $C_{28}H_{50}N_2S_4Sn$ (%): C, 50.8; H, 7.6; N, 4.2. Found: C, 51.0; H, 7.6; N, 4.1.

[$Ph_2SnCl(EtACDA)$] (**4**) Complex **4** was prepared as **1** with Ph_2SnCl_2 (1.72 g, 5 mmol) and EtACDA (0.935 g, 5 mmol). Yield 85%, M.p. 210°C (dec.). λ_{max}(nm) (CH_2Cl_2): 326, 396 (log ε 3.81, 4.59). *Anal.* Calcd. for $C_{20}H_{22}ClNS_2Sn$ (%): C, 48.5; H, 4.4; N, 2.8. Found: C, 48.7; H, 4.5; N, 2.8.

[$Ph_3Sn(EtACDA)$] (**5**) Complex **5** was prepared as **1** with Ph_3SnCl (1.93 g, 5 mmol) and EtACDA (0.935 g, 5 mmol). Yield 55%, M.p. 205°C (dec.). λ_{max}(nm) (CH_2Cl_2): 325, 400 (log ε 4.14, 4.63). *Anal.* Calcd. for $C_{26}H_{27}NS_2Sn$ (%): C, 58.2; H, 5.0; N, 2.6. Found: C, 58.3; H, 5.0; N, 2.6.

[$Bu_2Sn(EtACDA)_2$] (**6**) Complex **6** was prepared as **3** with Bu_2SnCl_2 (1.52 g, 5 mmol), EtACDA (1.87 g, 10 mmol) and $AgNO_3$ (1.70 g, 10 mmol). Yield 75%, M.p. 215°C (dec.). λ_{max}(nm) (CH_2Cl_2): 338, 405 (log ε 4.19, 4.88). *Anal.* Calcd. for $C_{24}H_{42}N_2S_4Sn$ (%): C, 47.6; H, 6.9; N, 4.6. Found: C, 47.9; H, 6.8; N, 4.8.

Crystallographic Study

Crystals suitable for X-ray studies were obtained by slow evaporation of a solution of the compounds in CH_2Cl_2/MeOH.

Yellow crystals with dimensions of 0.06 × 0.18 × 0.36 mm for **1** and 0.12 × 0.12 × 0.45 mm for **3** were used for crystal data collection. X-ray crystallographic measurements were carried out at 152 K on a Siemens LT-2A low-temperature apparatus attached to a Siemens SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) in the θ range 1.15–27.00° for **1** and 1.44–27.00° for **3**. Initial cell parameters were determined from analysis of three orthogonal sets of 20 detector frames. The orientation matrix was passed to SAINT for integration of the intensity data. No decay was observed through the data collection. Absorption corrections were applied using Sheldricks' SADABS program. The structures were solved by direct methods with the Siemens SHELXTL-PLUS program package. All non-hydrogen atoms were modeled with anisotropic parameters for thermal motion. Hydrogen atoms in **1** were added at calculated positions, then allowed to ride on the position of the parent atom through refinement. Hydrogen atoms in **3** were added at calculated positions, then allowed to refine freely using isotropic thermal parameters. The structure of **1** showed two independent molecules in the unit cell. Table I summarizes the crystal data, experimental details and refinement results.

RESULTS AND DISCUSSION

The suggested structure for *N*-alkylated 2-amino-1-cyclopentene-1-carbodithioic acids (RACDA) is shown below [19].

