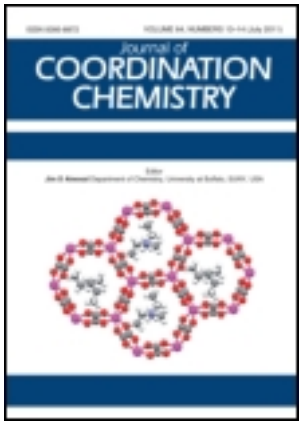

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Synthesis and characterization of stannacyclododecane-yl-dithiocarbamates

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Synthesis and characterization of stannacyclododecane-yl-dithiocarbamates

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Thirteen new stannacyclododecane dithiocarbamate complexes have been prepared by reacting 12-chloro-12-*n*-butyl-1,11-dioxa-4,8-dithia-12-stannacyclododecane (**1**) and 12-chloro-12-*n*-butyl-1,4,8,11-tetrathia-12-stannacyclododecane (**2**) with pyrrolidine-, morpholine-, thiomorpholine-, piperidine-, piperazinebis-, and 3-pyrroline-carbodithioates, respectively, as well as with diethyl-dithiocarbamate. All complexes were characterized by elemental analyses, IR, EI-MS, and NMR (^{1}H, ^{13}C, and ^{119}Sn) studies. The spectroscopic data suggest the replacement of the chlorides by the corresponding dithiocarbamates with monodentate coordination, leading to six-coordinate tin atoms in all the cases.

Keywords: Dithiocarbamates; Tin complexes; Organotin

1. Introduction

We have been interested in studying the influence of 1,1-dithiolates, dithiophosphinates (S_2PR_2) [1–3], dithiophosphates $S_2P(OR)_2$ [4], and dithiocarbamates (S_2CNR_2) [5] on the structural preference of main group cations in metallocene structures. Furthermore, dithiocarbamates have been used with heavy *p*-block metals leading to a variety of structural arrangements [6]. We reported [7] the synthesis of two tin(IV) twelve-membered metallacycles, 12-chloro-12-*n*-butyl-1,11-dioxa-4,8-dithia-12-stannacyclododecane (**1**) and 12-chloro-12-*n*-butyl-1,4,8,11-tetrathia-12-stannacyclododecane (**2**).

The coordination chemistry of this type of polydentate thioethers with transition cations has been studied in detail across the transition series, as well as studies with dithiocarbamates and transition elements [8]. There are reports of rhodium complexes [9] in which the length of the chain has been changed, in order to study *cis versus trans* preferences for the complex. Such studies show that a short chain prefers the *cis* isomer

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while a larger chain prefers the *trans* isomer. Although both isomers are observed when the chain size is similar to the chain in **1** and **2**, compounds containing main group elements have been much less studied. Exchange of chloride by a potential bidentate ligand, such as a dithiocarbamate, can lead to increased coordination numbers for tin.

Herein, we report the preparation of 13 organotin(IV) derivatives of **1** and **2** containing dithiocarbamates and their characterization by elemental analyses, IR, EI-MS, and NMR (^{1}H, ^{13}C, and ^{119}Sn) with the goal of obtaining compounds in which the tin has a high coordination number in a ring system, and to study the influence of dithiolate ligands in coordination of tin.

2. Experimental

2.1. *Materials and methods*

All reagents were of commercial grade and used as received. Compounds **1** and **2** were prepared by procedures reported in the literature [6]. IR spectra were recorded from 4000 to 400 cm^{-1} as KBr pellets using a Bruker-Vector spectrometer. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ were obtained on a Varian Unity Inova System 400 MHz operating at 399.747 (^{1}H), 100.515 MHz (^{13}C). ^{119}Sn NMR spectra were obtained on a Bruker 300 MHz operating at 111.853 MHz. The chemical shifts reported are relative to internal Me_4Si (^{1}H, ^{13}C) and external Me_4Sn (^{119}Sn) for the indicated nuclei. Mass spectra were performed on a Hewlett-Packard MS/GS 598 instrument by electron impact at 70 eV.

2.2. *General synthetic procedure*

To a dichloromethane solution of 12-chloro-12-*n*-butyl-1,11-dioxa-4,8-dithia-12-stannacyclododecane (**1**) or 12-chloro-12-*n*-butyl-1,4,8,11-tetrathia-12-stannacyclododecane (**2**) was added a stoichiometric quantity of the corresponding dithiocarbamate salt (Na dtc) and stirred overnight. The precipitated sodium chloride was filtered after drying over anhydrous Na_2SO_4, the filtrate was concentrated in vacuum to give the derivative, which was then purified by recrystallization from hot hexanes.

