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Study on the intramolecular transannular chalcogen-tin interactions in dithiastannecine compounds

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ABSTRACT

Dithiastannecine compounds of the type [{ $D(C_6H_4CH_2S)_2$]SnR¹R²] with different donor atoms **D** were prepared, where **D** = O and R¹ = R² = Ph (**4a**); R¹ = Ph, R² = Cl (**5a**); R¹ = *n*-Bu, R² = Cl (**6a**); **D** = S and R¹ = R² = Ph (**4b**); R¹ = Ph, R² = Cl (**5b**); R¹ = *n*-Bu, R² = Cl (**6b**). The molecular structures of the monochloro compounds **5a**, **5b**, **6a**, and **6b** were established by single-crystal X-ray diffraction and exhibit trigonal bipyramidal geometry at the tin atom with different degrees of distortion being due a **D** ··· Sn interaction. The spiro compounds [{ $D(C_6H_4CH_2S)_2$]sn] with **D** = O (**7a**) and **D** = S (**7b**) were also synthesized and structurally characterized; the molecular structure of **7a** showed the tin atom with a bicapped tetrahedral geometry. The behavior of all tin compounds in solution was investigated by NMR spectroscopy revealing that the **D** ···Sn interaction in solution was practically absent on the basis of the NMR chemical shifts values. DFT calculations with ADF package using VWN/QZ4P were carried out for the **6a** and **6b** compounds and showed that, in the topological analysis, bond critical points are present along the **D** ···Sn direction.

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1. Introduction

The heavy group 14 metals have attracted great interest because their environmental and toxicologic relevance [1], broad diversity in coordination numbers [2], and unusual molecular and supramolecular structures [3] as well as NMR properties [4,5].

On the other hand, the hypervalence of these heavy elements have been extensively studied in a number of eight-membered heterocycles containing one of these elements as electron-acceptor atom **A** and the dithioligands { $D(CH_2CH_2S)_2$ }²⁻ (type I), [2,6,7] { $D(C_6H_4S)_2$ }²⁻ (type II) [8–10], and { $D(C_6H_4S)_2O$ }²⁻ (type III) [11] where **D** is an electron-donor atom as nitrogen, oxygen, or sulfur (Scheme 1). These studies have shown that the expected tetrahedral geometry of **A** (**A** = Ge, Sn, Pb) is modified by the existence of a non-covalent **D** · · **A** transannular interaction, leading to geometries close to trigonal bipyramidal (tbp). For a given **A** acceptor, these structural modifications are dependent on several factors such as the donor abilities of **D**, the nature of the pendant ligands R attached to **A** that influences its Lewis acidity, and the flexibility of the dithioligand. Respect to this last point, we have reported some germanium compounds of the type III containing rigid ligands and observed that the interaction $D \cdots A$ was modulated according to the nature of the R groups [11]. Thus, we decided to study more flexible ligands attached to tin that could form larger rings in order to gain a deeper insight into the nature of the transannular interaction in larger heterocyclic compounds; to our knowledge, there is no report on dithioligands coordinated to heavy p-block elements able to form 10-membered rings of the type IV, although several dialkoxide analogous ligands able to form this type of rings were coordinated to different acceptor atoms as Al, Ti, Ta, and Zr [12,13]. Other examples containing 10-membered rings are those with tridentate trithioligands such as the tripodal tris-(2mercaptobenzyl)amine with nitrogen as donor atom that were coordinated to Ga and In, where the existence of a transannular interaction $N \cdot \cdot A$ (A = Ga, In) leaded to tbp geometries in these atrane compounds [14].

Following up on our studies on heterocyclic compounds of heavy p-block metals, here we report the synthesis, structural characterization, and a theoretical study of heterocyclic tin compounds containing a flexible 10-membered ring of the type IV with D = 0, S, where the $D \cdots$ Sn interaction influences the local geometry of the acceptor tin atom, despite the greater size of the central ring compared with that observed in compounds of types I–III where the interaction $D \cdots A$ is well documented.



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Scheme 1. Heterocyclic compounds of heavy group 14 elements **A** containing dithioligands with donor atoms **D** that lead to donor–acceptor interactions.

2. Experimental

2.1. Materials and physical measurements

All the starting reagents were of analytical grade and used without further purification. Solvents were dried by standard methods and distilled prior to use. O(C₆H₅)₂, S(C₆H₅)₂, n-BuLi 2.5 M in hexanes, N,N,N',N'-tetramethylethylendiammine (TMEDA), paraformaldehyde powder, Ph₂SnCl₂, n-BuSnCl₃, SnCl₄, Me₂SnCl₂, 1,4diazabicyclo-[2.2.2]-octane (DABCO), and hydrochloric acid were purchased from Aldrich and used as supplied. Melting points of the compounds determined on a Mel-Temp II instrument are reported without correction. Elemental analyses were recorded on a Perkin-Elmer Series II CHNS/O Analyzer. Electron-impact mass spectra (EI-MS) were measured on either Finnigan MAT 8230 or Varian MAT CH5 instrument. The IR spectra (4000–400 cm⁻¹) were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer as KBr pellets and in CsI films. The Raman spectra in solid state (4000-100 cm⁻¹) were recorded on a Perkin-Elmer Spectrum GX NIR FT-RAMAN spectrometer with 10-280 mW laser power and 4 cm⁻¹ resolution. ¹H, ¹³C{¹H}, and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Jeol Eclipse 400 spectrometer operating at 399.78, 100.53, and 149.03 MHz, respectively. The chemical shifts are reported in ppm with respect to the references and stated relative to external tetramethylsilane (TMS) for ¹H and ¹³C NMR, and Me₄Sn for ¹¹⁹Sn NMR spectroscopy. All the spectra were acquired at room temperature (25 °C).

2.2. General synthesis of the diols $D(C_6H_4CH_2OH)$ (**D** = 0, **1a**; S, **1b**)

TMEDA was added to a solution of $D(C_6H_5)_2$ in hexane and the resulting mixture was cooled to 0 °C and then *n*-BuLi 2.5 M in hexanes was added slowly. After the mixture was stirred for 24 h, paraformaldehyde in small portions was added and then refluxed for 48 h. The mixture was acidified using HCl to pH 2, and the compound was extracted with chloroform. The organic layer was dried by means of a column filled with Celite and anhydrous Na₂SO₄ and then evaporated to dryness; a solid was obtained and washed with a solvent mixture of hexane–ethyl acetate.

2.2.1. O(C₆H₄CH₂OH)₂ (**1a**)

The above procedure was adopted to obtain 1a using the following compounds: $O(C_6H_5)_2$ (7.6 mL, 48 mmol), hexane (30 mL), TME-DA, (20.9 mL, 139 mmol), n-BuLi 2.5 M (50 mL, 125 mmol), paraformaldehyde (20.10 g, 670 mmol), chloroform (two portions 50 mL). Yield 48% (5.23 g). Mp 90 °C. Anal. Calc. for $C_{14}H_{14}O_3{:}$ C, 73.03; H, 6.13. Found: C, 73.01; H, 6.06%. IR (CsI): v = 3342(OH), 3065, 3039, 2932, 2878, 1603, 1581, 1485, 1452, 1234, 1190, 1112, 1039, 1012, 882, 795, 752 cm⁻¹. Raman (420 mW): v = 3066, 2887, 1604, 1212, 1448, 1212, 1160, 1038, 790, 751 cm⁻¹. NMR: ¹H (CDCl₃) δ = 7.35 dd [1H, H-3, ³J_{H3-H4} = 7.69 Hz, ${}^{4}J_{\text{H3-H5}}$ = 1.46 Hz], δ = 7.23 td [1H, H-5, ${}^{3}J_{\text{H5-H6}}$ = 7.69 Hz, ${}^{3}J_{\text{H4-}}$ $_{H5} = 7.69 \text{ Hz}, \ {}^{4}J_{H3-H5} = 1.46 \text{ Hz}], \ \delta = 7.09 \text{ td} [1H, H-4, \ {}^{3}J_{H4-}]_{H5} = 7.69 \text{ Hz}, \ {}^{3}J_{H3-H4} = 7.69 \text{ Hz}, \ {}^{4}J_{H4-H6} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 6.81 \text{ dd} [1H, H-4]_{H5} = 1.46 \text{ Hz}], \ \delta = 1.4$ H-6, ${}^{3}J_{\text{H5-H6}} = 7.69 \text{ Hz}$, ${}^{4}J_{\text{H4-H6}} = 1.46 \text{ Hz}$], $\delta = 4.61 \text{ s}$ [2H, H-1], $\delta = 3.54 \text{ s}$ [1H, OH]; ${}^{13}\text{C}{}^{1}\text{H}$ (CDCl₃): $\delta = 154.8$ (C7), 131.3 (C2), 130.2 (C3), 129.4 (C5), 123.7 (C4), 117.9 (C6), 61.4 (C1). EI-MS: m/ z (% intensity) 230 (10) [M]⁺, 212 (90) $[O(C_6H_4CH_2)_2O]^{+}$, 195 (90) [C₁₄H₁₁O]⁺, 181 (100) [C₁₃H₉O]⁺.