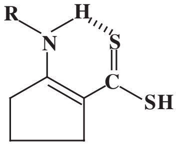

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TABLE I Crystal data and structure refinement for Complexes **1** and **3**

	[SnPh$_2$Cl(BuACDA)] (*1*)	*[SnBu$_2$(BuACDA)$_2$]* (*3*)
Formula	$C_{22}H_{26}ClNS_2Sn$	$C_{28}H_{50}N_2S_4Sn$
M (g/mol)	522.70	661.63
Color	Yellow	Yellow needle
Crystal size (mm)	0.06 × 0.18 × 0.36	0.12 × 0.12 × 0.45
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.162(4)	11.472(3)
b (Å)	14.278(10)	11.666(2)
c (Å)	17.713(9)	14.479(4)
α (°)	92.17(2)	111.14(2)
β (°)	93.816(11)	108.822(18)
γ (°)	92.268(12)	97.375(18)
V(Å^3)	2308(2)	1643.7(7)
Z	4	2
d_c (g/cm^3)	1.504	1.337
μ (mm^{-1})	1.411	1.050
λ (Å)	0.71073	0.71073
T (K)	152(2)	152(2)
Reflections collected	24 694	17 700
Unique reflections	10 054 ($R_{int}=0.0421$)	7150 ($R_{int}=0.0340$)
Abs. reflections	8429	6244
R_1	0.0949	0.0610
wR_2	0.2270	0.1449
Weighting coeffs.	$a=0.0000$ $b=4.5161$	$a=0.1122$ $b=0.1122$
Goodness-of-fit	1.208	1.022

The organotin(IV) chlorides R_nSnCl_{4-n} ($n=2$, $R={}^n$Bu or Ph; and $n=3$, R = Ph) react in methanol solution with RACDA ($R={}^n$Bu, Et) to give compounds **1**–**6**, in which the entering ligand replaces the chloride. In all cases the structures of the compounds have been characterized by their analytical and spectral data. The structures of **1** and **3** have also been confirmed by single crystal X-ray crystallography.

X-ray Structures

[Ph$_2$SnCl(BuACDA)] (*1*) The crystal consists of two independent molecules in the unit cell with their corresponding bond distances and angles being slightly different. Fig. 1(a) shows the crystal structure of one of the molecules with the atom-numbering scheme and Fig. 1(b) shows the structure around the tin. Table II gives selected bond distances and angles for the two molecules. The geometry around the Sn atom is described as a distorted trigonal bipyramid. The three atoms S(2), C(21) and C(31) lie on the equatorial plane of the bipyramid. The sum of the equatorial angles formed at the Sn atom is 358.5(10) instead of the ideal 360°, owing to the slight displacement of Sn out of the plane. The Cl and S(1) atoms occupy apical positions. Owing to the constraint of the chelate, the average angle between these axial groups is 156.84(10)°. As in the other known organotin dithiolates [14,15,20–22], an anisobidentate coordination is observed for this complex. The Average of the shorter Sn–S bond lengths is 2.453(3) Å which is very close to the sum of the covalent radii of tin and sulfur (2.42 Å), and the average of the longer Sn–S distances is 2.730(3) Å, which

