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Synthesis and crystal structures of new complexes of di- and tribenzyltin *N*-ethyl and *N*-benzyl-2-amino cyclopent-1-ene-1-carbodithioates

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Abstract

The dithiocarboxylato complexes of tin, $Bz_2SnCl(EtACDA)$ (**1a**) Bz = benzyl, $Bz_2Sn(EtACDA)_2$ (**1b**), and $Bz_3Sn(EtACDA)$ (**1c**) have been synthesized by the reaction of Bz_2SnCl_2 or Bz_3SnCl with 2-*N*-ethylamino-1-cyclopentene-1-carbodithioic acid (HEt-ACDA). The reaction of 2-amino-1-cyclopente-1-carbodithioic acid (H_2ACDA) with benzylamine, gave 2-*N*-benzylamino-1-cyclopente-1-carbodithioic acid (HBzACDA) (**2**), which reacts with Bz_2SnCl_2 or Bz_3SnCl to give $Bz_2SnCl(BzACDA)$ (**3a**), $Bz_2Sn(BzACDA)_2$ (**3b**) and $Bz_3Sn(BzACDA)$ (**3c**). The products were characterized by IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopies and elemental analysis. The crystal structures of **1c**, **2** and **3b** have also been determined. In all the complexes Sn is bound asymmetrically to the dithiocarboxylato ligand through two sulfur atoms. The orientation of the ligands is determined by NH···S hydrogen bonds. © 2002 Published by Elsevier Science B.V.

*Keywords:* Tin complexes; Organotin(IV) compounds; Dithiocarboxylato ligands; Crystal structures

1. Introduction

Organotin complexes are used as bactericides, fungicides, acaricides and industrial biocides. Their antitumor activity and their implications in antioncogenesis have been investigated. Several organotin complexes are effective antineoplastic (mainly antileukaemic) and antivirial agents [1–4]. In view of antifungal properties of 2-*N*-alkylamino-1-cyclopentene-1-carbodithioic acids (HRACDA) [5] we considered it of interest to synthesize organotin compounds containing these ligands.

2-Amino-1-cyclopentene-1-carbodithioic acid (H_2ACDA) contains the skeletal unit –NH–C=C–C(=S)SH and so it can be ambidentate. In many metal ion complexes the N and S sites are involved in bond formation (Scheme 1a) but with Co(II), Ni(II) and some other metal ions disulfur chelation (Scheme 1b) is common [5–11].

We report here the synthesis of new organotin(IV) complexes made by the reaction of Bz_2SnCl_2 or Bz_3SnCl with *N*-ethyl (HEtACDA) or *N*-benzyl (HBzACDA) derivatives of H_2ACDA, in which Sn is bound to the ligand exclusively through two sulfur atoms (Scheme 1b). Elemental analyses as well as IR and NMR spectra confirm the structures of the products and the spectra show that the ligands bind to tin through the sulfur atoms.
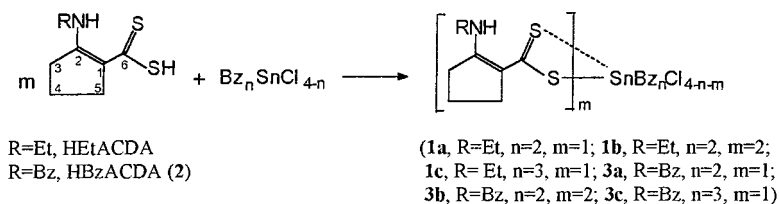
Crystallographic studies of organotin dithioate complexes have revealed a variety of coordination geometries around the Sn atom. Remarkable diversity in
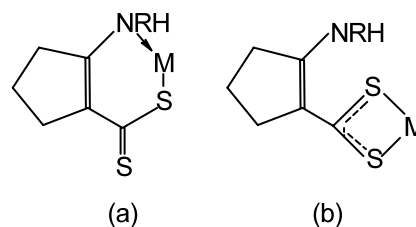
Scheme 1.

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Scheme 2.

structure may be observed even when only small changes in chemistry exist, so that for the diorganotin bis(1,1-dithiolates) four structural motifs are found [12]. Therefore, it was considered interesting to study the crystal structures especially for **3b**. The coordination geometry depends upon the bonding mode of the dithioate, which acts as a mono- or bi-dentate ligand. In this paper, we report the crystal structures of **1c** and **3b** in which the RACDA ligands are anisobidentate. The crystal structure of **2** is also described.