2.2.2. $S(C_6H_4CH_2OH)_2$ (**1b**)

S(C₆H₅)₂ (8.05 mL, 48 mmol), hexane (30 mL), TMEDA, (20.9 mL, 139 mmol), *n*-BuLi 2.5 M (50 mL, 125 mmol), paraformaldehyde (20.10 g, 670 mmol), chloroform (two portions 50 mL). Yield 52% (6.16 g). Mp 84–85 °C. *Anal.* Calc. for C₁₄H₁₄O₂S: C, 68.26; H, 5.73. Found: C, 68.41; H, 5.84%. IR (Csl): v = 3324(OH), 3059, 2875, 1589, 1568, 1466, 1441, 1196, 1031, 752 cm⁻¹. Raman (410 mW): $v = 3066, 3054, 1587, 1196, 1036, 796, 685 cm⁻¹. NMR: ¹H (CDCl₃) <math>\delta = 7.47$ dd [1H, H-3, ³*J*_{H3–H4} = 7.69 Hz, ⁴*J*_{H3–H5} = 1.49 Hz], $\delta = 7.29$ ddd [1H, H-4, ³*J*_{H3–H4} = 7.69 Hz, ³*J*_{H4–H5} = 7.32 Hz, ⁴*J*_{H4–H6} = 1.49 Hz], $\delta = 7.21$ ddd [1H, H-5, ³*J*_{H5–H6} = 7.69 Hz, ³*J*_{H4–H5} = 7.32 Hz, ⁴*J*_{H4–H6} = 1.49 Hz], $\delta = 4.75$ s [2H, H-1], $\delta = 2.25$ s [1H, OH]; ¹³C{¹H} (CDCl₃): $\delta = 141.2$ (C7), 133.3 (C2), 132.3 (C6), 128.8 (C3), 128.7 (C5), 128.0 (C4), 63.6 (C1). EI-MS: *m/z* (% intensity) 246 (88) [M]⁺, 228 (91) [M–H₂O]⁺, 211 (65) [C₁₄H₁₃S]⁺, 197 (100) [C₁₃H₇S]⁺.

2.3. General synthesis of the dibromo compounds $D(C_6H_4CH_2Br)$ (D = 0, 2a; S, 2b)

Aqueous HBr was added to a solution of **1** dissolved in toluene; the resulting mixture was refluxed for 24 h. After the reaction, the compound **2** was extracted by using chloroform; the organic layer was dried by means of a column filled with Celite and anhydrous Na_2SO_4 . After evaporation to dryness, a solid was obtained and washed with ethanol.

2.3.1. $O(C_6H_4CH_2Br)_2$ (**2a**)

Compound **1a** (1.00 g, 4.3 mmol), toluene (15 mL), HBr (1.5 mL, 13.04 mmol). Yield 91% colorless crystals (1.4 g). Mp 77–78 °C. *Anal.* Calc. for C₁₄H₁₂Br₂O: C, 47.23; H, 3.40. Found: C, 47.48; H, 3.31%. IR (CsI): v = 3036, 2981, 1579, 1486, 1450, 1241, 1220, 1185, 1086, 899, 755, 605 cm⁻¹. Raman (60 mW): v = 3058, 2983, 1608, 1225, 1158, 1039, 797, 602 cm⁻¹. NMR: ¹H (CDCl₃) $\delta = 7.47$ dd [1H, H-3, ³*J*_{H3–H4} = 8.06 Hz, ⁴*J*_{H3–H5} = 1.47 Hz], $\delta = 7.25$ td [1H, H-5, ³*J*_{H5–H6} = 8.06 Hz, ³*J*_{H4–H5} = 8.06 Hz, ⁴*J*_{H3–H5} = 1.47 Hz], $\delta = 6.83$ d [1H, H-6, ³*J*_{H5–H6} = 8.06 Hz], $\delta = 4.64$ s [2H, H-1]; ¹³C{¹H} (CDCl₃): $\delta = 154.9$ (C7), 131.5 (C3), 130.3 (C5), 129.0 (C2), 124.0 (C4), 118.6 (C6), 28.2 (C1). EI-MS: m/z (% intensity) 355 (5) [M]⁺-1, 275 (40) [C14H12OBr]⁺, 195 (100) [C1₄H₁₁O]⁺, 181 (30) [C₁₃H₉O]⁺.

2.3.2. $S(C_6H_4CH_2Br)_2$ (2b)

Compound **1b** (2.00 g, 7.6 mmol), toluene (15 mL), HBr (2.8 mL, 24.1 mmol). Yield 95% colorless crystals (2.67 g). Mp 65–66 °C. *Anal.* Calc. for $C_{14}H_{12}Br_2S$: C, 45.19; H, 3.25. Found: C, 45.71; H,

3.44%. IR (CsI): v = 3058, 2966, 1586, 1468, 1441, 1219, 1037, 818, 756, 605 cm⁻¹. Raman (25 mW): v = 3058, 2971, 1587, 1219, 1038, 602, 444 cm⁻¹. NMR: ¹H (CDCl₃) $\delta = 7.46$ d [1H, H-3, ³*J*_{H3-H4} = 7.33 Hz], $\delta = 7.25$ dd [1H, H-4, ³*J*_{H4-H5} = 8.06 Hz, ³*J*_{H3-H4} = 7.33 Hz], $\delta = 7.21$ dd [1H, H-5, ³*J*_{H4-H5} = 8.06 Hz, ³*J*_{H5-H6} = 7.33 Hz], $\delta = 7.16$ d [1H, H-6, ³*J*_{H5-H6} = 7.33 Hz], $\delta = 4.70$ s [2H, H-1]; ¹³C{¹H} (CDCl₃): $\delta = 138.5$ (C7), 135.2 (C2), 133.1 (C6), 131.1 (C3), 129.7 (C5), 128.2 (C4), 31.8 (C1). EI-MS: *m/z* (% intensity) 372 (30) [M]⁻⁺, 291 (45) [M-Br]⁺, 211 (100) [C₁₄H₁₁S]⁺, 197 (55) [C₁₃H₇S]⁺.

2.4. General synthesis of the dithiol compounds $D(C_6H_4CH_2SH)$ (D = O, **3a**; S, **3b**)

To a solution of **2** dissolved in acetone, thiourea was added and the solution mixture was refluxed for 24 h; when the solution was cooled to room temperature, a white solid obtained was filtered off and then it was mixed with an aqueous solution of potassium hydroxide. The resulting mixture was refluxed for 4 h and then let it to reach room temperature. The mixture was acidified with HCI to pH 2, extracted with chloroform and the organic layer was dried by means of a column filled with Celite and anhydrous Na₂SO₄. After evaporation of the organic solvent, an oily compound was obtained.

2.4.1. $O(C_6H_4CH_2SH)_2$ (**3a**)

Compound **2a** (1.50 g, 4.16 mmol), ethanol (30 mL), thiourea (0.70 g, 9.19 mmol), KOH (0.90 g, 16.7 mmol), ethanol (30 mL). Yield 75% Yellow oil (0.83 g). *Anal.* Calc. for $C_{14}H_{12}OS_2$: C, 64.08; H, 5.38. Found: C, 63.53; H, 5.27%. IR (CsI): v = 3090, 3035, 2937, 2554 (SH), 1578, 1484, 1451, 1236, 1186, 1103, 792, 752 cm⁻¹. Raman (420 mW): v = 3060, 2938, 2569 (SH), 1606, 1249, 1216, 1157, 1039, 785, 680 cm⁻¹. NMR: ¹H (CDCl₃) $\delta = 7.39$ d [1H, H-3, ³ $J_{H4} = 7.32$ Hz], $\delta = 7.20$ dd [1H, H-5, ³ $J_{H5-H5} = 8.06$ Hz, ³ $J_{H4-H5} = 7.69$ Hz], $\delta = 7.09$ dd [1H, H-4, ³ $J_{H4-H5} = 7.69$ Hz, $\delta = 7.09$ dd [1H, H-4, ³ $J_{H4-H5} = 7.69$ Hz, $\delta = 1.99$ t [1H, SH, ³ $J_{H1-SH} = 8.06$ Hz]; ¹³C{¹H} (CDCl₃): $\delta = 154.3$ (C7), 132.2 (C2), 130.2 (C3), 128.6 (C5), 123.8 (C4), 118.2 (C6), 23.8 (C1). EI-MS: m/z (% intensity) 262 (30) [M]:⁺, 228 (55) [O($C_6H_4CH_2)_2S$]:⁺, 195 (100) [$C_{14}H_{11}O$]⁺, 183 (70) [$C_{13}H_{10}$]⁺ 181 (70) [$C_{13}H_9O$]⁺.