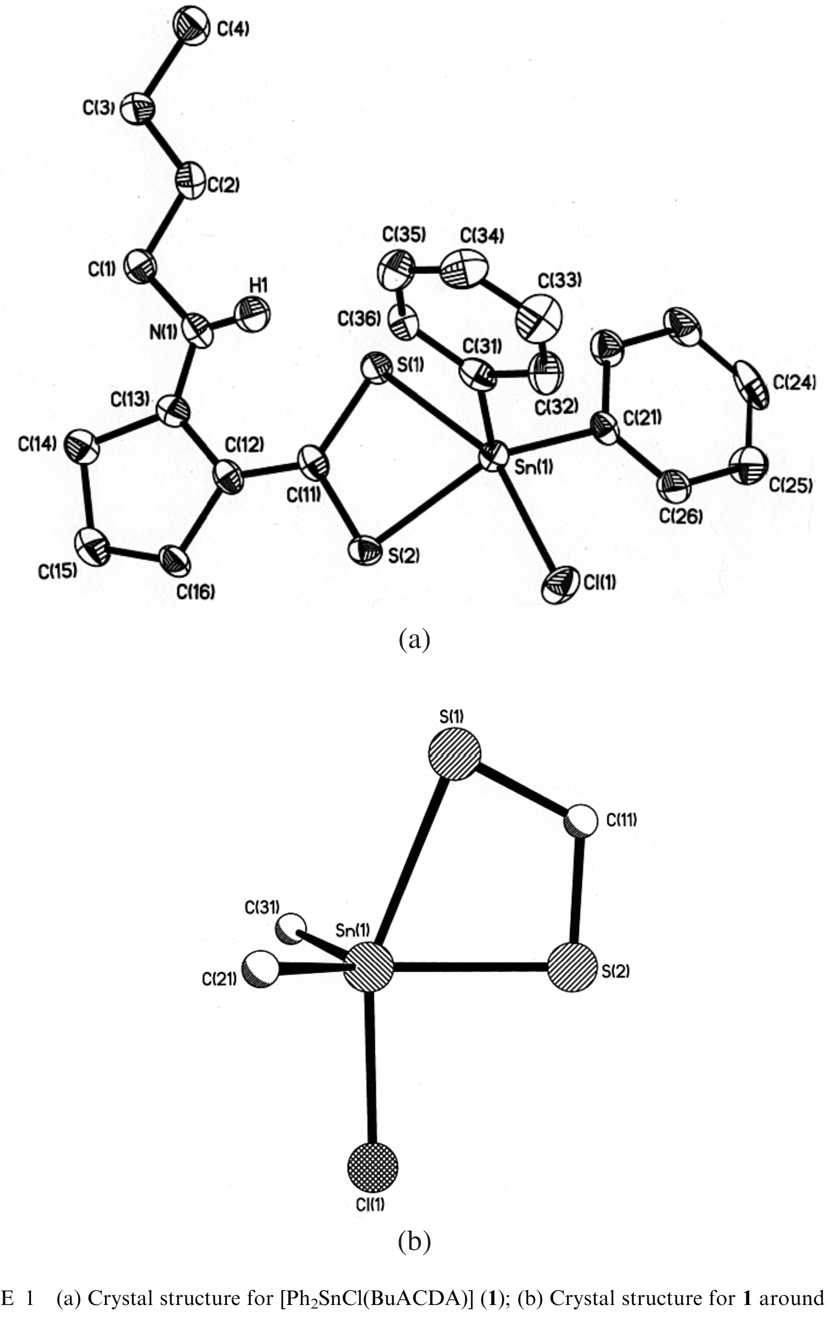


FIGURE 1 (a) Crystal structure for [$Ph_2SnCl(BuACDA)$] (**1**); (b) Crystal structure for **1** around tin atom.

is significantly less than the sum of van der Waals radii (4.0 Å) [23]. The longer C–S bond is associated with the shorter Sn–S bond, and likewise, the shorter C–S′ bond is associated with the longer Sn–S′ bond. The Sn–C bond distances are unremarkable.

The average distances between S(1) and the H atom of the amine group [S(1)–H(1), 2.324 Å] are similar to the value reported for NH ··· S hydrogen bonds (~2.4 Å) [24].

TABLE II Bond distances (Å) and angles (°) for [$Ph_2SnCl(BuACDA)$] (**1**)