Characterization of 3. **IR** (KBr): $\nu = 2953$, 2869, 1447, 1512, 1050, 690, 1252, 945, 1004, 1335. **EI MS** (70 eV): 358 $[C_7H_{12}S_3O_2NSn]^+$, 266 $[C_5H_8S_2NSn]^+$, 178 $[C_7H_{14}S_2O]^+$, 151 $[C_5H_{11}S_2O]^+$, 107 $[C_3H_7S_2]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): δ 0.97 (3H, t, $\mathbf{CH_3}CH_2CH_2CH_2$–, $J = 7.2$,), 1.51 (2H, sext, $CH_3\mathbf{CH_2}CH_2CH_2$–, $J = 7.2$), 1.89 (4H, q, $CH_3CH_2\mathbf{CH_2}CH_2$–, $-CH_2\mathbf{CH_2}CH_2$–, $J = 7.2$), 2.17 (6H, m, $CH_3CH_2CH_2\mathbf{CH_2}$–, $-NCH_2\mathbf{CH_2}\mathbf{CH_2}CH_2$), 2.66 (4H, t, $-\mathbf{CH_2}CH_2\mathbf{CH_2}$–, $J = 7.2$), 2.73 (4H, t, $-S\mathbf{CH_2}CH_2O$–, $J = 5.6$), 3.70 (4H, t, $-SCH_2\mathbf{CH_2}O$–, $J = 5.6$), 3.74 (4H, t, $-N\mathbf{CH_2}CH_2CH_2\mathbf{CH_2}$, $J = 5.6$). **^{13}C NMR** (ppm): 13.69, 25.50, 27.13, 29.72 (*n*-Bu), 27.24 ($-NCH_2\mathbf{CH_2}\mathbf{CH_2}CH_2$), 30.78 ($-\mathbf{CH_2}CH_2\mathbf{CH_2}$–), 35.60 ($-S\mathbf{CH_2}CH_2O$–), 37.85 ($-CH_2\mathbf{CH_2}CH_2$–), 56.12 ($-N\mathbf{CH_2}CH_2CH_2\mathbf{CH_2}$), 60.81 ($-SCH_2\mathbf{CH_2}O$–), 190.05 ($-S\mathbf{C}S$–). **^{119}Sn NMR** (ppm): −280.91 Anal. Calcd for $C_{16}H_{31}NO_2S_4Sn$ (%): C, 37.21; H, 6.05. Found: C, 37.09; H, 5.83.

Characterization of 4. **IR** (KBr): **ν** = 2955, 2861, 1432, 1495, 1023, 997, 684, 1238, 1302. **EI MS** (70 eV): 501 $[C_{16}H_{31}S_3NO_3Sn]^+$, 374 $[C_7H_{12}S_3O_3NSn]^+$, 282 $[C_5H_8S_2NOSn]^+$, 151 $[C_5H_{11}S_2O]^+$, 88 $[C_4H_8S]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.2$), 1.51 (2H, sext, $CH_3CH_2CH_2CH_2$–, $J = 7.2$), 1.88 (4H, q, $CH_3CH_2CH_2CH_2$–, –$CH_2CH_2CH_2$–, $J = 7.2$), 2.26 (2H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.2$), 2.66 (4H, t, –$CH_2CH_2CH_2$–, $J = 6.8$), 2.73 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 3.74 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 3.82 (4H, t, –$NCH_2CH_2OCH_2CH_2$, $J = 4.8$), 3.92 (4H, t, –$NCH_2CH_2OCH_2CH_2$, $J = 4.8$). **^{13}C NMR** (ppm): 13.68, 18.60, 27.60, 29.75 (*n*-Bu), 30.82 (–$CH_2CH_2CH_2$–), 35.61 (–SCH_2CH_2O–), 37.84 (–$CH_2CH_2CH_2$–), 53.05 (–$NCH_2CH_2OCH_2CH_2$), 60.84 (–SCH_2CH_2O–), 65.95 (–$NCH_2CH_2OCH_2CH_2$), 194.72 (–SCS–). **^{119}Sn NMR** (ppm): −205.76 Anal. Calcd for $C_{16}H_{31}NO_3S_4Sn$ (%): C, 36.10; H, 5.87. Found: C, 37.92; H, 5.91.