2.4.2. $S(C_6H_4CH_2SH)_2$ (**3b**)

Compound **2b** (1.46 g, 3.92 mmol), acetone (30 mL), thiourea (0.66 g, 8.7 mmol), KOH (0.88 g, 15.7 mmol), water (10 mL). Yield 70% Yellow oil (0.77 g). *Anal.* Calc. for C₁₄H₁₄S₃: C, 60.39; H, 5.07. Found: C, 59.85; H, 5.07%. IR (CsI): v = 3055, 3008, 2933, 2561 (SH), 1586, 1466, 1439, 1247, 1039, 755 cm⁻¹. Raman (360 mW): v = 3051, 2936, 2563(SH), 1586, 1247, 1039, 685 cm⁻¹. NMR: ¹H (CDCl₃) $\delta = 7.38$ d [1H, H-3, ³*J*_{H3-H4} = 7.32 Hz], $\delta = 7.25$ t [1H, H-4, ³*J*_{H3-H4} = 7.32 Hz, ³*J*_{H4-H5} = 7.32 Hz], $\delta = 7.15$ m [2H, H-5, H-6], $\delta = 3.88$ d [2H, H-1, ³*J*_{H1-SH} = 7.81 Hz], $\delta = 2.01$ t [1H, SH, ³*J*_{H1-SH} = 7.81 Hz]; ¹³C{¹H} (CDCl₃): $\delta = 141.1$ (C7), 133.8 (C2), 132.6 (6), 129.8 (C3), 128.3 (C5), 128.1 (C4), 27.6 (C1). EI-MS: *m/z* (% intensity) 278 (50) [M]⁻⁺, 244 (15) [M-H₂S]⁺, 211 (90) [C₁₄H₁₁S]⁺, 197 (100) [C₁₃H₉S]⁺.

2.5. General synthesis of the dithiastannecine compounds 4-7

A tin compound $(R_n \text{SnCl}_{4-n})$ was added to a solution of **3** and DABCO in chloroform; the reaction mixture was stirred for 24 h. After the reaction, the DABCO chlorohydrate was filtered off and the remaining solution was slowly evaporated to dryness to get a solid product.

2.5.1. [$\{O(C_6H_4CH_2S)_2\}SnPh_2$] (4a)

Ph₂SnCl₂ (0.42 g, 1.21 mmol), **3a** (0.3 g, 1.14 mmol), DABCO (0.13 g 1.19 mmol) dichloromethane (30 mL) Yield 40% (0.25 g).

Mp 62–64 °C. Anal. Calc. for C₂₆H₂₂OS₂Sn: C, 58.56; H, 4.16. Found: C, 59.40; H, 4.28%. IR (CsI): v = 3065, 3017, 2917, 2849, 1485, 1453, 1430, 1241, 1216, 1187, 755, 697, 667 cm⁻¹. Raman (360 mW): *v* = 3052, 2933, 1603, 1577, 1235, 1216, 1156, 1038, 997, 758, 666, 342 (C-Sn) cm⁻¹. NMR: ¹¹⁹Sn (CDCl₃) δ = 33.6; ¹H (CDCl₃) δ = 7.51 m [2H, H-9], δ = 7.44 dd [1H, H-3, ${}^{3}J_{H3-H4}$ = 7.32 Hz, ${}^{4}J_{H3-H4}$ _{H5} = 1.83 Hz], δ = 7.37 m [3H, H-10, H-11], δ = 7.20 td [1H, H-5, ${}^{3}J_{\text{H5}-\text{H6}}$ = 7.69 Hz, ${}^{3}J_{\text{H4}-\text{H5}}$ = 7.69 Hz, ${}^{4}J_{\text{H3}-\text{H5}}$ = 1.83 Hz], δ = 7.14 ddd [1H, H-4, ${}^{3}J_{H4-H5}$ = 7.69 Hz, ${}^{3}J_{H3-H4}$ = 7.32 Hz, ${}^{4}J_{H4-H6}$ = 1.46 Hz], δ = 6.60 dd [1H, H-6, ${}^{3}J_{H5-H6}$ = 7.69 Hz, ${}^{4}J_{H4-H6}$ = 1.46 Hz], δ = 4.03 s [2H, H-1, ${}^{3}J_{H1-119}S_{n} = 6.12$], 13C{¹H} (CDCl₃): $\delta = 153.7$ (C7), 139.1 (C8), 136.0 (C9), 133.3 (C2), 130.7 (C3), 130.0 (C11), 128.9 (C10), 128.6 (C5), 124.3 (C4), 118.0 (C6), 27.1 (C1). EI-MS: m/z (% intensity) 534 (3) [M]⁺, 457 (5) [C₂₀H₁₇OS₂Sn]⁺, 260 (15) $[C_{14}H_{12}OS_2]^{+}$, 227 (40) $[C_{14}H_{11}OS]^{+}$, 195 (100) $[C_{14}H_{11}O]^{+}$, 181 $(27) [C_{13}H_9O]^+$.

2.5.2. [$\{O(C_6H_4CH_2S)_2\}$ SnPhCl] (**5a**)

PhSnCl₃ (0.57 g, 1.88 mmol), **3a** (0.5 g, 1.90 mmol), DABCO (0.21 g 1.90 mmol) dichloromethane (30 mL) Yield 65% (0.61 g). Mp 122–123 °C. *Anal.* Calc. for C₂₀H₁₇ClOS₂Sn: C, 48.86; H, 3.49. Found: C, 48.59; H, 3.41%. IR (Csl): v = 3064, 2932, 1579, 1484, 1452, 1431, 1232, 1183, 1099, 900, 754, 728 cm⁻¹. Raman (360 mW): v = 3062, 2938, 1604, 1238, 1214, 1157, 1033, 997, 660, 328, 243 cm⁻¹. NMR: ¹¹⁹Sn (CDCl₃) $\delta = 19.5$; ¹H (CDCl₃) $\delta = 7.40$ m [4H, H-9, H10], $\delta = 7.32$ m [3H, H-3, H-11], $\delta = 7.17$ m [4H, H-4, H-5], $\delta = 6.48$ d [2H, H-6, ³*J*_{H5–H6} = 7.32 Hz], $\delta = 4.03$ s [2H, H-1, ³*J*_{H1–¹¹⁹Sn} = 93.7], 13C{¹H} (CDCl₃): $\delta = 153.2$ (C7), 138.8 (C8), 134.7 (C9), 132.7 (C2), 131.1 (C11), 130.4 (C3), 129.4 (C5, C10), 125.1 (C4), 118.0 (C6), 28.2 (C1). EI-MS: m/z (% intensity) 492 (5) [M]⁻⁺, 457 (5%) [M–CI]⁺, 415 (<5%) [M–Ph]⁺ 195 (100) [C₁₄H₁₁0]⁺, 181 (25) [C₁₃H₉O]⁺.