Sn(1)–C(21)	2.135(11)	Sn(1)–C(31)	2.166(11)
Sn(1)–Cl(1)	2.444(3)	Sn(1)–S(2)	2.457(3)
Sn(1)–S(1)	2.709(3)	N(1)–C(13)	1.307(14)
S(2)–C(11)	1.760(12)	S(1)–C(11)	1.725(11)
C(11)–C(12)	1.379(15)	C(12)–C(13)	1.449(16)
S(1)–H(1)	2.311()		
Sn(1′)–C(21′)	2.146(10)	Sn(1′)–C(31′)	2.117(11)
Sn(1′)–Cl(1′)	2.451(3)	Sn(1′)–S(2′)	2.448(3)
Sn(1′)–S(1′)	2.751(3)	N(1′)–C(13′)	1.304(14)
S(2′)–C(11′)	1.749(11)	S(1′)–C(11′)	1.717(11)
C(11′)–C(12′)	1.394(15)	C(12′)–C(13′)	1.408(15)
S(1′)–H(1′)	2.338()		
C(21)–Sn(1)–C(31)	118.1(4)	C(21)–Sn(1)–Cl(1)	98.2(3)
C(31)–Sn(1)–Cl(1)	96.0(3)	C(21)–Sn(1)–S(2)	114.3(3)
C(31)–Sn(1)–S(2)	126.1(3)	Cl(1)–Sn(1)–S(2)	88.0(10)
C(21)–Sn(1)–S(1)	96.1(3)	C(31)–Sn(1)–S(1)	93.4(3)
Cl(1)–Sn(1)–S(1)	156.60(10)	S(2)–Sn(1)–S(1)	69.20(9)
C(11)–S(2)–Sn(1)	91.4(4)	C(11)–S(1)–Sn(1)	84.0(4)
C(11)–S(1)–H(1)	83.8	H(1)–S(1)–Sn(1)	166.5
C(12)–C(11)–S(1)	126.9(9)	C(12)–C(11)–S(2)	118.0(9)
S(1)–C(11)–S(2)	115.1(6)		
C(21′)–Sn(1′)–C(31′)	123.0(4)	C(21′)–Sn(1′)–Cl(1′)	97.4(3)
C(31′)–Sn(1′)–Cl(1′)	96.5(3)	C(21′)–Sn(1′)–S(2′)	117.2(3)
C(31′)–Sn(1′)–S(2′)	118.2(3)	Cl(1′)–Sn(1′)–S(2′)	88.49(10)
C(21′)–Sn(1′)–S(1′)	96.1(3)	C(31′)–Sn(1′)–S(1′)	91.5(3)
Cl(1′)–Sn(1′)–S(1′)	157.09(9)	S(2′)–Sn(1′)–S(1′)	68.86(9)
C(11′)–S(2′)–Sn(1′)	91.7(4)	C(11′)–S(1′)–Sn(1′)	82.7(4)
C(11′)–S(1′)–H(1′)	83.8	H(1′)–S(1′)–Sn(1′)	166.1
C(12′)–C(11′)–S(1′)	125.9(8)	C(12′)–C(11′)–S(2′)	117.4(8)
S(1′)–C(11′)–S(2′)	116.7(6)		

Estimated standard deviations are given in parentheses.

This suggests an intramolecular hydrogen bond between sulfur and proton of the amine group.

[$Bu_2Sn(BuACDA)_2$] (*3*) Figure 2(a) shows the crystal structure of **3** with the atom numbering scheme. Figure 2(b) shows the crystal structure only around the tin atom. Bond distances and angles are given in Table III.

The molecular structure shows an unsymmetrical environment for the tin atom. One sulfur atom of each ligand is covalently bonded with an average distance of 2.5137 Å, only 0.09 Å longer than the sum of the covalent radii (2.42 Å), while the other is located at an average distance of 2.9831 Å. This may be considered as a weak coordinate bond corresponding to an anisobidentate ligand. The long Sn–S distances are significantly less than the sum of the van der Waals radii (4.0 Å), and the coordination number of tin is unambiguously assigned as six. The overall geometry at tin is, however, highly distorted from *trans* octahedral. The C–Sn–C angle is only 134.45(14)°, intermediate between *cis* and *trans*. The tin and four sulfur atoms of BuACDA are nearly coplanar but are highly distorted from square-planar geometry, *cis* S–Sn–S angles range from 64.79(3)° to 152.04(3)°. The deviations from regular octahedral geometry may be a result of the difference in the steric effect and the electronegativity of ligand groups attached to the Sn atom. Similar to **1**, the distances between S and the H atom of the NHR group are 2.3203 and 2.2494 Å for S(1)–H(1A) and S(3)–H(2A), respectively. This again suggests an intramolecular hydrogen bond between sulfur and the proton of the amine (–C=S 1$\cdots$HN–).