Characterization of 5. **IR** (KBr): **ν** = 2925, 2861, 1444, 1514, 1053, 1007, 682, 1138, 1243. **EI MS** (70 eV): 497 $[C_{17}H_{31}S_3O_2NSn]^+$, 475 $[C_{13}H_{25}S_4O_2NSn]^+$, 372 $[C_{11}H_{24}S_2O_2Sn]^+$, 280 $[C_6H_{10}S_2NSn]^+$, 128 $[C_6H_{10}SN]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.4$), 1.50 (2H, sext, $CH_3CH_2CH_2CH_2$–, $J = 7.4$), 1.77 (6H, $CH_3CH_2CH_2CH_2$–, –$CH_2CH_2CH_2$–, –$NCH_2CH_2CH_2CH_2CH_2$, m), 1.89 (4H, t, –$NCH_2CH_2CH_2CH_2CH_2$, $J = 6.0$), 2.23 (2H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.4$), 2.66 (4H, t, –$CH_2CH_2CH_2$–, $J = 7.4$), 2.74 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 3.74 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 3.86 (4H, t, –$NCH_2CH_2CH_2CH_2CH_2$, $J = 6.0$). **^{13}C NMR** (ppm): 13.76, 22.45, 25.49, 29.44 (*n*-Bu), 25.89 (–$NCH_2CH_2CH_2CH_2CH_2$), 27.53 (–$NCH_2CH_2CH_2CH_2CH_2$), 30.50 (–$CH_2CH_2CH_2$–), 35.39 (–SCH_2CH_2O–), 37.22 (–$CH_2CH_2CH_2$–), 55.03 (–$NCH_2CH_2CH_2CH_2CH_2$), 60.56 (–SCH_2CH_2O–), 191.43 (–SCS–). **^{119}Sn NMR** (ppm): −292.93 Anal. Calcd for $C_{17}H_{33}NO_2S_4Sn$ (%): C, 38.49; H, 6.27. Found: C, 38.62; H, 6.34.

Characterization of 6. **IR** (KBr): **ν** = 2925, 2864, 1444, 1528, 1067, 685, 1149, 910, 1012, 1278. **EI MS** *m/z*: 344 $[C_7H_{14}S_3ONSn]^+$, 268 $[C_5H_{10}S_2NSn]^+$, 178 $[C_7H_{14}S_2O]^+$, 151 $[C_5H_{11}S_2O]^+$, 107 $[C_3H_7S_2]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.4$), 1.37 (3H, t, CH_3CH_2N–, $J = 7.4$), 1.51 (2H, sext, $CH_3CH_2CH_2CH_2$–, $J = 7.4$), 1.89 (4H, q, $CH_3CH_2CH_2CH_2$–, –$CH_2CH_2CH_2$–, $J = 7.4$), 2.24 (2H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.4$), 2.66 (4H, t, $CH_2CH_2CH_2$–, $J = 7.4$), 2.73 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 3.71 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 3.77 (4H, c, CH_3CH_2N–, $J = 7.4$). **^{13}C NMR** (ppm): 12.15 (CH_3CH_2N–), 13.74, 25.47, 27.53, 29.46 (*n*-Bu), 30.53 (–$CH_2CH_2CH_2$–), 35.39 (–SCH_2CH_2O–), 37.19 (–$CH_2CH_2CH_2$–), 51.86 (CH_3CH_2N–), 60.58 (–SCH_2CH_2O–), 192.85 (–SCS–). **^{119}Sn NMR** (ppm): −287.21 Anal. Calcd for $C_{16}H_{33}NO_2S_4Sn$ (%): C, 37.07; H, 6.42. Found: C, 36.83; H, 6.17.

Characterization of 7. **IR** (KBr): **ν** = 2953, 2859, 1628, 1447, 1490, 1353, 1181, 1049, 998, 672, 953. **EI MS** *m/z*: 355 $[C_7H_9S_3O_2NSn]^+$, 264 $[C_5H_6S_2NSn]^+$, 178 $[C_7H_{14}S_2O]^+$, 151 $[C_5H_{11}S_2O]^+$, 107 $[C_3H_7S_2]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.0$), 1.51 (2H, sext, $CH_3CH_2CH_2CH_2$–, $J = 7.0$), 1.89 (4H, q, $CH_3CH_2CH_2CH_2$–, –$CH_2CH_2CH_2$–, $J = 7.0$), 2.27 (4H, t, $CH_3CH_2CH_2CH_2$–, $J = 7.0$), 2.66 (4H, t, –$CH_2CH_2CH_2$–, $J = 7.0$), 2.73 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 3.74 (4H, t, –SCH_2CH_2O–, $J = 5.8$), 4.44 (4H, d, –$NCH_2CHCHCH_2$, $J = 5.8$), 5.89 (2H, d, –$NCH_2CHCHCH_2$, $J = 5.8$). **^{13}C NMR** (ppm): 13.74, 25.48, 27.53, 31.08 (*n*-Bu), 30.54 (–$CH_2CH_2CH_2$–), 35.38 (–SCH_2CH_2O–), 38.07 (–$CH_2CH_2CH_2$–),

60.61 (–N**C**H$_2$CHCH**C**H$_2$), 62.00 (–SCH$_2$**C**H$_2$O–), 126.02 (–NCH$_2$**C**H**C**HCH$_2$), 191.23 (–S**C**S–). **^{119}Sn NMR** (ppm): −268.00 Anal. Calcd for $C_{16}H_{29}NO_2S_4Sn$ (%): C, 37.36; H, 5.68. Found: C, 37.51; H, 5.84.