2.5.3. $[{O(C_6H_4CH_2S)_2}Sn(n-Bu)Cl]$ (**6a**)

n-BuSnCl₃ (0.54 g, 2.09 mmol), **3a** (0.5 g, 1.90 mmol), DABCO (0.21 g 1.90 mmol) dichloromethane (30 mL) Yield 41% (0.36 g). Mp 103 °C. Anal. Calc. for C₁₈H₂₁ClOS₂Sn: C, 45.84; H, 4.49. Found: C, 45.61; H, 4.62%. IR (CsI): v = 3090, 2958, 2927, 2870, 1579, 1485, 1453, 1229, 1181, 1097, 900, 795, 755, 668 cm⁻¹. Raman (420 mW): v = 3061, 2962, 2933, 1605, 1234, 1215, 1154, 1036, 679, 596, 351, 333, 241 (C-Sn) cm⁻¹. NMR: ¹¹⁹Sn (CDCl₃) δ = 75.6; ¹H (CDCl₃) δ = 7.38 d [1H, H-3, ³J_{H3-H4} = 7.69 Hz], δ = 7.25 t [1H, H-5, ³J_{H5-H6} = 7.69 Hz, ³J_{H4-H5} = 7.69 Hz], δ = 7.17 t [1H, H-4, ${}^{3}J_{H4-H5}$ = 7.69 Hz, ${}^{3}J_{H3-H4}$ = 7.69 Hz], δ = 6.71 d [1H, H-6, ${}^{3}J_{\text{H5}-\text{H6}}$ = 7.69 Hz], δ = 3.92 s [2H, H-1, ${}^{3}J_{\text{H1}-119}\text{Sn}$ = 83.1 Hz], δ = 1.90 t [2H, H-8, ${}^{3}J_{H8-H9}$ = 7.69, ${}^{3}J_{H8-^{119}Sn}$ = 78.7 Hz], δ = 1.50 q [2H, H-9, ${}^{3}J_{H8-H9}$, ${}^{3}J_{H9-H10}$ = 7.69, ${}^{3}J_{H8-^{119}Sn}$ = 12.19 Hz], δ = 1.27 sx [2H, H-10, ${}^{3}J_{H9-H10}$, ${}^{3}J_{H10-H11}$ = 7.69], δ = 0.79 t [3H, H-11, ${}^{3}J_{H10-}$ $_{H11} = 7.69$] $^{13}C{^{1}H}$ (CDCl₃): $\delta = 153.0$ (C7), 133.2 (C2), 130.6 (C3), 129.5 (C5), 125.3 (C4), 118.0 (C6), 27.8 (C1), 27.1 (C9), 26.2 (C8), 25.7.1 (C10), 13.6 (C11). EI-MS: m/z (% intensity) 472 (3) [M]⁺, 437 (7) $[C_{18}H_{21}OS_2Sn]^+$, 415 (8) $[C_{14}H_{12}OS_2SnCl]^+$, 379 (5) $[C_{14}H_{11}OS_2Sn]^+$, 260 (15) $[C_{14}H_{12}OS_2]^{++}$, 227 (40) $[C_{14}H_{11}OS]^+$, 195 $(100) [C_{14}H_{11}O]^+, 181 (35) [C_{13}H_9O]^+.$

2.5.4. [$\{O(C_6H_4CH_2S)_2\}_2Sn$] (**7a**)

SnCl₄ (0.14 g, 0.56 mmol), **3a** (0.3 g, 1.14 mmol), DABCO (0.13 g 1.19 mmol) dichloromethane (30 mL) Yield 45% (0.33 g). Mp 174 °C. *Anal.* Calc. for C₂₈H₂₄O₂S₄Sn: C, 52.59; H, 3.78. Found: C, 52.32; H, 3.73%. IR (CsI): v = 3090, 2917, 2848, 1579, 1483, 1452, 1235, 1184, 1097, 900, 794, 752, 666 cm⁻¹. Raman (420 mW) v = 3067, 3048, 2952, 2926, 1603, 1236, 1217, 1152, 1035, 667, 322 (C-Sn) cm⁻¹. NMR: ¹¹⁹Sn (CDCl₃) $\delta = 125.4$; ¹H (CDCl₃) $\delta = 7.28$ d [1H, H-3, ³J_{H3-H4} = 7.32 Hz], $\delta = 7.18$ dd [1H, H-5, ³J_{H5-H6} = 8.06 Hz, ³J_{H4-H5} = 7.32 Hz], $\delta = 7.05$ t[1H, H-4, ³J_{H4-H5} = 7.32 Hz, ³J_{H3-H4} = 7.32 Hz], $\delta = 6.73$ d[1H, H-6, ³J_{H5-H6} = 8.06 Hz], $\delta = 3.92$ s [2H, H-1, ${}^{3}J_{H1-119}{}_{Sn} = 88.17$], ${}^{13}C{}^{1}H{}(CDCl_{3}): \delta = 153.5 (C7), 132.6 (C2), 130.5 (C3), 128.7 (C5), 124.2 (C4), 117.9 (C6), 28.2 (C1). EI-MS: <math>m/z$ (% intensity) 640 (1) [M]⁺, 260 15) [C₁₄H₁₂OS₂] ⁻⁺, 228 (35) [C₁₄H₁₂OS]⁺, 195 (100) [C₁₄H₁₁O]⁺, 181 (35) [C₁₃H₉O]⁺.

2.5.5. $[{S(C_6H_4CH_2S)_2}SnPh_2]$ (4b)

Ph₂SnCl₂ (0.62 g, 1.80 mmol), **3b** (0.5 g, 1.80 mmol), DABCO (0.20 g 1.78 mmol) dichloromethane (30 mL) Yield 45% (0.44 g). Mp 53–55 °C. *Anal.* Calc. for C₂₆H₂₂S₃Sn: C, 56.84; H, 4.04. Found: C, 57.18; H, 4.24%. IR (Csl): v = 3062, 3010, 2928, 1585, 1478, 1467, 1429, 1231, 1071, 759, 730, 696, 448 cm⁻¹. Raman (340 mW): v = 3048, 2927, 1586, 1233, 1198, 1160, 1038, 997, 655, 347, 236 cm⁻¹. NMR: ¹¹⁹Sn (CDCl₃) $\delta = 37.5$; ¹H (CDCl₃) $\delta = 7.77$ m [2H, H-9], $\delta = 7.47$ m [3H, H-10, H-11], $\delta = 7.38$ d [1H, H-3, ³J_{H3-H4} = 7.69 Hz], $\delta = 7.28$ td [1H, H-4, ³J_{H3-H4} = 7.69 Hz, ⁴J_{H4-H6} = 1.83 Hz], $\delta = 7.23$ m [2H, H-5, H-6], $\delta = 4.06$ s [2H, H-1, ³J_{H1-119Sn} = 55.0]; 13C{¹H} (CDCl₃): $\delta = 143.4$ (C7), 140.7 (C8), 136.3 (C2), 135.9 (C9), 133.8 (C6), 130.5(C3), 130.2 (C11), 129.1 (C10), 128.7 (C5), 128.0 (C4), 31.1 (C1). EI-MS: m/z (% intensity) 550 (5) [M]⁺, 473 (70) [M–Ph]⁺, 396 (9) [M–2Ph]⁺, 211 (100) [C₁₄H₁₁S]⁺, 197 (73) [C₁₃H₇S]⁺.

2.5.6. [{S(C₆H₄CH₂S)₂}SnPhCl] (**5b**)

PhSnCl₃ (0.55 g, 1.82 mmol), **3b** (0.5 g, 1.80 mmol), DABCO (0.20 g 1.78 mmol) dichloromethane (30 mL) Yield 50% (0.46 g). Mp 116–117 °C. *Anal.* Calc. for $C_{20}H_{17}ClS_3Sn:$ C, 47.31; H, 3.37. Found: C, 46.58; H, 3.20%. IR (CsI): v = 3062, 3009, 2927, 1585, 1468, 1443, 1431, 1232, 1038, 759, 730, 693, 666, 445 cm⁻¹. Raman (260 mW): v = 3056, 3014, 2925, 1585, 1233, 1200, 1161, 1036, 996, 660, 356, 307, 236, 199 cm⁻¹. NMR ¹¹⁹Sn (CDCl₃) $\delta = -42.3$ Hz; ¹H (CDCl₃) $\delta = 7.65$ m [2H, H-9], $\delta = 7.46$ m [3H, H-10, H-11], $\delta = 7.37$ m [2H, H-3, H-4], $\delta = 7.24$ m [2H, H-5, H-6], $\delta = 3.24$ s [2H, H-1, ³ $J_{H1^{-119}Sn} = 94.5$]; 13C{¹H} (CDCl₃): $\delta = 142.7$ (C7), 130.9 (C8), 134.4 (C2, C9), 130.4 (C6), 129.6 (C3), 130.4 (C11), 129.8 (C10), 128.8 (C5, C4), 31.4 (C1). EI-MS: m/z (% intensity) 276 (36) [$C_{14}H_{12}S_{3}$]⁺, 211 (63) [$C_{14}H_{12}S$]⁺, 197 (44) [$C_{13}H_7S$]⁺.