2. Results and discussion

2.1. Synthesis

Bz$_2$SnCl(EtACDA) (**1a**) was obtained from the reaction of Bz$_2$SnCl$_2$ with HEtACDA in 1:1 molar ratio. In the presence of triethylamine (TEA), treatment of Bz$_2$SnCl$_2$ with two equivalents of HEtACDA gave Bz$_2$Sn(EtACDA)$_2$ (**1b**). The reaction between Bz$_3$SnCl and HEtACDA in the presence of TEA gave a good yield of Bz$_3$Sn(EtACDA) (**1c**).

The benzyl derivative HBzACDA (**2**), which was prepared from the reaction of benzylamine with H$_2$ACDA, did not react with Bz$_2$SnCl$_2$ or Bz$_3$SnCl in the absence of TEA, but in the presence of an appropriate amount of TEA, Bz$_2$SnCl(BzACDA) (**3a**) and Bz$_2$Sn(BzACDA)$_2$ (**3b**) were obtained by reaction of Bz$_2$SnCl$_2$ and **2** in 1:1 and 1:2 molar ratios, respectively. The reaction between **2**, Bz$_3$SnCl and TEA in 1:1:1 molar ratio produced Bz$_3$Sn(BzACDA) (**3c**) (See Scheme 2).

The IR spectra of HEtACDA and HBzACDA exhibit weak intensity bands at 2430 and 2546 cm^{-1}, respectively, due to the –SH group. This band is absent in the spectra of the corresponding complexes, but a new band in the 350–370 cm^{-1} range may be assigned to ν(Sn–S). The strong bands observed at 1605–1580, 1490–1480, 1345–1315 and 1290–1270 cm^{-1} in the spectra of the ligands and their complexes may be assigned to the combination bands of ν(NH$_2$ + C=C), ν(CH$_2$ + C=C), ν(C=N + C=S) and ν(C=S + C=N), respectively [9]. The band due to ν_{asym} CSS at ≈ 900 cm^{-1} of the ligand spectra is diagnostic in deciding the mode of sulfur attachment to the tin center. It is

symmetrically split for **1c** and **3c** indicating the unidentate mode of chelation, but the appearance of asymmetrically split bands for **1a**, **1b**, **3a** and **3b** indicates the unequal involvement of the two S atoms in the complexation. Compounds **1a** and **3a** exhibit sharp and weak bands at 289 and 282 cm^{-1}, respectively, assignable to ν(Sn–Cl).

A comparison of ^{1}H-NMR spectra of di- and tribenzyltin(IV) complexes with those of the corresponding ligands shows the disappearance of the signal for the –SH proton on the formation of the Sn–S bond. In the spectra of the complexes in CDCl$_3$ solution, the –NH signals observed in the acids (HEtACDA and HBzACDA) shift to upfield. This shift may be ascribed to the weakening of the NH···S=C hydrogen bond on complexation. The signals assigned to the protons of ethyl or benzyl groups attached to nitrogen are not shifted indicating that nitrogen atom is not involved in the bonding to tin [9,13]. Likewise the position of signals assigned to H(3), H(4) and H(5) do not change.

In the ^{13}C-NMR spectra of the complexes, chemical shifts are quite similar to those of the parent ligands. Only a small shift in the position of C(6) is seen due to the deshielding of this carbon upon deprotonation of the thiol group and coordination through the other sulfur atom.

The ^{119}Sn-NMR data for the tin complexes shown in Table 1 suggest that the geometries in solution are similar to those in the crystal. Although the shifts are dependent on the nature of the substituents at the tin atom, the values obtained for **1c** and **3c** are consistent with the presence of four-coordinate organotin(IV) dithioate species for which a range of 144 to −120

Table 1
^{119}Sn chemical shifts for di- and tribenzyltin(IV) chlorides and their dithiocarboxylate complexes in CDCl$_3$

Species	$\delta(^{119}$Sn$)$
Bz$_2$SnCl$_2$ (in CH$_2$Cl$_2$)	−35
Bz$_3$SnCl	−52
Bz$_2$SnCl(EtACDA)	−168
Bz$_2$SnCl(BzACDA)	−166
Bz$_2$Sn(EtACDA)$_2$	−222
Bz$_2$Sn(BzACDA)$_2$	−221
Bz$_3$Sn(EtACDA)	−38
Bz$_3$Sn(BzACDA)	−36