Characterization of 8. **IR** (KBr): **ν** = 2921, 2864, 1428, 1484, 1278, 1150, 1044, 999, 683. **EI MS** *m*/*z*: 372 $[C_7H_{12}N_2O_2S_3Sn]^+$, 252 $[C_4H_6NS_2Sn]^+$, 151 $[C_5H_{11}S_2O]^+$, 107 $[C_3H_7S_2]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.98 (6H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.4), 1.51 (4H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.4) 1.89 (8H, q, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, *J* = 7.4), 2.30 (4H, t, CH$_3$CH$_2$CH$_2$C**H$_2$**–, *J* = 7.4), 2.66 (8H, t, –C**H$_2$**CH$_2$C**H$_2$**–, *J* = 7.4), 2.74 (8H, t, –SC**H$_2$**CH$_2$O–, *J* = 5.8), 3.74 (8H, t, –SCH$_2$C**H$_2$**O–, *J* = 5.8), 4.17 (8H, sa, –NC**H$_2$**C**H$_2$**N–). **^{13}C NMR** (ppm): 13.78, 22.51, 27.60, 29.48 (*n*-Bu), 30.55 (–**C**H$_2$CH$_2$**C**H$_2$–), 35.49 (–S**C**H$_2$CH$_2$O–), 38.47 (–CH$_2$**C**H$_2$CH$_2$–), 51.08 (–N**C**H$_2$**C**H$_2$N–), 60.59 (–SCH$_2$**C**H$_2$O–), 197.64 (–S**C**S–). **^{119}Sn NMR** (ppm): −245.3 Anal. Calcd for $C_{28}H_{54}N_2O_4S_8Sn_2$ (%): C, 34.43; H, 5.57. Found: C, 34.09; H, 5.35.

Characterization of 9. **IR** (KBr): **ν** = 2919, 2862, 1503, 1446, 1251, 1157, 945, 998, 692. **EI MS** *m*/*z*: 492 $[C_{12}H_{22}S_6NSn]^+$, 266 $[C_5H_8S_2NSn]^+$, 147 $[C_5H_8S_2N]^+$, 167 $[C_5H_{11}S_3]^+$, 107 $[C_3H_7S_2]^+$, 61 $[C_2H_5S]^+$. **^{1}H NMR** (ppm): 0.96 (3H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.2), 1.49 (2H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.2), 1.87 (4H, q, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, *J* = 7.2), 2.13 (6H, CH$_3$CH$_2$CH$_2$C**H$_2$**–, –NCH$_2$C**H$_2$**C**H$_2$**CH$_2$, m), 2.71 (12H, –C**H$_2$**S–, m,), 3.69 (4H, t, –NC**H$_2$**CH$_2$CH$_2$C**H$_2$**, *J* = 6.8). **^{13}C NMR** (ppm): 13.73, 24.88, 25.75, 31.09 (*n*-Bu), 26.89 (–NCH$_2$**C**H$_2$**C**H$_2$CH$_2$), 27.95 (–SCH$_2$**C**H$_2$SSn–), 30.89 (–**C**H$_2$CH$_2$**C**H$_2$–), 35.38 (–CH$_2$**C**H$_2$CH$_2$–), 36.35 (–S**C**H$_2$CH$_2$SSn–), 55.43 (–N**C**H$_2$CH$_2$CH$_2$**C**H$_2$), 191.74 (–S**C**S–). **^{119}Sn NMR** (ppm): −295.00 Anal. Calcd for $C_{16}H_{31}NS_6Sn$ (%): C, 35.03; H, 5.70. Found: C, 34.31; H, 5.98.

