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Synthesis, crystal structures and coordination modes of some triorganotin(IV) complexes with 2-N-propyl and 2-N-benzyl-amino-1-cyclopentene-1-dithiocarboxylates

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ABSTRACT

The syntheses and characterization of six new triorganotin(IV) complexes, Ph_3Sn(PrACDA) (**1**), Bu_3Sn(-PrACDA) (**2**), Ph_3Sn(BzACDA) (**3**), Bu_3Sn(BzACDA) (**4**), Me_3Sn(BzACDA) (**5**) and Cy_3Sn(BzACDA) (**6**) (ACDA = 2-amino-1-cyclopentene-1-carbodithioate anion) are reported. Compounds **1**–**6** were synthesized by the reaction between the sodium salts of 2-*N*-propyl- or 2-*N*-benzyl-2-amino-1-cyclopentene-1-carbodithioate and R_3SnCl (R = Ph, Bu, Me, Cy) in a 1:1 M ratio. The complexes were characterized by elemental analyses, IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy and by FAB^+ mass spectrometry. The experimental data reveal that the tin atom is coordinated to the ligand by means of the two sulfur atoms from the carbodithioate group in an anisobidentate mode, while the $^{119}Sn\{^1H\}$ NMR spectra suggest a pentacoordinate metal center in **1**–**4** and a tetracoordinate tin atom for **5** and **6**. The molecular structures of complexes **1**, **3** and **5** were confirmed by single crystal X-ray diffraction analysis showing the presence of N–H···S hydrogen bonding and a distorted trigonal bipyramid geometry for the tin atoms.

1. Introduction

The coordination chemistry of organometallic tin complexes has been widely studied, possible the most important scientific contributions correspond to the development of tin compounds with biological activity, particularly anti-tumor activity, novel supramolecular arrangements, including new host guest host relationships [1,2] and the synthesis of compounds with unprecedented geometric arrangements [3,4] promoted by the presence of soft donor atoms.

Organotin(IV) compounds are important agrochemicals, biocides, catalysts and stabilizers in PVC [5]. However, along with this utility there is great concern about their toxic impact on the environment [6]. An option for reducing such bioimpact is to block available coordination sites around the tin atom by promoting intramolecular Sn···E (E = S, O, N) bonding [7]. Moreover, this type of secondary bonding has been suggested to be relevant to the biological activity of organotin(IV) species [8]. Indeed, organotin(IV) compounds of general formula, R_nSnL_{4-n} are able to exhibit a variety of interesting biological effects that depend on the number *n* and type of organic group R bonded to the metal ion, and on the nature of the ligand L. It is known that the number and nature of the organic groups bound to the central Sn atom essentially determine the biological activity while the nature of the anionic group is of only secondary importance [9]. The biological activity ranges from compounds with severe toxicity to compounds with good potential pharmacological applications. In this way, organotin(IV) compounds are known to exhibit important cytotoxic effects and are actively investigated as possible commercial antitumor compounds [10–13]. Nonetheless, their mechanism of action is still not totally understood, but it has been suggested that organotin(IV) compounds exert their effects through binding to the thiol groups of proteins [14].

The 2-Amino-1-cyclopentene-1-carbodithioate anion (ACDA) and its *N*-derivatives are versatile chelating agents [15] and their related complexes have been recently used as precursors in the synthesis of nanoparticles [16,17]. These ligands can coordinate to

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the metal center through a bidentate *N*∩*S* mode [18] or solely through the carbodithioate moiety in a mono- or bidentate fashion, where the latter can be done in a iso- or anisobidentate mode, that is the most frequently observed pattern for main group elements [19].

The biological activity of organotin(IV) compounds and the interesting versatile behavior of ACDA type ligands, as well as the possibility of the use of the new complexes as precursors for the preparation of nanomaterials, motivated us to synthesize some new ACDA/Sn compounds. Therefore, following up on our studies on organotin(IV) complexes bearing 1,1-dithiolates, we now report on the synthesis of six triorganotin (IV) complexes using 2-*N*-propyl-amino-(**PrACDA**) and 2-*N*-benzyl-amino-1-cyclopentene-1-carbodithioic acids (**BzACDA**) as ligands (Fig. 1).