Table 2
Selected bond lengths (Å) and bond angles (°) for **1c**

| Bond lengths			
Sn–C(14)	2.160(3)	Sn–C(7)	2.166(3)
Sn–C(21)	2.171(3)	Sn–S(1)	2.4577(8)
Sn···S(2)	3.1001(10)	S(1)–C(1)	1.767(4)
S(2)–C(1)	1.699(4)	N–C(6)	1.294(6)
N–C(28)	1.469(6)	C(1)–C(2)	1.394(5)
C(2)–C(6)	1.401(5)	C(7)–C(8)	1.504(5)
Bond angles			
C(14)–Sn–C(7)	115.87(14)	C(14)–Sn–C(21)	106.66(13)
C(7)–Sn–C(21)	107.53(15)	C(14)–Sn–S(1)	116.87(10)
C(7)–Sn–S(1)	111.18(10)	C(21)–Sn–S(1)	96.31(10)
C(1)–S(1)–Sn	98.82(12)	S(2)–C(1)–S(1)	118.5(2)
C(8)–C(7)–Sn	110.9(2)	C(15)–C(14)–Sn	114.3(2)
C(22)–C(21)–Sn	112.8(2)		

Estimated standard deviations in parentheses.
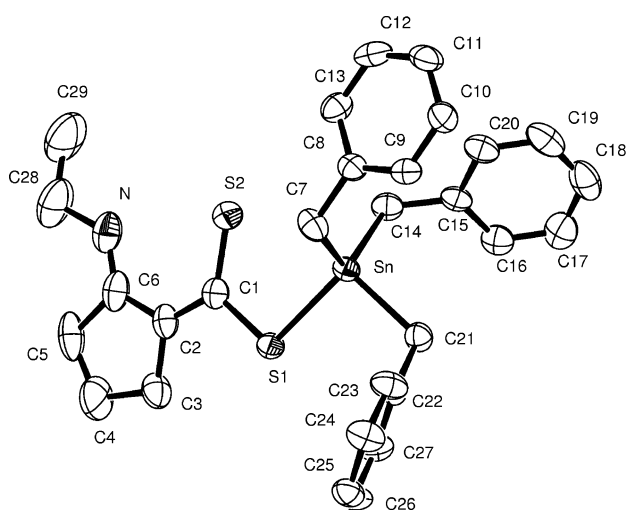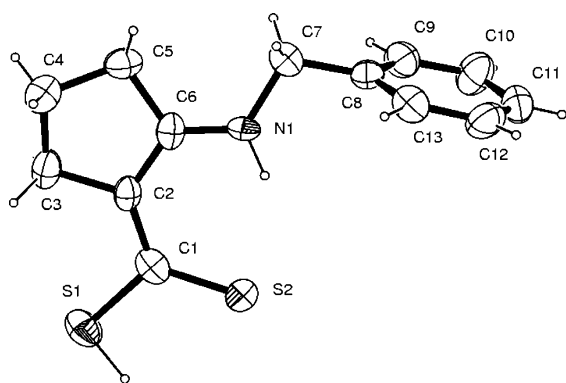

Fig. 1. Crystal structure of Bz$_3$Sn(EtACDA) (**1c**).

Fig. 2. Crystal structure of BzACDA (**2**).

ppm was reported earlier [14]. Chemical shifts of **1a** and **3a** are in the expected range of −150 to −250, for the five-coordinated tin(IV) species [13]. The chemical shifts for **1b** and **3b** are somewhat different from the values, −300 to −500 ppm, expected for the six coordinated

tin(IV) compounds, suggesting that the coordination is asymmetrical, with two S atoms held more weakly than the other two.

2.2. Description of the crystal structures

2.2.1. Bz$_3$Sn(EtACDA) (1c)

In the unit cell of this compound, there are two crystallographically independent molecules that show only minor differences. Selected bond lengths and bond angles for one of the molecules are given in Table 2 and its view is shown in Fig. 1. The molecules contain essentially the four-coordinate tin, but with distortion from the normal tetrahedral environment. However, the long Sn···S(2) interactions (3.1001(10) Å) can be regarded as weak coordinate bonds corresponding to an anisobidentate ligand [15]. The tin atom is also coordinated to the other sulfur atom and to the one carbon atom of each of the three benzyl groups. The Sn–S(1) bond length lies toward the middle of the range reported for triphenyl thiolates (2.405–2.481 Å) close to the sum of the covalent radii of tin and sulfur (2.42 Å) [15,16]. Around the tin, the angles C(14)–Sn–C(7), C(14)–Sn–S(1) and C(7)–Sn–S(1) are wider and C(14)–Sn–C(21), C(7)–Sn–C(21) and especially C(21)–Sn–S(1) are narrower than the ideal tetrahedral angle. This might suggest the description of the tin environment as *cis*-trigonal bipyramid with S(2) and C(21) in the apical positions and S(1), C(7) and C(14) in the equatorial positions, but this bipyramid is extremely distorted: the sum of the equatorial angles is only 344° and the axial Sn–C bond lengths are very similar to the equatorial ones. Thus, the environment of tin is best described as distorted tetrahedral. [16,17].