Characterization of 10. **IR** (KBr): **ν** = 2955, 2855, 1437, 1503, 1267, 1199, 1113, 1025, 994, 754. **EI MS** *m*/*z*: 345 $[C_7H_{13}S_4Sn]^+$, 281 $[C_5H_7S_2NOSn]^+$, 226 $[C_7H_{14}S_4]^+$, 161 $[C_7H_{13}S_2]^+$, 186 $[S_2H_2Sn]^+$, 97 $[C_5H_7NO]^+$, 55 $[C_4H_7]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.2), 1.49 (2H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.2), 1.88 (4H, q, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, *J* = 7.2), 2.15 (2H, t, CH$_3$CH$_2$CH$_2$C**H$_2$**–, *J* = 7.2), 2.86 (12H, –C**H$_2$**S–, m), 3.80 (4H, t, –NC**H$_2$**CH$_2$OCH$_2$C**H$_2$**, *J* = 5.2), 3.95 (4H, t, –NCH$_2$C**H$_2$**OC**H$_2$**CH$_2$, *J* = 5.2). **^{13}C NMR** (ppm): 13.83, 25.85, 28.07, 31.76 (*n*-Bu), 29.56 (–SCH$_2$**C**H$_2$SSn–), 31.17 (–**C**H$_2$CH$_2$**C**H$_2$–), 36.27 (–CH$_2$**C**H$_2$CH$_2$–), 38.90 (–S**C**H$_2$CH$_2$SSn–), 52.34 (–N**C**H$_2$CH$_2$OCH$_2$**C**H$_2$), 66.01 (–NCH$_2$**C**H$_2$O**C**H$_2$CH$_2$), 197.32 (–S**C**S–). **^{119}Sn NMR** (ppm): −243.13 Anal. Calcd for $C_{16}H_{31}NOS_6Sn$ (%): C, 34.04; H, 5.53. Found: C, 34.27; H, 5.72.

Characterization of 11. **IR** (KBr): **ν** = 2953, 2867, 1504, 1437, 1282, 1197, 1025, 998, 684. **EI MS** *m*/*z*: 298 $[C_5H_8S_3NSn]^+$, 225 $[C_3H_5S_2Sn]^+$, 178 $[C_5H_8S_3N]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.2), 1.49 (2H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.2), 1.88 (4H, q, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, *J* = 7.2), 2.15 (2H, t, CH$_3$CH$_2$CH$_2$C**H$_2$**–, *J* = 7.2), 2.90 (16H, −C**H$_2$**S–, m), 4.22 (4H, t, –NC**H$_2$**CH$_2$SCH$_2$C**H$_2$**, *J* = 5.4). **^{13}C NMR** (ppm): 13.85, 25.86, 28.09, 29.88 (*n*-Bu), 27.85 (–SCH$_2$**C**H$_2$SSn–), 29.56 (–**C**H$_2$CH$_2$**C**H$_2$–), 31.18 (–NCH$_2$**C**H$_2$S**C**H$_2$CH$_2$), 35.42 (–CH$_2$**C**H$_2$CH$_2$–), 36.28 (–S**C**H$_2$CH$_2$SSn–), 55.26 (–N**C**H$_2$CH$_2$SCH$_2$**C**H$_2$), 197.48 (–S**C**S–). **^{119}Sn NMR** (ppm): −275.38 Anal. Calcd for $C_{16}H_{31}NS_7Sn$ (%): C, 33.10; H, 5.38. Found: C, 32.85; H, 5.03.

Characterization of 12. **IR** (KBr): **ν** = 2921, 2855, 1507, 1441, 1242, 1136, 1004, 972, 687. **EI MS** *m/z*: 381 $[C_5H_9S_6Sn]^+$, 358 $[C_7H_{12}S_4NSn]^+$, 336 $[C_{16}H_{20}S_2NSn]^+$, 114 $[C_5H_8SN]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.4), 1.49 (2H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.2), 1.82 (10H, m, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, –NCH$_2$C**H$_2$**C**H$_2$**C**H$_2$**CH$_2$), 2.13 (2H, t, CH$_3$CH$_2$CH$_2$C**H$_2$**–, *J* = 7.4), 2.90 (12H, m, –C**H$_2$**S–), 3.88 (4H, –NC**H$_2$**CH$_2$CH$_2$**H$_2$**CH$_2$C**H$_2$**, s.a). **^{13}C NMR** (ppm): 13.82, 22.73, 27.97, 31.03 (*n*-Bu), 24.89 (–NCH$_2$CH$_2$**CH$_2$**CH$_2$CH$_2$), 28.85 (–NCH$_2$**CH$_2$**CH$_2$**CH$_2$**CH$_2$CH$_2$), 29.46 (–SCH$_2$**CH$_2$**SSn–), 30.82 (–**CH$_2$**CH$_2$**CH$_2$**–), 36.26 (–CH$_2$**CH$_2$**CH$_2$–), 36.31 (–S**CH$_2$**CH$_2$SSn–), 54.26 (–N**CH$_2$**CH$_2$CH$_2$**H$_2$**CH$_2$**CH$_2$**), 193.63 (–S**C**S–). **^{119}Sn NMR** (ppm): −310.48 Anal. Calcd for $C_{17}H_{33}NS_6Sn$ (%): C, 36.30; H, 5.91. Found: C, 36.09; H, 5.74.