2. Experimental

2.1. Materials and methods

Commercial starting materials were used as received and all solvents were dried and distilled prior to use. 2-*N*-propyl-amino-1-cyclopentene-1-carbodithioic acid (**PrACDA**) and 2-N-benzyl-amino-1-cyclopentene-1-carbodithioic acid (**BzACDA**) were synthesized as described previously in the literature [20,21]. IR spectra were obtained using KBr disks on a Bio-Rad FTIR spectrophotometer in the range $\tilde{\nu}$400–4000 cm^{-1}. Mass spectra were obtained on Jeol JMS 700 equipment. NMR spectra were recorded on a Varian Gemini 200 MHz and Varian Unity Inova 400 MHz spectrometers using $CDCl_3$ as solvent. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were reported with reference to TMS (internal), while $^{119}Sn\{^1H\}$ NMR spectra were referenced to the external references $SnMe_4$. Elemental analyses (C and H) were carried out on an Elemental Vario EI TCD instrument.

2.2. X-ray structure determination

Single crystals were mounted on a Bruker APEX DUO diffractometer equipped with an Apex II CCD detector at 100 K. Frames were collected using omega scans and integrated with SAINT [22]. Multi-scan absorption correction (SADABS, TWINABS) [22] was applied. The structures were solved by direct methods (SHELXS) [23] or using intrinsic phasing (SHELXT) [24] and refined using full-matrix least-squares on F^2 with SHELXL [25] using the ShelXle GUI [26]. Weighted *R* factors, R_w and all goodness-of-fit indicators, are based on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the C–H bonds were placed in idealized positions, whereas the hydrogen atoms from the NH moieties in **1**, **3** and **5** were localized from the difference electron density map and their position was refined with U_{iso} tied to the parent atom with distance restraints (DFIX). Compound **3** crystallized as a non-merohedral twin with the ratio of the two domains 3:1. The molecular graphics were prepared using GRETEP, POV-RAY and GIMP [27].

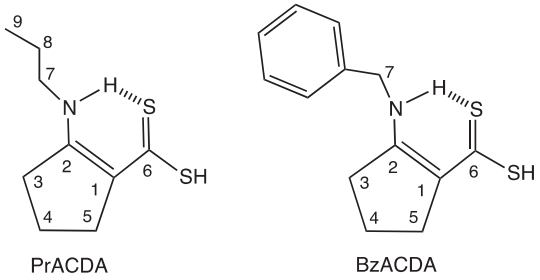
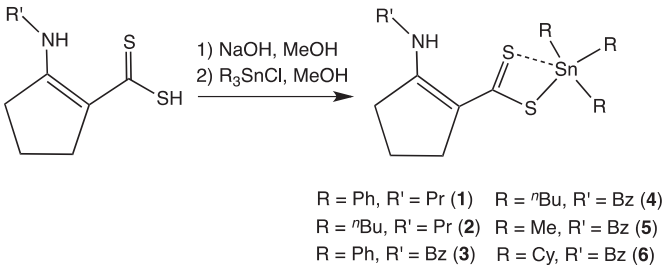


Fig. 1. The structures of the N-substituted ACDA ligands.



Scheme 1. Synthetic procedure for the preparation of the compounds **1**–**6**.

2.3. Preparation of the complexes

2.3.1. General synthetic procedure for the triorganotin(IV) complexes *1*–*6*

Ph_3Sn(PrACDA) (1): A solution of NaOH (0.020 g, 0.518 mmol) in methanol (10 mL) was added dropwise to a solution of **PrACDA** (0.104 g, 0.518 mmol) in methanol (10 mL). The reaction mixture was stirred for 10 min at 24 °C and then was added dropwise to a solution of Ph_3SnCl (0.2 g, 0.518 mmol) in methanol. The mixture was stirred overnight and a pale yellow precipitate formed. The solid was filtered and washed with MeOH and recrystallized from a CH_2Cl_2/hexane mixture to give pale yellow crystals. Yield: 66% (0.18 g). M.p. 183–185 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$3423 ν(N–H), 1605 ν(NH + C=C), 1500 ν(CH_2+C=C), 944–907 ν(CS_2), 500, 451 ν(C–Sn). ^1H NMR ($CDCl_3$, 25 °C, TMS): δ 0.9 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, *H*-9), 1.5 (m, 2H, *H*-8), 1.8 (m, 2H, *H*-4), 2.6 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *H*-3), 2.9 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *H*-5), 3.2 (m, 2H, *H*-7), 7.3–8.0 (m, 15H, m, Ar–*H*), 11.2 (br s, 1H, N*H*). $^{13}C\{^1H\}$NMR ($CDCl_3$, 25 °C, TMS): δ 11.7 (*C*-9), 20.0 (*C*-4), 23.1 (*C*-8), 33.4 (*C*-3), 35.5 (*C*-5), 47.8 (*C*-7), 119.8 (*C*-2), 128.4 (*p*-*C*), 129.0 (*o*-*C*), 137.0 (*m*-*C*), 141.9 (*i*-*C*), 170.3 (*C*-1), 192.9 (*C*-6). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 25 °C, TMS): δ −155.8. MS(FAB^+): *m/z* (%) 551 (M^+, 10), 474 (M^+–Ph, 60), 383 (Ph_3SnS^+, 10), 351 (Ph_3Sn^+, 60), 168 ($C_9H_{14}NS^+$, 100). Elemental analysis (%) calcd. for $C_{27}H_{29}NS_2Sn$ (550.37): C 58.92, H 5.31. Found: C 58.79, H 5.19.