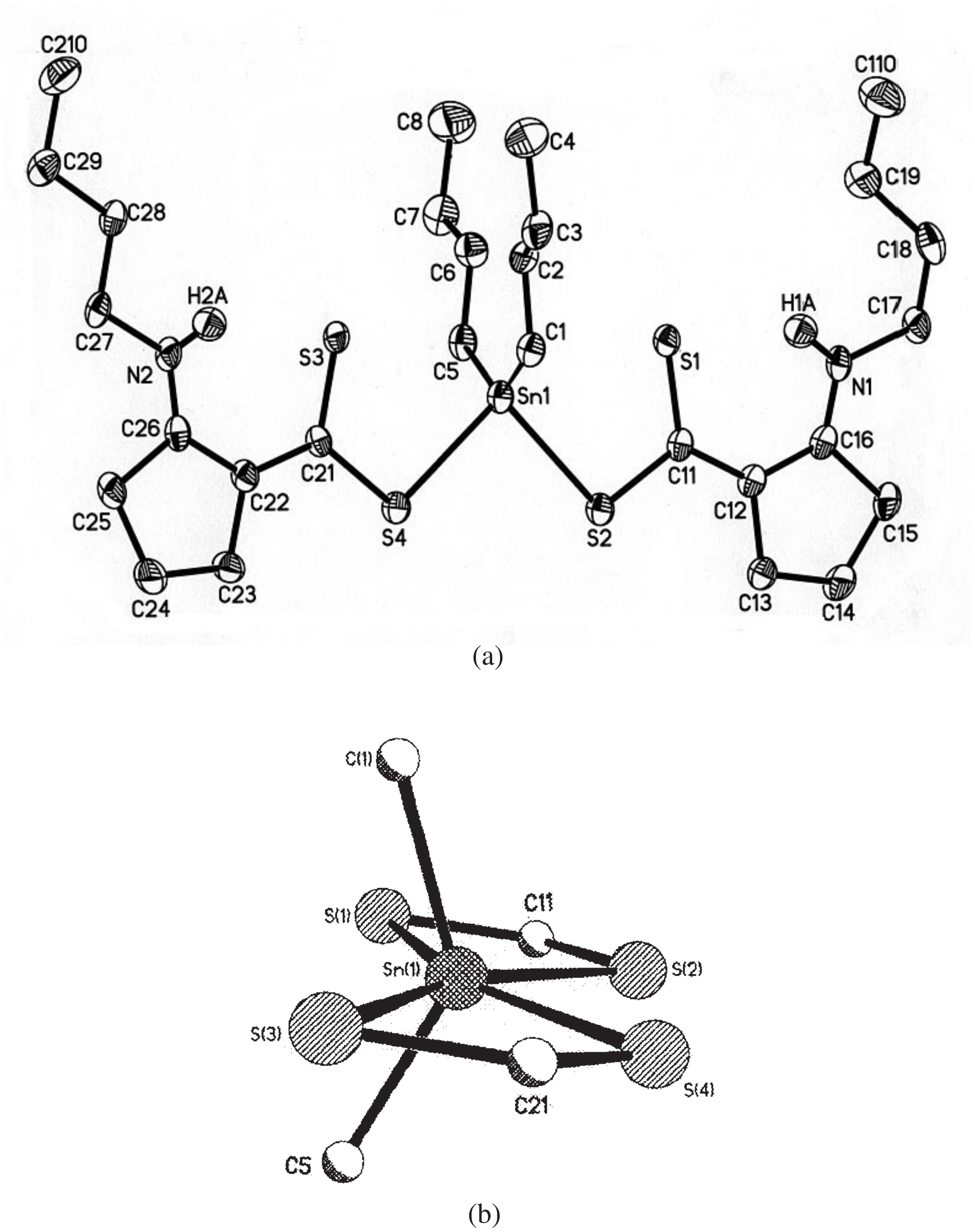


FIGURE 2 (a) Crystal structure of [$Bu_2Sn(BuACDA)_2$] (**3**); (b) Crystal structure of **3** around tin atom.