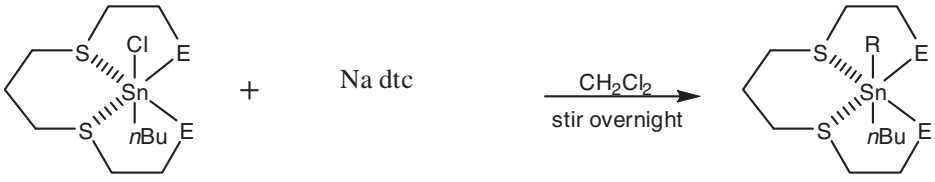
Characterization of 13. **IR** (KBr): **ν** = 2922, 2863, 1513, 1436, 1274, 1199, 1071, 989, 687. **EI MS** *m/z*: 360 $[C_7H_{14}S_4NSn]^+$, 268 $[C_5H_{10}S_2NSn]^+$, 194 $[C_7H_{14}S_3]^+$, 167 $[C_5H_{11}S_3]^+$, 107 $[C_3H_7S_2]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.97 (3H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.2), 1.35 (6H, t, –NCH$_2$C**H$_3$**, *J* = 7.2), 1.50 (2H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.2), 1.88 (4H, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, m), 2.13 (2H, t, CH$_3$CH$_2$CH$_2$C**H$_2$**–, *J* = 7.2), 2.91 (12H, m, –C**H$_2$**S–), 3.74 (4H, c, –NC**H$_2$**CH$_3$, *J* = 7.2). **^{13}C NMR** (ppm): 13.80, 24.89, 25.75, 30.83 (*n*-Bu), 12.14 (–NCH$_2$**CH$_3$**), 27.97 (–SCH$_2$**C**H$_2$SSn–), 29.45 (–**C**H$_2$CH$_2$**C**H$_2$–), 31.03 (–CH$_2$**C**H$_2$CH$_2$–), 36.27 (–S**C**H$_2$CH$_2$SSn–), 51.08 (–NC**H$_2$**CH$_3$), 197.42 (–S**C**S–). **^{119}Sn NMR** (ppm): −300.76 Anal. Calcd for $C_{16}H_{33}NS_6Sn$ (%): C, 34.91; H, 6.04. Found: C, 33.79; H, 5.82.

Characterization of 14. **IR** (KBr): **ν** = 2920, 2855, 1627, 1506, 1449, 1252, 1184, 1077, 996, 673. **EI MS** *m/z*: 387 $[C_7H_9S_5NSn]^+$, 264 $[C_5H_6S_2NSn]^+$, 194 $[C_7H_{14}S_3]^+$, 167 $[C_5H_{11}S_3]^+$, 107 $[C_3H_7S_2]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.98 (3H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.4), 1.51 (2H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.4), 1.89 (4H, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, q, *J* = 7.4), 2.18 (2H, t, CH$_3$CH$_2$CH$_2$C**H$_2$**–, *J* = 7.4), 2.80 (12H, m, –C**H$_2$**S–), 4.46 (4H, sa, –NC**H$_2$**CHCHC**H$_2$**), 5.90 (2H, sa, –NCH$_2$C**H**C**H**CH$_2$). **^{13}C NMR** (ppm): 13.82, 24.91, 25.80, 30.88 (*n*-Bu), 27.97 (–SCH$_2$**C**H$_2$SSn–), 29.50 (–**C**H$_2$CH$_2$**C**H$_2$–), 31.07 (–CH$_2$**C**H$_2$CH$_2$–), 36.16 (–S**C**H$_2$CH$_2$SSn–), 61.44 (–N**C**H$_2$CHCH**C**H$_2$), 125.94 (–NCH$_2$**C**H**C**HCH$_2$), 198.43 (–S**C**S–). **^{119}Sn NMR** (ppm): −284.32 Anal. Calcd for $C_{15}H_{27}NS_6Sn$ (%): C, 35.16; H, 5.35. Found: C, 35.29; H, 5.56.

Characterization of 15. **IR** (KBr): **ν** = 2921, 2857, 1425, 1473, 1274, 1126, 1028, 995, 683. **EI MS** *m/z*: 404 $[C_7H_{12}N_2S_5Sn]^+$, 252 $[C_4H_6NS_2Sn]^+$, 167 $[C_5H_{11}S_3]^+$, 107 $[C_3H_7S_2]^+$, 57 $[C_4H_9]^+$. **^{1}H NMR** (ppm): 0.95 (6H, t, C**H$_3$**CH$_2$CH$_2$CH$_2$–, *J* = 7.2), 1.47 (4H, sext, CH$_3$C**H$_2$**CH$_2$CH$_2$–, *J* = 7.2), 1.85 (8H, CH$_3$CH$_2$C**H$_2$**CH$_2$–, –CH$_2$C**H$_2$**CH$_2$–, m), 2.17 (4H, t, CH$_3$CH$_2$CH$_2$C**H$_2$**–, *J* = 7.2), 2.90 (24H, m, –C**H$_2$**S–), 4.14 (8H, s.a, –NC**H$_2$**C**H$_2$**N–). **^{13}C NMR** (ppm): 13.82, 25.03, 25.88, 31.17 (*n*-Bu), 28.16 (–SCH$_2$**C**H$_2$SSn–), 29.90 (–**C**H$_2$CH$_2$**C**H$_2$–), 31.34 (–S**C**H$_2$CH$_2$SSn–), 31.95 (–CH$_2$**C**H$_2$CH$_2$–), 50.66 (–N**C**H$_2$**C**H$_2$N–), 199.66 (–S**C**S–). **^{119}Sn NMR** (ppm): −254.05 Anal. Calcd for $C_{28}H_{54}N_2S_{12}Sn_2$ (%): C, 32.31; H, 5.23. Found: C, 32.07; H, 4.96.