2.2.2. HBzACDA (2)

The molecular structure of **2** is shown in Fig. 2 and selected bond lengths and bond angles are given in Table 3. The bond lengths and bond angles within this ligand are insignificantly different from those in **3b** described below. In **2** there are intramolecular hydrogen

Table 3
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
S(1)–C(1)	1.753(7)	S(2)–C(1)	1.694(7)
N(1)–C(6)	1.318(7)	N(1)–C(7)	1.468(9)
C(1)–C(2)	1.411(9)	C(2)–C(6)	1.397(9)
S(1)–HS	1.23	S(2)···HS	2.99
N(1)–HN	0.92	S(2)···HN	2.24
Bond angles			
C(6)–N(1)–C(7)	123.5(6)	C(2)–C(1)–S(2)	125.5(5)
C(2)–C(1)–S(1)	114.6(5)	S(2)–C(1)–S(1)	119.9(5)
C(6)–C(2)–C(1)	127.3(5)	N(1)–C(6)–C(2)	126.4(6)
S(1)–HS···S(2)	123	N(1)–H–S(2)	145

Estimated standard deviations in parentheses.
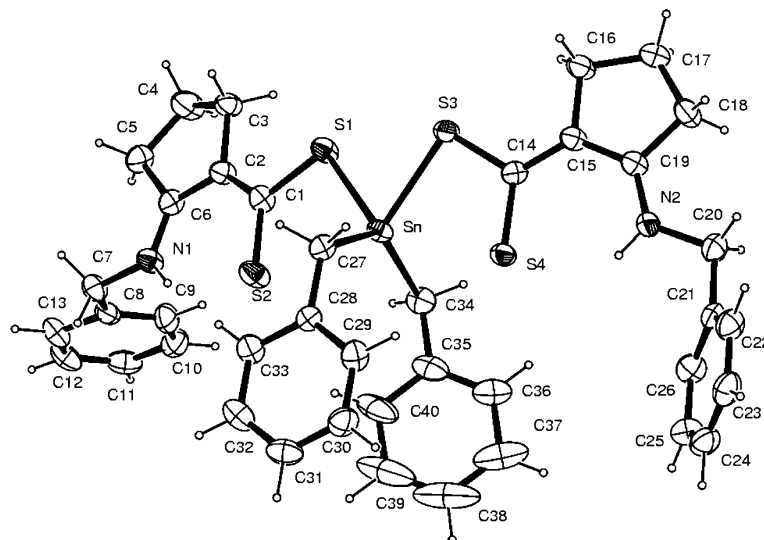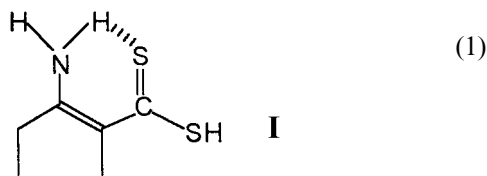
Fig. 3. Crystal structure of $Bz_2Sn(BzACDA)_2$ (**3b**).

bonds between N(1)H···S(2) and intermolecular bonds between S(1)H and S(2) [$-x + 1.5, y - 0.5, -z + 1.5$]. Based on the NMR data Singh et al. showed that among the possible tautomeric forms for H_2ACDA, form **I** exists exclusively [5]. This is confirmed by the crystal structure of **2**.

(1)

2.2.3. $Bz_2Sn(BzACDA)_2$ (**3b**)

The molecular structure and the numbering scheme are shown in Fig. 3 and selected bond lengths and bond angles are listed in Table 4.

The tin atom has a highly distorted octahedral environment in which the four S atoms lie in the equatorial plane. The atoms C(27) and C(34) of the benzyl groups define a C–Sn–C angle of 129.22(16)° which is intermediate between those for *cis*- and *trans*-substitution [18]. The deviation from the regular octahedral geometry may result from steric effects and differences in the electronegativities of the ligands attached to the tin atom [19]. The S–Sn–S bond angles range from 79° in the chelate ring to 154° for the angle between the ligands.

The BzACDA ligands are anisobidentately chelated to Sn, with one longer and one shorter Sn–S bond [19,20]. The much smaller differences between Sn–S distances in *cis*-$Cl_2Sn(S_2CNEt_2)_2$ was attributed to packing forces and coordination geometry [21]. The Sn–S–C–S′ bonding system in **3b** is easy to discern [13].