Infrared Spectra

The band in the region of 2550–2430 cm^{-1}, which appears in the free ligand spectra as ν(S–H) vibration, is absent in the spectra of all complexes, indicating participation of the carbodithioate group in the tin–ligand bonding. The bands attributed to ν(N–H) in the free ligand do not shift upon complexation, attesting to no participation

TABLE III Bond distances (Å) and angles (°) for [$Bu_2Sn(BuACDA)_2$] (**3**)

Sn(1)–C(5)	2.144(4)	Sn(1)–C(1)	2.152(3)
Sn(1)–S(2)	2.5093(10)	Sn(1)–S(4)	2.5182(10)
Sn(1)–S(3)	2.9805(10)	Sn(1)–S(1)	2.9858(10)
N(1)–C(16)	1.312(5)	N(1)–C(17)	1.470(4)
N(2)–C(26)	1.301(5)	N(2)–C(27)	1.462(4)
S(1)–C(11)	1.721(4)	S(1)–H(1A)	2.3203
S(2)–C(11)	1.742(4)	S(3)–C(21)	1.717(3)
S(3)–H(2A)	2.2494()	S(4)–C(21)	1.747(4)
C(11)–C(12)	1.413(5)	C(12)–C(16)	1.388(5)
C(22)–C(26)	1.396(6)	C(21)–C(22)	1.411(4)
C(5)–Sn(1)–C(1)	134.45(14)	C(5)–Sn(1)–S(2)	107.65(10)
C(1)–Sn(1)–S(2)	107.66(10)	C(5)–Sn(1)–S(4)	103.91(10)
C(1)–Sn(1)–S(4)	105.63(10)	S(2)–Sn(1)–S(4)	87.22(3)
C(5)–Sn(1)–S(3)	81.61(10)	C(1)–Sn(1)–S(3)	80.53(10)
S(2)–Sn(1)–S(3)	152.04(3)	S(4)–Sn(1)–S(3)	64.84(3)
C(5)–Sn(1)–S(1)	84.27(9)	C(1)–Sn(1)–S(1)	85.60(9)
S(2)–Sn(1)–S(1)	64.79(3)	S(4)–Sn(1)–S(1)	151.96(3)
S(3)–Sn(1)–S(1)	143.17(3)	C(16)–N(1)–C(17)	124.8(3)
C(26)–N(2)–C(27)	127.2(3)	C(11)–S(1)–H(1A)	85.1
C(11)–S(1)–Sn(1)	80.85(12)	H(1A)–S(1)–Sn(1)	165.9
C(11)–S(2)–Sn(1)	95.99(12)	C(21)–S(3)–H(2A)	85.6
C(21)–S(3)–Sn(1)	81.10(11)	H(2A)–S(3)–Sn(1)	166.0
C(21)–S(4)–Sn(1)	95.57(11)	C(12)–C(11)–S(1)	123.8(3)
C(12)–C(11)–S(2)	118.0(3)	S(1)–C(11)–S(2)	118.2(2)
C(22)–C(21)–S(3)	123.5(3)	C(22)–C(21)–S(4)	118.2(3)
S(3)–C(21)–S(4)	118.26(18)		

Estimated standard deviations are given in parentheses.

of nitrogen in coordination to the tin center. The complexes of Ph_2SnCl_2 and Ph_3SnCl also show the typical IR bands for phenyltin complexes [25].