2.5.7. $[{S(C_6H_4CH_2S)_2}Sn(n-Bu)Cl]$ (**6b**)

n-BuSnCl₃ (0.51 g, 1.82 mmol), **3b** (0.5 g, 1.80 mmol), DABCO (0.20 g 1.78 mmol) dichloromethane (30 mL) Yield 55% (0.48 g). Mp 95–96 °C. *Anal.* Calc. for C₁₈H₂₁ClS₃Sn: C, 44.33; H, 4.34. Found: C, 44.51; H, 3.40%. IR (CsI): *v* = 3059, 3008, 2957, 2925, 2869, 1586, 1467, 1442, 1231, 1038, 760, 666 cm⁻¹. Raman (360 mW): *v* = 3061, 2929, 2908, 1587, 1234, 1225, 1204, 1160, 1036, 512, 369, 345, 241 cm⁻¹. NMR: ¹¹⁹Sn (CDCl₃) δ = 13.2; ¹H (CDCl₃) δ = 7.35 m [1H, H-3], δ = 7.12 m [3H, H-4, H-5, H-6], δ = 3.85 s [2H, H-1, ³J_{H1-119}Sn = 80.9 Hz], δ = 2.18 t [2H, H-8, ³J_{H8-H9} = 7.86, ³J_{H1-119}Sn = 129.6 Hz], δ = 1.44 sextuplet [2H, H-10, ³J_{H9-H10}, ³J_{H10-H11} = 7.69]; δ = 0.89 t [3H, H-11, ³J_{H10-H11} = 7.69]; ¹³C{¹H} (CDCl₃): δ = 142.6 (C7), 132.5 (C2), 130.5 (C6), 129.9 (C3), 128.8 (C5, C4), 31.7 (C8), 31.2 (C1), 27.9 (C9), 25.8 (C10), 13.7 (C11). EI-MS: *m/z* (% intensity) 488 (5%) [M]⁻⁺, 431 (87) [M-*n*Bu]⁺, 396 (10) [M–Cl–*n*Bu]⁺, 211 (100) [C₁₄H₁₁S]⁺, 197 (75) [C₁₃H₇S]⁺.

2.5.8. $[{S(C_6H_4CH_2S)_2}_2Sn]$ (7b)

SnCl₄ (0.22 g, 0.85 mmol), **3b** (0.5 g, 1.80 mmol), DABCO (0.20 g 1.78 mmol) dichloromethane (30 mL) Yield 35% (0.42 g). Mp 155 °C. *Anal.* Calc. for C₂₈H₂₄S₆Sn: C, 50.07; H, 3.60%. Found: C, 49.35; H, 3.87%. IR (CsI): *ν* = 3056, 2927, 1717, 1465, 1439, 1219, 1038, 771, 752 cm⁻¹. Raman (260 mW): *ν* = 3066, 2937, 1585, 1567, 1223, 1199, 1030, 817, 663, 328, 245 cm⁻¹. NMR: ¹¹⁹Sn (CDCl₃) δ = -95.8; ¹H (CDCl₃) δ = 7.29 d [1H, H-3, ³J_{H3-H4} = 7.32 Hz], δ = 7.23 m [1H, H-4], δ = 7.16 m [2H, H-5, H-6], δ = 4.10 s [2H, H-1, ³J_{H1-119}_{Sn} = 82.4 Hz]; ¹³C{¹H} (CDCl₃): δ = 142.8 (C7), 133.8 (C2), 133.5 (C6), 130.0 (C3), 128.7 (C5), 128.1 (C4), 32.5 (C1). EI-MS: m/z (% intensity) 276 (25%) $[C_{14}H_{12}S_3]^+$, 244 (78) $[C_{14}H_{12}S_2]^+$, 211 (100) $[C_{14}H_{11}S]^+$, 197 (37) $[C_{13}H_7S]^+$.

2.6. X-ray crystallography and structure solution

Suitable single crystals of compounds 1a, 6b, and 7a were grown from a chloroform solution by slow evaporation; crystals of **5a**, **5b**, and **6a** were grown form dichloromethane solution. X-ray diffraction data of **1a** were collected at room temperature on a CCD SMART 6000 diffractometer through the use of MoK α radiation ($\lambda = 0.71073$ Å, graphite monochromator). Data were integrated, scaled, sorted, and averaged using the SMART software package. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program sADABS [15]. X-ray diffraction data of 5a, 6a, 6b, and 7a were collected at 141 K on an Oxford Diffraction Gemini CCD diffractometer with graphite-monochromated MoK α radiation $(\lambda = 0.71073 \text{ Å})$; for **5b** CuK α radiation $(\lambda = 1.54184 \text{ Å})$ was used. Data were integrated, scaled, sorted, and averaged using the CrysAlis software package [16]. An analytical numeric absorption correction using a multifaceted crystal model was applied by using the CrysAlis software. The structures were solved by direct methods, using SHELXTL NT Version 5.10 and refined by full-matrix least squares against F^2 [17]. The displacement parameters of nonhydrogen atoms were anisotropically refined. The positions of the hydrogen atoms were kept fixed with a common isotropic displacement parameter. The absolute structure of **6a** was determined following the reported methods with a Flack parameter of -0.014(12) [18]. Selected crystallographic data are given in Table 6.

3. Results and discussion

3.1. Synthesis of the dithioligands $D(C_6H_4CH_2SH)_2$ (**D** = 0, S)

Ditihioligands **3a** and **3b** were prepared by linear synthesis from diphenylether and diphenylthioether, respectively (the letter **a** refers to the compound with D = oxygen and **b** to the compound with D = sulfur, see Scheme 2 and Section 2, for details).

3.2. Synthesis of the tin compounds 4-7

The reaction of **3a** or **3b** with the corresponding tin chloride compound dissolved in chloroform in the presence of the deprotonating agent DABCO yielded the corresponding compounds **4–7** with yields ranging from 65% to 40%. All tin compounds are air-stable and soluble in chloroform or in toluene.

3.3. Vibrational spectroscopy

The IR spectra as well as the Raman spectra (data in parentheses) of ligands **3a** and **3b** display bands of medium intensity at 2564 (2570) and 2561 (2565) cm⁻¹ assigned to the –SH vibration group; these bands vanished in the corresponding spectra of the compounds **4–7**, thus indicating that the deprotonation of the thiol groups occurred upon complex formation. This is consistent with the appearance of bands in the Raman spectra (356–328 cm⁻¹) assignable to the tin–sulfur and tin–chloride stretching vibration [19].

3.4. NMR spectra

NMR spectra of all compounds were recorded in CDCl₃ solutions at 25 °C; the assignment of the signals was carried out by the



Scheme 2. Synthesis of compounds 4-7. (i) n-BuLi/(CH₂O)_n/THF; (ii) HBr/toluene; (iii) Thiourea/KOH/H⁺; (iv) R_nSnCl_{4-n}/DABCO/CHCl₃.

heteronuclear and homonuclear correlation of two dimensional experiments (HSOC and HMBC). In solution, the DC₆H₄CH₂S moieties are equivalent for all compounds. For the organic compounds 1-3, the signals of the aromatic protons of the ligand framework were observed as an ABCD pattern. The -CH₂-X hydrogen resonances were observed around 4.75-3.83 ppm; in the case of the dithioligands **3a** and **3b** (X = SH) these CH_2 signals were observed as doublets due to the coupling with the -SH group observed as a triplet at ca. 2.0 ppm $({}^{3}J^{1}_{H^{-}H} = 8.06$ for **3a** and 7.81 Hz for **3b**). However, these couplings vanished when the ligand was coordinated with the starting material of tin and new ${}^{3}I_{sn-H}^{119}$ couplings –CH₂–S–Sn appeared ranging from 55 Hz (for the diphenyltin compound 4b) to 94 Hz (for the chlorotin compound 5b). The coupling of these $-CH_2$ -S hydrogen nuclei with the aromatic framework is practically absent making, therefore, the analysis of the signals easier than that carried out in the more flexible stannocane compounds of the type I with A = Sn. This situation allowed us to explore the magnetic environmental changes in our compounds after tin was bonded to sulfur. Hence, two different values of ³J $^{119}_{Sn-H}$ couplings for the CH₂-S-Sn system were observed: one ranging from 55 to 61 Hz and the other one from 80 to 94 Hz. The first range is associated with the diphenyltin compounds $[{D(C_6H_4CH_2S)_2}SnPh_2]$ **4a** (**D** = 0) and **4b** (**D** = S). The second one is associated with the chloromonoorganotin compounds 5a-6b; these greater values can be related to the enhanced Lewis acidity over the tin atom. This acidity is expected because of the presence of the electronegative chloro ligand, promoting the presence of a transannular $D \cdots$ Sn interaction.