The longer C–S bond is associated with the shorter Sn–S bond, and the shorter C–S′ bond is associated with the longer Sn–S′ bond. The long Sn–S distances are significantly shorter than the sum of the van der Waals radii (4.0 Å) and the coordination number of Sn is effectively six [22].

The bond distances and bond angles within the five-member rings and benzyl groups are unexceptional. Intramolecular hydrogen bonds between S and the adjacent amine groups are observed. The distances between S and H atoms are 2.33 and 2.38 Å for S(2)–H(1) and S(4)–H(2), respectively.

Table 4
Selected bond lengths (Å) and bond angles (°) for **3b**

Bond lengths			
Sn–C(34)	2.158(4)	Sn–C(27)	2.165(4)
Sn–S(3)	2.5072(3)	Sn–S(1)	2.5157(3)
Sn···S(2)	3.1030(3)	Sn···S(4)	2.9564(3)
S(1)–C(1)	1.755(4)	S(2)–C(1)	1.702(4)
S(3)–C(14)	1.749(4)	S(4)–C(14)	1.722(4)
N(1)–C(6)	1.328(5)	N(1)–C(7)	1.459(5)
N(1)–H(1)	0.84	N(2)–H(2)	0.87
S(2)···H(1)	2.33	S(4)···H(2)	2.38
Bond angles			
C(34)–Sn–C(27)	129.22(16)	C(34)–Sn–S(3)	116.94(12)
C(27)–Sn–S(3)	104.78(11)	C(34)–Sn–S(1)	104.71(12)
C(27)–Sn–S(1)	110.37(11)	S(3)–Sn–S(1)	79.574(9)
S(2)···Sn···S(4)	153.76(1)	C(1)–S(1)–Sn	99.02(14)
C(14)–S(3)–Sn	95.77(13)	S(2)–C(1)–S(1)	117.7(2)
S(4)–C(14)–S(3)	116.3(2)	C(28)–C(27)–Sn	115.6(3)
C(35)–C(34)–Sn	116.2(3)	N(1)–H(1)–S(2)	138
N(2)–H(2)–S(4)	134		

Estimated standard deviations in parentheses.

3. Experimental

3.1. General procedure

Starting materials were purchased from commercial sources and used without further purification, except for benzyl chloride and Et$_3$N, which were distilled before use. HEtACDA, Bz$_2$SnCl$_2$ and Bz$_3$SnCl were prepared using the literature methods [23 and 24, respectively]. IR spectra were obtained in FT BOMEM MB102 or SHIMADZU IR-470 infrared spectrometers from KBr disks. ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded with a Bruker DRX500 ADVANCE spectrometer.

3.2. Synthesis of Bz$_2$SnCl(EtACDA) (1a)

A solution of HEtACDA (0.400 g, 2.14 mmol) in warm MeOH (20 cm^3) was added dropwise to a solution of Bz$_2$SnCl$_2$ (0.796 g, 2.14 mmol) in the same solvent (10 cm^3). A pale yellow precipitate was formed almost immediately. This was filtered, washed with MeOH and recrystallized from CH$_2$Cl$_2$–MeOH to give pale yellow crystals, m.p. (dec) 157 °C. Yield: 0.93 g (83%). Anal. Calc. for C$_{22}$H$_{26}$ClNS$_2$Sn: C, 50.55; H, 5.01; N, 2.68. Found: C, 50.09; H, 5.02; N, 2.75%. ^{1}H-NMR: δ 1.32 ($^3J_{HH}$ = 7.3 Hz, 3H, t, CH$_2$–CH$_3$), 1.85 ($^3J_{HH}$ = 7.5 Hz, 2H, tt, H(4)), 2.70 (4H, m, H(3) and H(5)), 3.14 ($^2J_{119SnH}$ = 86 Hz, 4H, s, CH$_2$–Ph), 3.43 (2H, m, CH$_2$–CH$_3$), 7.04–7.21 (10H, m, aromatic-H), 9.56 (1H, s, –NH). ^{13}C-NMR: δ 15.0 (CH$_2$–CH$_3$), 19.7 (C(4)), 33.6 (C(3)), 34.5 (C(5)), 36.1 (CH$_2$–Ph), 41.6 (CH$_2$–CH$_3$), 120.1 (C(1)), 124.9 (m-C), 128.3 (p-C), 128.4 (o-C), 138.3 (i-C), 172.3 (C(2)), 190.7(C(6)).