^{1}H NMR Spectra

The ^{1}H NMR data of the synthesized complexes and the free ligands are given in Table IV. For all complexes ^{1}H NMR spectra show removal of the –SH proton indicating formation of an Sn–ligand bond through sulfur. The chemical shifts due to *N*-alkyl groups remain practically unchanged in the complex with respect to the ligand. This means that nitrogen is not involved in bonding with tin. If this bond was formed, there would have been a large downfield shift particularly for the H(7) protons. In free RACDA, the signal due to the NH proton appears downfield (~12 ppm), because of hydrogen bonding through the sulfur atom (N–H···S=). On complexation, this signal shifts upfield, particularly in **1** and **4**, evidence for (S, S^-) type bonding and weakening of hydrogen bonding in the complex. We suggest that the stronger the metal sulfur bond (–C=S–Sn), the weaker the hydrogen bonding (NH···S=). The central tin atom in Ph_2SnCl(S–S) complexes should display enhanced acceptor strength owing to the presence of the more electronegative Cl atom in comparison to the other complexes. Such an enhancement in acidity of the tin center should spread over both the coordination sites of the NCS_2 skeleton, strengthening the bonding interaction of the ligand (–C=S–Sn) and weakening the hydrogen bonding (NH···S=). In the chlorophenyltin complexes (**1** and **4**) chemical shift values for the proton of the amine group are at much lower frequencies than those observed in other synthesized complexes.

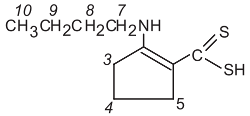
The ^{1}H NMR spectra of the phenyl derivatives show two multiplets attributable to the H(2,6) and H(3,4,5) protons of phenyl rings. The signal of H(2,6) has $^{117/119}$Sn

TABLE IV ^{1}H and ^{119}Sn NMR data for free ligands and synthesized complexes in $CDCl_3$ (δ in ppm and J in Hz)

Compound	*RACDA*[a]								*Ph*				*^{119}Sn data*
	H(3)	*H(4)*	*H(5)*	*H(7)*	*H(8)*	*H(9)*	*H(10)*	*NH*	*$H_{2,6}$*	*$H_{3,4,5}$*	*$^{3}J(^{119}Sn,H)$*		
BuACDA	2.6–2.8 t	1.9–2.1 qui	3–3.2 t	3.3 m	1.6 m	1.4 m	0.8 t	12.6 s					
EtACDA	2.66 t	1.86 qui	2.66 t	3.40 m	1.32 t			12.1 s					
1	2.68 t	1.86 qui	2.79 t	3.37qua	1.67qui	1.43 m	0.98t	9.63 s	8.01 m	7.46 m	94		−183.5
2	2.59 t	1.80 qui	2.87 t	3.25 qua	1.58qui	1.40 m	0.92t	11.09 s	7.69 m	7.33 m	65.5		−153.2
4	2.63 t	1.80 qui	2.71 t	3.39 qui	1.28t			9.53 s	7.98 m	7.37 m	95.8		−252.3
5	2.62 t	1.83 qui	2.89 t	3.39 qui	1.28t			11.05 s	7.67 m	7.33 m	65		−155.1
$SnPh_2Cl_2$[b]									7.7 m	7.56 m	81.7		−27
$SnPh_3Cl$[b]									7.67	7.47	60.4		−48
									Bu				
									H_α	*H_β*	*H_γ*	*H_δ*	
3	2.67 t	1.82 qui	2.87 t	3.34 qua	1.65 qui	1.43 m	0.9–1.0 m	11.09 s	1.94 m	1.94 m	1.43 m[c]	0.9–1.0 m[d]	−183.7
6	2.69 t	1.82 qui	2.71 t	3.40m	1.33t			11.08 s	1.94 m	1.94 m	1.44 m	0.92 t	−185.4
$SnBu_2Cl_2$[e]									1.8 m	1.41 m	1.4 m	0.95 t	122

s: singlet, d: doublet, t: triplet, qua: quartet, qui: quintet, m: multipet

[a] Numbering scheme:



[b] Ref. [26]; [c] mixed with H_9; [d] mixed with H_{10}; [e] Ref. [27].

satellites and indicates an increasing coupling constant $^3J(^{119}Sn,^1H)$ on complexation, suggesting a higher coordination number at the tin atom, particularly in diphenyltin complexes. The ^1H NMR spectra of butyltin complexes show a triplet upfield due to $–CH_3$ and a *pseudo* sextet due to $–CH_2(\gamma)$, owing to the coupling with the $–CH_3$ and $–CH_2(\beta)$. These signals remain unaffected on complexation. The $–CH_2(\alpha)$ and $–CH_2(\beta)$ groups give overlapping multiplets and show downfield shifts relative to uncomplexed Bu_2SnCl_2. In the spectra of these butyltin complexes, tin satellites are undetectable and the $^2J(^{119}Sn,^1H)$ values cannot be extracted, because of the complexity of the methylene multiplets.

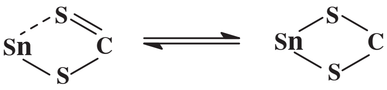
The ^1H NMR spectra of **3** in toluene-d_8 have also been examined as a function of temperature in the range from 100 to -50°C, to evaluate the behavior of the –NH proton within the complex. At high temperature, NMR spectra show only one singlet for the –NH proton. Upon cooling, this singlet splits and, after broadening, a triplet appears. This splitting is due to coupling with nitrogen ($I = 1$) in which the rate of spin relaxation would be slow with lowering temperature and therefore coupling with the proton could be observed. Upon varying the temperature, the position of the –NH signal shows no significant shift in the range from 100 to -50°C. So variation of temperature has no significant effect on the hydrogen bonding in the complex. These effects seem unique and deserve further study.

^{119}Sn NMR Spectra

The $^{119}Sn\{H\}$ NMR data for all complexes are given in Table IV. In the spectrum of these complexes only a sharp singlet appears, indicating the formation of a single product. The $^{119}Sn\{H\}$ chemical shifts for all these new complexes are at much higher field than those of the original chloroorganotin(IV) compounds, because the electronegative group has been removed and the coordination number has increased. On the basis of the chemical shift ranges proposed for some of the tin(IV) dithiocarbamato complexes [27], it appears reasonable to assume that in all of the complexes the effective coordination number in solution is five. However, these NMR data themselves do not indicate whether in solution the dithioate ligands are symmetrically or asymmetrically coordinated to tin. In most dithioates one of the Sn–S bonds is weaker than the other, so that there are two sets of intramolecular distances [20,21]. In ^1H NMR spectra of complexes **3** and **6** only one signal was observed for −NH, indicating that the two RACDA groups are chemically equivalent. Each dithioate ligand effectively behaves as a bidentate sulfur donor ligand coordinated asymmetrically to the metal center. The distribution of charge on tin leads to shifts in the ^{119}Sn NMR spectra consistent with a coordination number of five.

Fluxional behavior of chelates, $S{=}C{–}S{–}Sn(S_2C) \leftrightarrow (CS_2)Sn{–}S{–}C{=}S$ in solution may also be responsible for the two equivalent NH features in the ^1H NMR spectrum and thus the effective coordination number of five in ^{119}Sn NMR

In the ^{119}Sn NMR spectrum of **4** after standing in $CDCl_3$, another signal at -157.6 ppm appeared. Apparently at room temperature, the dithioate ligand can undergo slow monodentate–bidentate equilibrium in solution [27,28]:



Appearance of an additional signal at higher frequency is consistent with an effective decrease in coordination number at the tin atom, which would arise from this intramolecular monodentate–bidentate exchange that is slow on the NMR timescale. This possibility will be investigated and reported on later.

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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