3. Results and discussion

Compounds **3–15** were synthesized by metathesis using stoichiometric ratios of **1** or **2** with the corresponding sodium dithiocarbamate in dichloromethane at ambient



1 E=O
2 E=S

3–15

3; R = pyrrolidine-carbodithioate, E = O
4; R = morpholine-carbodithioate, E = O
5; R = piperidine-carbodithioate, E = O
6; R = diethyl-dithiocarbamate, E = O
7; R = 3-pyrroline-carbodithioates, E = O
8; R = piperazinebis-carbodithioate, E = O
9; R = pyrrolidine-carbodithioate, E = S
10; R = morpholine-carbodithioate, E = S
11; R = thiomorpholine-carbodithioate, E = S
12; R = piperidine-carbodithioate, E = S
13; R = diethyl-dithiocarbamate, E = S
14; R = 3-pyrroline-carbodithioates, E = S
15; R = piperazinebis-carbodithioate, E = S

Scheme 1. Synthetic method.

Table 1. IR frequencies for **3–15**.

	Frequencies												
Compound	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
νC–H	2953f	2955f	2925f	2925f	2953f	2921f	2919f	2955f	2953f	2921f	2922f	2920f	2921f
(CH_2,CH_3)	2869m	2861m	2861m	2864m	2859m	2864m	2862m	2855m	2867m	2855m	2863m	2855m	2857m
δC–H	1447f	1432f	1444f	1444f	1447f	1428f	1446f	1437f	1437f	1441f	1436f	1449f	1425f
(CH_2,CH_3)													
νN–C = S	1512f	1495f	1514f	1528f	1490f	1484f	1503f	1503f	1504f	1507f	1513f	1506f	1473f
νC–O	1050m	1108f	1107d	1049f	1049m	1050m		1113f					
νC–S	690d	684d	682d	685m	672m	683d	692m	754m	684m	687m	687m	673f	683m
νC = S	1252d	1238f	1138d	1200m	1181m	1229m	1157m	1199m	1197m	1136d	1199f	1184f	1126m
νCSS	945d	997m	1007m	1012m	953m	1044m	945m	994m	998m	972d	989m	996m	995m
	1004m	1023m	1053m	1067m	998m	999f	998d	1025m	1025d	1004m	1071m	1077d	1028d
νC–N	1335m	1302d	1243f	1278m	1353m	1278m	1251m	1267f	1282f	1242f	1274f	1252m	1274m
νC = C					1628d							1627d	
νSn–O	462d	541f	513d	494d	468d	489m							
νSn–S							459d	410f	500f	510f	501d	501d	445d

temperature (scheme 1). Compounds **3–15** are colorless and viscous liquids, moisture, and air stable for short periods of time (1 or 2 weeks). However, upon standing for longer periods **3–15** appear to decompose to a mixture of different compounds as shown in the ^{119}Sn NMR.

IR spectra of all compounds (table 1) reveal a strong band between 1473 and 1528 cm^{-1} assigned to the thioureide, which is observed in dithiocarbamates due to C–N vibration [10]. Two other absorptions are observed at 945 and 1053 cm^{-1} from the $\nu(CS_2)$ vibration. This suggests monodentate coordination of the dithiocarbamates to tin [11]. Furthermore, a single band between 1238 and 1126 cm^{-1} corresponding to νC=S indicates monodentate coordination for **3-15**.

Table 2. Chemical shifts for ^{119}Sn NMR.

Compound	Shift (ppm)
3	−280.91
4	−205.76
5	−292.93
6	−287.21
7	−268.00
8	−243.30
9	−295.00
10	−243.13
11	−275.38
12	−310.48
13	−300.76
14	−284.32
15	−254.05

The EI mass spectra do not exhibit the molecular ion, but the data are easily related to the proposed structures. All spectra show the fragment from loss of the *n*-butyl group for the molecular ion, as well as fragments corresponding to the fragmentation pattern of **1** and **2** and fragments owing to the dithiocarbamate ligand [7]. It is important to note that all spectra also show fragments corresponding to tin bonded to dithiocarbamate.