The related triorganotin(IV) complexes **2**–**6** were prepared using a similar method as described for **1**.

Bu_3Sn(PrACDA) (2): Yield: 66% (0.16 g). M.p. 156–158 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3453 ν(N–H), 1615 ν(NH + C=C), 1500 ν(CH_2+C=C), 948-912 ν(CS_2), 502, 422 ν(C–Sn). ^1H NMR ($CDCl_3$, 25 °C, TMS): δ 0.9 (t, $^3J_{H-H}$ = 7.2 Hz, 9H, $CH_3(CH_2)_2CH_2Sn$), 1.0 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, *H*-9), 1.4 (m, 6H, $CH_3CH_2(CH_2)_2Sn$), 1.7 (m, 2H, *H*-8), 1.8 (m, 2H, *H*-4), 1.9 (m, 6H, $CH_3CH_2CH_2CH_2Sn$), 2.0 (m, 6H, $CH_3(CH_2)_2CH_2Sn$), 2.7 (m, 2H, *H*-3), 2.9 (m, 2H, *H*-5), 3.3 (m, 2H, *H*-7), 11.1 (br s, 1H, N*H*). $^{13}C\{^1H\}$NMR ($CDCl_3$, 25 °C, TMS): δ 11.7 (*C*-9), 14.0 ($CH_3(CH_2)CH_2Sn$), 19.9 (*C*-4), 23.3 (*C*-8), 16.7 ($CH_3CH_2(CH_2)_2Sn$), 26.8 ($CH_3CH_2CH_2CH_2Sn$), 30.6 ($CH_3(CH_2)_2CH_2Sn$), 33.7 (*C*-3), 35.3 (*C*-5), 47.7 (*C*-7), 118.3 (*C*-2), 169.0 (*C*-1), 192.5 (*C*-6). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 25 °C, TMS): δ −184.4. MS(FAB^+): *m/z* (%) 491 (M^+, 10), 434 (M^+–^{n}Bu, 75), 323 ($^nBu_3SnS^+$, 35), 291($^nBu_3Sn^+$, 10), 168 ($C_9H_{14}NS^+$, 100). Elemental analysis (%) calcd. for $C_{21}H_{41}NS_2Sn$ (490.40): C 51.43, H 8.43. Found: C 51.35, H 8.33.

Ph_3Sn(BzACDA) (3): Yield: 68% (0.21 g) M.p. 191–193 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3413 ν(N–H), 1592 ν(NH + C=C), 1493 ν(CH_2+C=C), 944–911 ν(CS_2), 513, 449 ν(C–Sn). ^1H NMR ($CDCl_3$, 25 °C, TMS): δ 1.74 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *H*-4), 2.5 (t, $^3J_{H-H}$ = 7.6 Hz 2H, *H*-3), 2.9 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *H*-5), 4.4 (m, 2H, *H*-7), 7.2–7.8 (m, 20H, Ar–*H*), 11.4 (br s, 1H, N*H*). $^{13}C\{^1H\}$NMR ($CDCl_3$, 25 °C, TMS): δ 19.9 (*C*-4), 33.7 (*C*-3), 35.7 (*C*-5), 49.7 (*C*-7), 120.1 (*C*-2), 127.2–141.0 (Ar–*C*),