The ¹¹⁹Sn NMR spectra of the **4–7** tin compounds recorded in the non-coordinating solvent CDCl₃ at room temperature displayed only a sharp signal in the –42 to 125 ppm range (Table 1) without a clear pattern. Generally, it is well known that the ¹¹⁹Sn chemical shifts move to lower frequencies when the coordination number increases, even though the shifting is somewhat dependent on the nature of the substituents attached to tin [20,21]. Thus, according to Otera's ranges [20], all the tin complexes would be fourcoordinate, indicating that the { $D(C_6H_4CH_2S)_2$ }^{2–} ligand is coordinated to the tin atom in a bidentate fashion, i.e., the presence of

ladie I		
119Sn{1H} NMR data (ppm) for	compounds 4-7 in	CDCl ₃ solution (25 °C).

D	4	5	6	7
0	33.6	19.5	75.6	125.4
S	37.5	42.5	13.2	95.8

the transannular interaction in **4–7** is practically absent in solution. Nevertheless, some additional comments with respect to the ¹¹⁹Sn chemical shifts of the chloromonophenyltin compounds **5a** and **5b** can be done: (i) they occur at lower frequencies than the corresponding shifts of the diphenyltin compounds **4a** and **4b** due to the enhanced Lewis acidity over the tin atom and, (ii) they are also more shifted than the chloromonobutyltin compounds **6a** and **6b** $[\Delta \delta = 55.9(2) \text{ ppm}$, low frequency] due to the nature of the phenyl group and its diamagnetic ring-current; a similar behavior was observed in the corresponding chloromonophenyl and -butyl [{ $D(CH_2 CH_2S)_2$ }SnRCI] stannocanes (D = O, S; R = Ph, *n*-Bu) [22,23]. In general, the $\Delta \delta$ values suggest significant changes in the coordination number of tin and should be considered in addition to the values of the ¹¹⁹Sn NMR chemical shifts.

3.5. Description of the solid state structures of dithiastannecines

The solid state molecular structures of **1a**, **5a**, **5b**, **6a**, **6b**, and **7a** were determined by single crystal X-ray diffraction analyses. The asymmetric unit of the compounds **5a** and **5b** contains two crystal-lographically independent molecules (herein after labeled as **5a**' and **5a**'' and **5b**'', respectively). The molecular drawings are depicted in Figs. 1–6 and selected bond lengths, angles, and torsion angles for tin compounds **5a**, **5b**, **6a**, **6b**, and **7a** are given in Table 2.

In the course of the synthesis the starting material **1a** was crystallized; the most relevant features in the structure are the angles C–O–C [117.1(3)°] and that between the two twisted benzenic planes [86.8(1)°]. The two –OH groups are pointed away from the oxygen ether-type; the crystal structure is stabilized by hydrogen bonding with the hydroxyl groups (Fig. 1).

3.5.1. Description of the structures of 5a, 5b, 6a, and 6b

The analogous monoorganotin compounds $[{D(C_6H_4CH_2S)_2} SnRCI]$ **5a** (D = O; R = Ph), **5b** (D = S; R = Ph), **6a** (D = O; R = n-Bu), and **6b** (D = S; R = n-Bu) are isostructural and contain a 10-membered central ring; although the ¹¹⁹Sn NMR data in solution suggest a four coordinated structures in solution, the molecular structures reveal five-coordinate tin atoms due to a transannular coordination by the D donor atom. The local geometry around the tin atom can be described as distorted trigonal bipyramidal where two equatorial bonds are formed with the thiolate-type sulfur atoms and the third one with the carbon of either Ph or n-Bu groups; the chloro and the donor D atoms occupy the axial positions. For the compounds, the Sn–S(thiolate-like) distances are in good agreement with those reported for eight-membered



Fig. 1. Hydrogen bonding in compound **1a**. Selected bond lengths (Å): O(1)-C(7), 1.400(4); O(1)-C(8), 1.402(4); O(2)-C(1), 1.400(5); O(3)-C(14), 1.426(5) $O(3)\cdots O(2A)$, 2.669(4). Selected bond angles and torsion angles (°): C(7)-O(1)-C(8), 117.1(3); O(2)-C(1)-C(2)-C(7), -178.6(3); C(8)-C(13)-C(14)-O(3), 174.8(3).

heterocycles and several other compounds with tin-sulfur bonds [22,24–32]. The **D** \cdots Sn distances are 2.888(2), 2.978(2), 2.9522

(18), 3.0799(18), 2.7126(14), and 3.0970(7) Å for **5a**', **5a**'', **5b**'', **5b**'', **6a**, and **6b**, respectively; these distances are 78.3%, 80.7%, 74.4%, 77.6%, 73.5%, and 78.0% of the corresponding van der Waals radii sum [Σr_{vdW} (Sn, **D**); **D** = 0, 3.69 Å; **D** = S, 3.97 Å] [33] and they influence the local geometry along the path from tetrahedral to trigonal bipyramidal. By considering several dithiotin compounds containing eight-membered rings where the coordination number of the tin acceptor atom is four or five¹, it is possible to observe that the magnitude of the angle S–Sn–S is roughly coupled with the transannular interaction **D**...Sn (**D** = O, S). The variability of these structural parameters is illustrated in Fig. 7; the corresponding parameters for **5a**', **5a**'', **5b**'', **6a**, and **6b** were also plotted for reasons of comparison.

From the scattergram it can be observed that the larger endocyclic S–Sn–S angle makes a shorter transannular distance. In spite of the greater size and flexibility of the compounds **5a'**, **5a''**, **5b'**, **5b''**, **6a**, and **6b**, it can be noted that the S–Sn–S angle is also enlarged by the presence of the transannular interaction. Thus, in order to evaluate distortions in geometry at the tin atom and the magnitude of the interaction, the difference between the sum of the equatorial and axial angles [$\Delta = \Sigma(\theta)_{equatorial} - \Sigma(\theta)_{axial}$] [19,24] and the Pauling-type Bond Order based on interatomic distances [34,27], respectively, were used. The data are listed in Table 3; the data for the corresponding [{D(CH₂CH₂S)₂}SnRCl] stannocanes (D = O, S; R = Ph, *n*-Bu) are also presented.



Fig. 2. Molecular structure of 5a' (left) and 5a'' (right). ORTEP at 50% probability. Selected torsion angles (°): C(7)-C(2)-C(1)-S(1), 83.6(4); C(8)-C(13)-C(14)-S(2), 79.0(4); C(27)-C(22)-C(21)-S(3), -78.7(4); C(28)-C(33)-C(34)-S(4), -83.9(4).



Fig. 3. Molecular structure of **5b**' (left) and **5b**'' (right). ORTEP at 50% probability. Selected torsion angles (°): C(7)-C(2)-C(1)-S(1), -81.3(8); C(8)-C(13)-C(14)-S(2), -82.1(7); C(27)-C(22)-C(21)-S(4), 81.2(7); C(28)-C(33)-C(34)-S(5), 81.6(8).



Fig. 4. Molecular structure of compound **6a**. ORTEP at 50% probability. Selected torsion angles (°): C(7)–C(2)–C(1)–S(1), –76.3(2); C(8)–C(13)–C(14)–S(2), –83.4(2).



Fig. 5. Molecular structure of compound **6b**. ORTEP at 50% probability. Selected torsion angles (°): C(7)-C(2)-C(1)-S(1), 81.1(3); C(8)-C(13)-C(14)-S(2), 78.5(3).



Fig. 6. Molecular structure of compound **7a**. ORTEP at 50% probability. Selected torsion angles (°): C(7)-C(2)-C(1)-S(1), -79.1(3); C(8)-C(13)-C(14)-S(2), -90.2(3); C(21)-C(16)-C(15)-S(3), 88.5(3); C(22)-C(27)-C(28)-S(4), 76.5(3).

The tbp % and bond orders are bigger for the stannocanes; however, the D···Sn–Cl angle is substantially larger for the 10-membered dithiastannecine compounds; this result is indicative of the abilities of the { $D(C_6H_4CH_2S)_2$ ²⁻ ligand to expand the coordination number of a central atom, especially if the Lewis acidity is greatly enhanced.