3.3. Synthesis of Bz$_2$Sn(EtACDA)$_2$ (1b)

Triethylamine (0.52 cm^3) was added to a suspension of HEtACDA (0.7 g, 3.74 mmol) in MeOH (10 cm^3). The clear solution was then added to a solution of Bz$_2$SnCl$_2$ (0.69 g, 1.85 mmol) in MeOH (10 cm^3). Formation of a yellow crystalline precipitate was observed after a few minutes. Stirring was continued overnight and then the product was filtered, washed with MeOH and recrystallized from MeOH–CH$_2$Cl$_2$ to give yellow crystals, m.p. 178–180 °C. Yield: 0.71 g (57%). Anal. Calc. for C$_{30}$H$_{38}$N$_2$S$_4$Sn: C, 53.49; H, 5.69; N, 4.16. Found: C, 53.36; H, 5.70; N, 4.25%. ^{1}H-NMR: δ 1.33 ($^3J_{HH}$ = 7.3 Hz, 6H, t, CH$_2$–CH$_3$), 1.79 ($^3J_{HH}$ = 7.5 Hz, 4H, tt, H(4)), 2.67 ($^3J_{HH}$ = 7.7 Hz, 4H, t, H(3)), 2.76 ($^3J_{HH}$ = 7.5 Hz, 4H, t, H(5)), 3.36 ($^2J_{119SnH}$ = 83 Hz, 4H, s, CH$_2$–Ph), 3.40 (4H, m, CH$_2$–CH$_3$), 6.99–7.29 (10H, m, aromatic-H), 10.85 (1H, s, –NH). ^{13}C-NMR: δ 15.3 (CH$_2$–CH$_3$), 19.7 (C(4)), 33.4 (C(3)), 35.0 (C(5)), 37.9 (CH$_2$–Ph), 40.6 (CH$_2$–CH$_3$), 119.8 (C(1)), 124.2 ($^4J_{SnC}$ = 31 Hz, m-C), 127.4 ($^5J_{SnC}$ = 25

Hz, p-C), 129.0 ($^3J_{SnC}$ = 44 Hz, o-C), 139.8 (i-C), 169.0 (C(2)), 198.0 (C(6)).

3.4. Synthesis of Bz$_3$Sn(EtACDA) (1c)

A solution of HEtACDA (0.500 g, 2.67 mmol) and Et$_3$N (0.37 cm^3) in CH$_2$Cl$_2$ (10 cm^3) was added to a solution of Bz$_3$SnCl (1.14 g, 2.67 mmol) in CH$_2$Cl$_2$ (10 cm^3). The mixture was stirred for 2 h and then MeOH (10 cm^3) was added and the solution was kept at –4 °C to give greenish-yellow plates, m.p. 95 °C. Yield: 1.2 g (78%). Anal. Calc. for C$_{29}$H$_{33}$NS$_2$Sn: C, 60.22; H, 5.74; N, 2.42. Found: C, 59.86, H, 5.75; N, 2.47. ^{1}H-NMR: δ 1.31 ($^3J_{HH}$ = 7.3 Hz, 3H, t, CH$_2$–CH$_3$), 1.81 ($^3J_{HH}$ = 7.4 Hz, 2H, tt, H(4)), 2.60 ($^2J_{119SnH}$ = 68 Hz, 6H, s, CH$_2$–Ph), 2.65 ($^3J_{HH}$ = 7.6 Hz, 2H, t, H(3)), 2.86 ($^3J_{HH}$ = 7.5 Hz, 2H, t, H(5)), 3.37 (2H, m, CH$_2$–CH$_3$), 6.77 (6H, d, o-H), 6.99 (3H, t, p-H), 7.14 (6H, t, m-H), 11.52 (1H, s, –NH). ^{13}C-NMR: δ 15.1 (CH$_2$–CH$_3$), 19.7 (C(4)), 25.2 ($^2J_{119SnC}$ = 301 Hz, CH$_2$–Ph), 33.2 (C(3)), 35.3 (C(5)), 40.6 (CH$_2$–CH$_3$), 120.4 (C(1)), 123.8 ($^4J_{SnC}$ = 21 Hz, m-C), 127.6 ($^5J_{SnC}$ = 30 Hz, p-C), 128.4 ($^3J_{SnC}$ = 17 Hz, o-C), 141.0 ($^2J_{SnC}$ = 43 Hz, i-C), 170.1 (C(2)), 195.0 (C(6)).