^{1}H NMR spectra confirm the identity of **3–15** showing the expected integration and multiplicities in comparison with **1** and **2**. Additionally, signals corresponding to the dithiocarbamate ligand are observed in the expected region. The ^{13}C NMR spectra of **3–15** exhibit a downfield shift for carbons of the CH_2SCH_2 fragments and the tin-bonded methylene of the *n*-butyl, compared to those on **1** and **2**. Studies on transition metal complexes of related ligands exhibit a mixture of *trans* and *cis* isomers according to their NMR spectra, which show a double set of ^{13}C NMR signals [9]. However, this is not the case for **3–15** in which the ^{13}C NMR display only one set of signals, suggesting the existence of a single isomer.

The ^{119}Sn chemical shift of a tin complex is influenced by the coordination number of Sn, the electronegative character of the ligands and the bond angles at tin [12–14]. When the coordination number on tin increases, the ^{119}Sn signal shifts to higher field. For six-coordinate tin compounds, δ ^{119}Sn ranges from −125 to −515 ppm [15]. The ^{119}Sn NMR spectra of **3–15** (table 2) show signals from −205 and −310 ppm, thus suggesting that only one sulfur from dithiocarbamate participates in bonding to tin. This is supported by the IR studies discussed before as well as by the ^{119}Sn NMR spectra reported for the stannacyclododecane-yl-dithiocarbamates in which the chemical shifts of five-coordinate complexes are typically between −150 and −195 ppm [5]. In comparison, ^{119}Sn shifts of **3–15** are at higher field, which suggests the coordination number for tin in these compounds is six.

4. Conclusion

It was possible to prepare 13 new stannacyclododecane dithiocarbamate complexes as viscous liquids, soluble in chloroform and dichloromethane. Spectroscopic techniques

suggest six-coordinate tin, as shown by IR and ^{119}Sn NMR, consistent with similar compounds reported before [6].

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References

[1] M.A. Muñoz-Hernández, R. Cea-Olivares, G. Espinosa-Pérez, S. Hernández-Ortega. *J. Chem. Soc., Dalton Trans.*, 4135 (1996).
[2] M.A. Muñoz-Hernández, R. Cea-Olivares, S. Hernández-Ortega. *Z. Anorg. Allg. Chem.*, **622**, 1392 (1996).
[3] M.A. Muñoz-Hernández, R. Cea-Olivares, G. Espinosa-Pérez, S. Hernández-Ortega. *Z. Anorg. Allg. Chem.*, **623**, 642 (1997).
[4] R. Cea-Olivares, M.A. Muñoz-Hernández, S. Hernández-Ortega, C. Silvestru. *Inorg. Chim. Acta*, **235**, 31 (1995).
[5] R. Cea-Olivares, V. García-Montalvo, R.A. Toscano, A. Gómez-Ortiz, R. Ferrari-Zijlstra, P. García y García, A.M. Cotero-Villegas, M. López-Cardoso. *Rev. Soc. Quim. Mex.*, **44**, 176 (2000).
[6] S. Khan, S.A.A. Nami, K.S. Siddiqi. *J. Organomet. Chem.*, **693**, 1049 (2008).
[7] G. Vargas-Pineda, M. López-Cardoso, P. García-García, R. Cea-Olivares. *Heteroatom Chem.*, **15**, 451 (2004).
[8] S. Khan, S.A.A. Nami, K.S. Siddiqi. *J. Organomet. Chem.*, **875**, 478 (2008).
[9] N. Goswami, R. Alberto, C.L. Barnes, S. Jurisson. *Inorg. Chem.*, **35**, 7546 (1996).
[10] H.M. Randle, R.G. Fowler, N. Fuson, J.R. Dangl. *Infrared Determination of Organic Structures*, Van Nostrand, New York (1949).
[11] F. Bonati, R. Ugo. *J. Organomet. Chem.*, **10**, 257 (1967).
[12] H.C. Clark, V.K. Jain, R.C. Mehrotra, B.P. Singh, G. Srivastava, T. Birchall. *J. Organomet. Chem.*, **279**, 385 (1985).
[13] P.J. Smith, A.P. Tupciauskas. *Ann. Rep. NMR Spectrosc.*, **8**, 291 (1978).
[14] H.C. Clark, V.K. Jain, I.J. McMahon, R.C. Mehrotra. *J. Organomet. Chem.*, **243**, 299 (1983).
[15] J.J. Otera. *J. Organomet. Chem.*, **221**, 57 (1981).