3.5.2. Description of the structure of 7a

The molecular structure of the spiro compound **7a** shows a tin atom covalently bonded to four sulfur atoms: in addition, two intramolecular interactions of both oxygen atoms with the central atom can be observed [O...Sn distances; 3.3106(17) and 3.3477(18) Å]. These distances are 89.7 and 90.7% of the Σr_{vdW} (Sn, O) sum (3.69 Å). The S–Sn–S angles are slightly distorted from the ideal tetrahedral value; the most deviated one is the angle between sulfurs S1 and S3 [100.21(2)°]. Moreover, these atoms and the two oxygen atoms are almost coplanar (mean deviation: 0.0578 Å). Hence, in order to assign the local geometry of the tin atom, we related the four covalent bonds plus the two short contacts to a method used to describe structural displacements of six-coordinate atoms between octahedral and bicapped tetrahedral idealized geometries. [35] Thus, by using the sum of the fifteen angles of a six-coordinate atom in an octahedron (1.620.00°) and in a bicapped tetrahedron (1549.47°) we observed for 7a a value of 1549.94°. corresponding to 99.3% of a bicapped tetrahedral geometry. With respect to the Pauling-type bond order [27,34], an averaged BO = 0.0211 for **7a** was calculated, which is one order of magnitude lower than that found for 5a, 5b, 6a, and 6b (Table 3). Therefore, we can conclude that the transannular interaction distorts the geometry of the tin atom, although is not as strong as that observed in the $[{D(C_6H_4CH_2S)_2}SnRC]$ compounds.

3.6. Theoretical study

The analogous compounds **6a** and **6b** are suitable systems to study the nature of the intramolecular interactions (D···Sn), hence, we present here the results of our theoretical results. Firstly, the molecular systems were optimized, and the nature of the chemical bonding was analyzed in terms of the topology of the electronic density [$\rho(\mathbf{r})$]. All calculations were performed with the help of the Amsterdam Density Functional (ADF) package [36–38] and the suite of programs in GAUSSIAN 09 [39]. The ground-state wavefunction was used for the calculation of "atoms in molecules" (AIM) [40] to determine bond critical points (BCPs) and ring critical points (RCPs); the results were analyzed in terms of electron densities, ρ , and their Laplacians, $\nabla^2 \rho$. The Bader theory is implemented in the AIM 2000 program [41].

Calculations of the compounds **6a** and **6b** were carried out by using Amsterdam Density Functional (ADF) 2008.01. Scalar Relativistic corrections were included via the ZORA to the Dirac equation [42,43]. The geometry optimization in gas phase was worked out using the Vosko–Wilk–Nusair functional. [44] The quadruple ζ quality with four polarization functions (QZ4P) basis of Slater-type orbitals provided with the ADF package was used for all atoms. Selected bond lengths and angles of the optimized structures are presented in Table 4, showing that the calculations at the level employed reproduce adequately the experimental overall geometries, mainly in the distances and angles parameters around the tin atom.

For the optimized system, the bond critical points of the electron density (BCPs) and the gradient paths were determined using the AIM program. The results of the topological analysis of the electron density are presented in Table 5 and the molecular graphs are depicted in Fig. 8 for compounds **6a** and **6b**.

The molecular graphs show that the BCP's are present along with the Sn···**D** directions (**D** = 0, S). The values of ρ_c (**D**···Sn) are the smallest (≈ 0.021 a.u.) and $\nabla^2 \rho_c$ is positive (in the table it is shown

¹ Data for stannocane structures were retrieved from the CSD (version 5.32, November 2010) with CSD codes CLOXSN, CLTHSN, COVQAF, COVQEJ, CXTHSN, DELWIA, DELXAT, KISDUL, LIHRUP, LIHSAW, LIHSEA, LIHSIE, MAXTOU, MAXTUA, PHOXSN, PHTHSN, XUYFIG, XUYFIG, YIFKON, YIFKUT, YIFLAA, YIFLEE, YIFLOO, YIFLUU; the deposition numbers of dibenzostannocine structures are 756927, 756928, 756929, 756930, 756931.

Table 2

Table 3

Selected bond lengths (Å) and bond angles (°) of 5a, 5b (both display two crystallographic independent molecules), 6a, 6b and 7a.							
	5a′	5a″	5b′	5b″	6a	6b	7a
D	0(1)	0(2)	S(3)	S(6)	O(1)	S(3)	O(1)
S ¹	S(1)	S(3)	S(1)	S(4)	S(1)	S(1)	S(1)
S ²	S(2)	S(4)	S(2)	S(5)	S(2)	S(2)	S(2)
R ¹	Cl(1)	Cl(2)	Cl(1)	Cl(2)	Cl(1)	Cl(1)	S(3)
R ²	C(15)	C(35)	C(15)	C(35)	C(15)	C(15)	S(4)
Sn-S ¹	2.3886(9)	2.3812(10)	2.4034(18)	2.3980(18)	2.3810(6)	2.3993(7)	2.3914(7)
Sn-S ²	2.3803(10)	2.3898(10)	2.3970(17)	2.3974(19)	2.3944(6)	2.3829(7)	2.3944(7)
Sn-R ¹	2.3709(10)	2.3575(10)	2.4000(18)	2.384(2)	2.3826(6)	2.4132(7)	2.4011(7)
Sn-R ²	2.115(3)	2.123(3)	2.106(6)	2.114(7)	2.146(2)	2.150(3)	2.3987(6)
D···Sn	2.888(2)	2.978(2)	2.9522(18)	3.0799(18)	2.7126(14)	3.0970(7)	3.3477(18)
O(2)···Sn	-	_	-			-	3.3106(17)
C(7) - D - C(8)	116.5(2)	-	105.9(3)	-	118.99(16)	102.50(12)	116.39(19)
C(27)-D-C(28)	-	116.0(3)	-	103.3(3)		-	
C(21)-O(2)-C(22)	-	-	-	-	-	-	117.48(19)
S ¹ -Sn-S ²	116.15(3)	114.67(3)	117.27(6)	116.82(6)	116.09(2)	114.40(2)	114.47(2)
S ¹ -Sn-R ¹	97.69(3)	100.73(4)	93.17(6)	96.67(7)	97.44(2)	96.29(3)	100.21(2)
S ¹ -Sn-R ²	117.86(10)	114.22(10)	121.10(17)	117.80(19)	115.66(6)	120.96(8)	110.95(2)
S ² -Sn-R ¹	97.70(4)	96.50(4)	96.15(6)	96.43(7)	91.53(2)	93.91(2)	111.94(2)
S ² -Sn-R ²	116.90(10)	119.34(10)	117.44(17)	117.51(19)	122.87(6)	119.46(8)	111.28(2)
R^1-Sn-R^2	104.91(9)	107.36(9)	101.11(17)	105.05(19)	104.19(6)	102.29(8)	107.30(2)
$D \cdot \cdot \cdot Sn - R^1$	176.92(5)	178.06(5)	175.29(5)	177.94(6)	175.20(4)	175.81(2)	168.66(3)
$O(2) \cdot \cdot \cdot Sn - S(1)$	-	-	-	-	-	-	178.66(3)



Fig. 7. Scattergram of transannular distance D. Sn (Å) as a function of the S-Sn-S angle (°) for dithiotin compounds (numbers in parentheses indicate the size of the central ring).

△ Trithiastannocannes (8)

× Dibenzotrithiastannocines (8)

▲ $[{S(C_6H_4CH_2S)_2}SnRCl](10)$

Comparison of geometrical bond parameters in the dithiastanne	cine compounds [{D(C6H4CH2S)2}SnRCl] and	d [{ $D(CH_2CH_2S)_2$ }SnRCl] stannocanes ($D = 0$,	S; $R = Ph$, $n-Bu$).

	R	D	$D \cdots Sn(Å)$	$D \cdots Sn-Cl$ (°)	tbp (%) ^a	$BO^b D \cdots Sn$
5a′	Ph	0	2.888(2)	176.92(5)	56.2	0.0882
5a″	Ph	0	2.978(2)	178.06(5)	48.6	0.0658
5b′	Ph	S	2.9522(18)	175.29(5)	72.6	0.1835
5b″	Ph	S	3.0799(18)	177.94(6)	60.0	0.1212
6a	n-Bu	0	2.7126(14)	175.20(4)	68.3	0.1558
6b	n-Bu	S	3.0970(7)	175.81(2)	69.3	0.1147
$[{D(CH_2CH_2S)_2}SnRC1]$	Ph	0	2.412	167.33	69.6	0.4135
$[{D(CH_2CH_2S)_2}SnRC1]$	Ph	S	2.805	174.24	81.4	0.2960
$[{D(CH_2CH_2S)_2}SnRC1]$	n-Bu	0	2.409	169.72	69.1	0.4176
$[{D(CH_2CH_2S)_2}SnRCl]$	<i>n</i> -Bu	S	2.786	170.23	83.5	0.3148

O Oxadithiastannocanes (8)

• $[{O(C_6H_4CH_2S)_2}SnRCl](10)$

^a Following the method of differences in angles $\Delta = \Sigma(\theta)_{\text{equatorial}} - \Sigma(\theta)_{\text{axial}}$. ^b Method of calculation BO = 10^{-(1.41 \(\Delta\)d)}, where $\Delta d = d_{\text{exp}} - \Sigma r_{\text{cov}}$, according to the covalent radii sum $\Sigma r_{\text{cov}}(\text{Sn}, \text{O}) = 2.14$ Å and $\Sigma r_{\text{cov}}(\text{Sn}, \text{S}) = 2.43$ Å.