3.5. Synthesis of BzACDA (2)

A solution of H$_2$ACDA (2.000 g, 12.58 mmol) and benzylamine (1.350 g, 12.58 mmol) in MeOH (40 cm^3) was stirred at room temperature (r.t.) for 24 h. Water (80 cm^3) was added to the solution and the mixture was filtered. The filtrate was cooled to 0 °C and neutralized with 2 N HCl to give crystalline orange precipitate, which was filtered, washed with MeOH and dried over CaCl$_2$. The dry product was then recrystallized from MeOH to give orange needles, m.p. 98 °C. Yield: 2.3 g (73%). Anal. Calc. for C$_{13}$H$_{15}$NS$_2$: C, 62.61; H, 6.06; N, 5.62. Found: C, 62.85; H, 6.08; N, 5.67%. ^{1}H-NMR: δ 1.86 ($^3J_{HH}$ = 7.5 Hz, 2H, tt, H(4)), 2.70 ($^3J_{HH}$ = 7.7 Hz, 2H, t, H(3)), 2.76 ($^3J_{HH}$ = 7.5 Hz, 2H, t, H(5)), 4.57 ($^3J_{HH}$ = 6.2 Hz, 2H, d, N–CH$_2$), 4.89 (1H, s, –SH), 7.27–7.38 (5H, m, aromatic-H), 12.72 (1H, s, –NH). ^{13}C-NMR: δ 20.1 (C(4)), 33.3 (C(3)), 34.1 (C(5)), 49.3 (N–CH$_2$), 119.0 (C(1)), 127.0 (m-C), 127.9 (p-C), 129.0 (o-C), 136.1 (i-C), 171.3 (C(2)), 191.0 (C(6)).

3.6. Synthesis of Bz$_2$SnCl(BzACDA) (3a)

A solution of HBzACDA (0.350 g, 1.41 mmol) and Et$_3$N (0.142 g, 1.41 mmol) in MeOH (15 cm^3) was added dropwise to a solution of Bz$_2$SnCl$_2$ (0.522 g, 0.141 mmol) in the same solvent (10 cm^3). The mixture was stirred for 3 h during which a pale yellow precipitate was formed. This was filtered, washed with MeOH and recrystallized from CH$_3$OH–CH$_2$Cl$_2$ to give pale yellow crystals, m.p. 121–123 °C. Yield: 0.65 g (79%).

Table 5
Crystal data and structure refinement parameters for **1c**, **2** and **3b**

	Bz$_3$Sn(EtACDA) (**1c**)	Bz$_2$Sn(BzACDA)$_2$ (**3b**)	BzACDA (**2**)
Empirical formula	C$_{29}$H$_{33}$NS$_2$Sn	C$_{40}$H$_{42}$N$_2$S$_4$Sn	C$_{13}$H$_{15}$NS$_2$
Formula weight	578.37	797.69	249.38
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
Unit cell dimensions			
a (Å)	13.1380(4)	11.1332(8)	8.708(2)
b (Å)	13.7351(6)	11.4042(7)	7.571(3)
c (Å)	16.4793(6)	15.3036(11)	19.448(5)
α (°)	91.907(2)	80.960(4)	90
β (°)	95.123(2)	87.516(3)	94.223(15)
γ (°)	110.975(2)	72.395(4)	90
Z	4	2	4
V (Å^3)	2758.8(2)	1829.0(2)	1278.7(6)
μ (mm^{-1})	1.094	0.96	0.39
Reflections collected	22 004	12 668	3940
Independent reflections	13 035 ($R_{int} = 0.063$)	6398 ($R_{int} = 0.059$)	1481 ($R_{int} = 0.166$)
Reflections observed [$I > 2\sigma(I)$]	10 529	5288	880
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.046$, $wR_2 = 0.098$	$R_1 = 0.045$, $wR_2 = 0.105$	$R_1 = 0.069$, $wR_2 = 0.109$
R indices (all data)	$R_1 = 0.062$, $wR_2 = 0.107$	$R_1 = 0.059$, $wR_2 = 0.113$	$R_1 = 0.137$, $wR_2 = 0.130$

Anal. Calc. for C$_{27}$H$_{28}$ClNS$_2$Sn: C, 55.45; H, 4.83; N, 2.40. Found: C, 54.96; H, 4.83; N, 2.45%. ^{1}H-NMR: δ 1.81 ($^3J_{HH} = 7.5$ Hz, 2H, tt, H(4)), 2.68 ($^3J_{HH} = 7.7$ Hz, 2H, t, H(3)), 2.70 ($^3J_{HH} = 7.4$ Hz, 2H, t, H(5)), 3.14 ($^2J_{119SnH} = 86$ Hz, 4H, s, Sn–CH_2), 4.54 ($^3J_{HH} = 6.2$ Hz, 2H, d, N–CH_2), 7.03–7.42 (15H, m, aromatic-H), 9.92 (1H, s, –NH). ^{13}C-NMR: δ 19.6 (C(4)), 33.9 (C(3)), 34.6 (C(5)), 36.0 (Sn–CH_2), 50.2 (N–CH_2), 120.5 (C(1)), 124.8–138.1 (aromatic-C), 172.5 (C(2)), 192.8 (C(6)).

3.7. Synthesis of Bz$_2$Sn(BzACDA)$_2$ (3b)

A solution of HBzACDA (0.400 g, 1.6 mmol) and Et$_3$N (0.162 g, 1.6 mmol) in MeOH (20 cm^3) was added to a solution of Bz$_2$SnCl$_2$ (0.299 g, 0.8 mmol) in the same solvent (5 cm^3). The mixture was stirred overnight. The resultant orange precipitate was filtered, washed with MeOH and dissolved in CH$_2$Cl$_2$ (10 cm^3). Methanol (5 cm^3) was added and the solution then was kept at −4 °C to give orange needles, m.p. (dec.) 177–199 °C. Yield: 0.46 g (72%). Anal. Calc. for C$_{40}$H$_{44}$N$_2$S$_4$Sn: C, 60.07; H, 5.54; N, 3.50. Found: C, 59.38; H, 5.30; N, 3.58%. ^{1}H-NMR: δ 1.78 ($^3J_{HH} = 7.4$ Hz, 4H, tt, H(4)), 2.67 ($^3J_{HH} = 7.7$ Hz, 4H, t, H(3)), 2.79 ($^3J_{HH} = 7.6$ Hz, 4H, t, H(5)), 3.38 ($^2J_{119SnH} = 88$ Hz, 4H, s, Sn–CH_2), 4.58 ($^3J_{HH} = 6.3$ Hz, 4H, s, N–CH_2), 6.97–7.41 (20H, m, aromatic-H), 11.23 (2H, s, –NH). ^{13}C-NMR: δ 19.7 (C(4)), 33.7 (C(3)), 35.2 (C(5)), 38.0 (Sn–CH_2), 49.4 (N–CH_2), 120.4 (C(1)), 124.3–139.7 (aromatic-C), 168.9 (C(2)), 200.6 (C(6)).

3.8. Synthesis of Bz$_3$Sn(BzACDA) (3c)

A solution of HBzACDA (0.300 g, 1.2 mmol) and Et$_3$N (0.121 g, 1.2 mmol) in MeOH (10 cm^3) was added to a solution of Bz$_3$SnCl (0.515 g, 1.2 mmol) in CH$_2$Cl$_2$ (10 cm^3). The mixture was stirred for 5 h and then the solvent was removed under vacuum to give a gummy solid, which gave an orange powder when treated with acetone. The powder was filtered and recrystallized from CH$_2$Cl$_2$–MeOH (2:1) to give orange plates, m.p. 124–126 °C. Yield: 0.47 g (61%). Anal. Calc. for C$_{34}$H$_{35}$NS$_2$Sn: C, 63.76; H, 5.51; N, 2.19. Found: C, 63.36; H, 5.62; N, 2.25%. ^{1}H-NMR: δ 1.80 ($^3J_{HH} = 7.4$ Hz, 2H, tt, H(4)), 2.61 ($^2J_{119SnH} = 67$ Hz, 6H, s, Sn–CH_2), 2.67 ($^3J_{HH} = 7.9$ Hz, 2H, t, H(3)), 2.89 ($^3J_{HH} = 7.5$ Hz, 2H, t, H(5)), 4.54 ($^3J_{HH} = 6.2$ Hz, 2H, d, N–CH_2), 6.76–7.38 (20H, m, aromatic-H), 11.88 (1H, s, –NH). ^{13}C-NMR: δ 19.7 (C(4)), 25.2 ($^1J_{SnC} = 280$ Hz, Sn–CH_2), 33.6 (C(3)), 35.5 (C(5)), 49.5 (N–CH_2), 120.9 (C(1)), 123.8–141.0 (aromatic-C), 170.0 (C(2)), 197.6 (C(6)).

3.9. X-ray structure analysis of 1c, 2 and 3b

Data were collected in Kappa CDD diffractometer at 173 K by using Mo–K radiation and the structures were solved by direct methods. Further details are given in Table 5. Full matrix least-squares against F^2 (SHELXL-97) was used for refinement with non-H atoms anisotropic and H atoms in riding mode anisotropic.

For **1c** and **3b** the amine H atom was refined freely and the rest were included in riding mode. For **2** all atoms were refined freely.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 165159, 165161 and 165160 for compounds **1c**, **2** and **3b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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