Table 4 Selected bond lengths (Å) and bond angles (°) of 6a and 6b.

	[{O(C ₆ H ₄ CH ₂ S) ₂ }Sn(<i>n</i> -Bu)Cl] (6a) Exp. Calc.		$[{S(C_6H_4CH_2S)_2}Sn(n-Bu)Cl] $ (6b)		
			Exp.	Calc.	
D Sn	2.7126(14)	2.881	3.0970(7)	3.030	
Sn-Cl	2.3826(6)	2.351	2.4132(7)	2.372	
Sn-S1	2.3810(6)	2.405	2.3993(7)	2.411	
Sn-S2	2.3944(6)	2.398	2.3829(7)	2.411	
Sn-C15	2.146(2)	2.142	2.150(3)	2.148	
S1-Sn-C15	115.66(6)	112.3	120.96(8)	116.0	
S2-Sn-S1	116.09(2)	114.5	114.40(2)	116.3	
C15-Sn-S2	122.87(2)	123.3	119.46(2)	123.9	
$D \cdots Sn-Cl$	175.20(4)	178.3	175.81(2)	178.7	

Table 5

Topological analysis of the electronic density for compounds **6a** and **6b**; ρ and L are the density and the Laplacian $(-1/4\nabla^2 \rho)$, respectively. All quantities are in atomic units.

	6a (D = 0)		6b (<i>D</i> = S)	
	ρ	L	ρ	L
D Sn1	0.017	-0.014	0.026	-0.014
Sn1-S1	0.082	-0.026	0.080	-0.025
Sn1-S2	0.082	-0.025	0.080	-0.025
Sn1-C15	0.104	-0.027	0.102	-0.026
Sn1-Cl1	0.078	-0.046	0.075	-0.044
C1-S1	0.168	0.056	0.169	0.056
C1-C2	0.266	0.183	0.266	0.183
C2-C7	0.314	0.245	0.308	0.234
C7- D	0.269	0.061	0.197	0.090
D -C8	0.267	0.067	0.199	0.093
C8-C13	0.317	0.248	0.308	0.234
C13-C14	0.266	0.182	0.266	0.184
C14-S2	0.170	0.056	0.171	0.059
H1A-H16A	0.005	-0.005	-	-
Cl1-H16B	-	-	0.009	-0.008

as L = -0.014 a.u.). It is important to note that the *L* values of all bond critical points connecting Sn with their neighbors are negative, ranging from -0.014 to -0.046 a.u.; they are indicative of an important ionic contribution. The topological analyses presented allow us to classify as intramolecular donor-acceptor compounds, in which Sn acts as an acceptor and the **D** atom as a donor (**D** = O, S).

4. Conclusion

The dithiastannecine compounds containing a 10-membered central ring shows that the dithioligands are able to expand the coordination number of the Sn acceptor atom by establishing the interaction $D \cdots Sn$ (D = O or S). For example, the spirocyclic compound **7a** displays a bicapped tetrahedral local geometry where the oxygen atoms cap two triangular faces; furthermore, the compounds [{ $D(C_6H_4CH_2S)_2$ }SnRCl] **5a** (D = O, R = Ph), **5b** (D = S, R = Ph), **6a** (D = O, R = n-Bu), and **6b** (D = S, R = n-Bu) in the solid state exhi-

bit a five-coordinate tin atom where the local geometry is described as a distorted trigonal bypyramidal. In all cases the organic R group is located at an equatorial position, and the chloro ligand occupies an axial position; the remaining axial position is occupied by the **D** donor atom. In contrast, in solution the ¹¹⁹Sn NMR experiments indicate the presence of a four-coordinate configuration around the tin atoms despite the significant change in $\Delta\delta$ values related to the coordination number of the tin atom, mainly in compounds **5** where the acidity of Sn has been enhanced. The DFT studies of **6a** and **6b** in gas phase satisfactorily reproduced the overall geometries observed in the solid state; the topological analysis showed bond critical points along the **D**...Sn interaction



Fig. 8. Critical points of the electron density (CPs) and the gradient paths in the compounds 6a and 6b (the small red and yellow spheres are the bond and ring critical points, respectively). Color online.

Table 6

Selected crystallographic data for compounds 1a, 5a, 5b, 6a, 6b, and 7a.

	1a	5a	5b	6a	6b	7a
Empirical formula	$C_{14}H_{14}O_3$	C ₂₀ H ₁₇ ClOS ₂ Sn	C ₂₀ H ₁₇ ClS ₃ Sn	C18H21ClOS2Sn	C18H21ClS3Sn	C ₂₈ H ₂₄ O ₂ S ₄ Sn
Formula weight	230.25	491.60	507.66	471.61	487.67	639.40
Temperature (K)	295(2)	131(2)	131(2)	131(2)	131(2)	131(2)
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	Pbcn	$P2_1/c$	$P2_1/c$	$P2_{1}2_{1}2_{1}$	P2 ₁ /c	$P2_1/n$
a (Å)	16.300(5)	28.8979(8)	28.8866(14)	10.3068(2)	9.1362(3)	10.3756(3)
b (Å)	7.533(2)	9.09834(19)	8.9857(5)	12.8059(2)	24.7690(12)	15.9807(5)
<i>c</i> (Å)	19.603(6)	15.2309(4)	15.9723(7)	14.7505(3)	8.7296(3)	16.6493(5)
β (°)	90	102.836(3)	103.249(5)	90	96.515(3)	107.803(3)
V (Å ³)	2406.8(13)	3904.48(17)	4035.5(4)	1946.89(6)	1962.70(14)	2628.43(14
Ζ	8	8	8	4	4	4
Wavelength (Å)	0.71073	0.71073	1.54184	0.71073	0.71073	0.71073
Absorption coefficient (mm ⁻¹)	0.089	1.665	14.186	1.665	1.754	1.315
F(000)	976	1952	2016	944	976	1288
θ range for data collection (°)	2.08-24.06	3.49-26.05	4.72-68.12	3.47-26.06	3.17-25.29	3.28-25.29
Reflections collected	17455	28270	26328	15082	8690	8769
Independent reflections	1914	7703	7366	3849	3567	4668
Completeness to θ	99.9	99.7	100.0	99.6	99.8	97.5
Data/restrains/parameters	1914/0/158	7703/0/451	7366/0/451	3849/0/209	3567/0/209	4668/0/316
Goodness-of-fit on F ²	1.010	1.050	1.037	1.026	1.151	0.987
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0596$,	$R_1 = 0.0344$,	$R_1 = 0.0473$,	$R_1 = 0.0169$,	$R_1 = 0.0225$,	$R_1 = 0.0243$,
	$wR_2 = 0.1572$	$wR_2 = 0.0631$	$wR_2 = 0.1044$	$wR_2 = 0.0348$	$wR_2 = 0.0520$	$wR_2 = 0.0591$
R indices (all data)	$R_1 = 0.1199$,	$R_1 = 0.0514$,	$R_1 = 0.0797$,	$R_1 = 0.0187$,	$R_1 = 0.0267$,	$R_1 = 0.0330$,
	$wR_2 = 0.1943$	$wR_2 = 0.0665$	$wR_2 = 0.1160$	$wR_2 = 0.0352$	$wR_2 = 0.0531$	$wR_2 = 0.0613$
Largest difference in peak and hole ($e \text{ Å}^{-3}$)	0.334 and -0.183	0.438 and -0.614	0.826 and -0.707	0.202 and -0.379	0.347 and –0.580	0.805 and -0.394

and their Laplacian values indicated an important ionic contribution. These results allow us to propose the wide coordination abilities of the $\{D(C_6H_4CH_2S)_2\}^{2-}$ ligand to increase the coordination number of tin as an acceptor atom as other well studied ligands that produce smaller central rings of the types I–III also do.

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Appendix A. Supplementary data

CCDC 830555, 830556, 830554, 830557, 830559, and 830558 contain the supplementary crystallographic data for **1a**, **5a**, **5b**, **6a**, **6b**, and **7a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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