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Diorganotin(IV) dithiocarbamate complexes as chromogenic sensors of anion binding

Juan Pablo Fuentes-Martínez, Isaim Toledo-Martínez, Perla Román-Bravo, Patricia García y García, Carolina Godoy-Alcántar *, Marcela López-Cardoso, Hugo Morales-Rojas *

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C.P. 62209 Cuernavaca, Mexico

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ABSTRACT

One dinuclear chlorodiphenyltin (IV) dithiocarbamate complex (**1**) and four mononuclear complexes of general formula $Ph_2Sn(S_2CNR)Cl$ (**2**, **3**, **5**, and **6**) have been synthesized and characterized both in solid-state and solution. X-ray structures for complexes **1**, **3** and **6** demonstrated a five-coordination geometry around of tin atoms, in which dithiocarbamate ligand chelates asymmetrically the metal center. As shown by ^{119}Sn NMR spectroscopy, five-coordination geometry observed in the solid-state remains in solution. The stability of these chlorodiphenyltin(IV) dithiocarbamate complexes in the presence of biologically relevant anions such as acetate, dicarboxylates of general formula $^{-}OOC\text{-}(CH_2)_n\text{-}COO^{-}$ ($n = 2$–8), dihydrogenphosphate, hydrogensulfate, and halides has been examined in acetonitrile solutions. For all of these organotin(IV) complexes the displacement of the coordinated ligands (*i.e.*, chloride and dithiocarbamate) from the organotin(IV) moiety occurred in the presence of monoanions like acetate, dihydrogenphosphate, hydrogensulfate and fluoride. A stepwise mechanism for ligand exchange is proposed based on UV–Vis, ^{1}H, ^{13}C and ^{119}Sn spectroscopic data, as well as mass spectrometry. From UV–Vis titration experiments it was found that dicarboxylates with small spacers like malonate and succinate, acted differently in the exchange of the dithiocarbamate group in comparison to other monoanionic *O* donor ligands or dicarboxylates with longer chains, perhaps by following an intramolecular displacement of the coordinated ligand.

The lability of these organotin(IV) dithiocarbamate compounds in solution hampers their use as stably host for anions, however, by taking advantage of the intrinsic chromogenic properties of free dithiocarbamate anions, or by attaching dithiocarbamate groups to well-known fluorescent moieties such as antracene, these complexes can sense the presence of *O*-donor anions at very low concentrations by displacement of the metal-coordinated dithiocarbamate.

1. Introduction

Anion recognition by Lewis acid moieties has received attention as an important strategy in developing supramolecular receptors [1]. Several organometallic compounds containing tin(IV) as electrodeficient center have been previously examined for ion recognition including macrocycles [2], cryptand-like [3] and calixarene shaped receptors [4], as well as ferrocene based complexes [5]. In general anion binding affinity was tested for monoanionic species such as halides (F^-, Cl^-, Br^-) in solvents like chloroform or dichloromethane using ^{119}Sn NMR spectroscopy as the main detection tool. Further attempts made by Dakternieks, Jurkshat and coworkers were based on bis(haloorganostannyl)alkanes that linked two tin(IV) centers [6]. These receptors were incorporated into polymeric membrane ion-selective electrodes and were highly selective for fluoride and phosphate ions, but somewhat unstable. A recent example of fluoride sensing with bis(di-*n*-alkyl(fluoro)stannyl)alkanes improved the performance of these ion carriers in polymeric matrixes [7]. Organotin(IV) sensors of anions based on optical signaling are scarce, interestingly, a recent report on tin(IV) complexes of *N*-confused porphyrins showed remarkable affinity and selectivity as fluorescent probes for halides, particularly fluoride, with binding constants in the order of $10^6\ M^{-1}$ in CH_2Cl_2 [8].

General interest in organotin complexes have been geared by their potential therapeutic use as antifungal, antibacterial, and antitumoral agents [9]. Mostly, these compounds are organotin(IV) derivatives with carboxylates [10], aminoacids [11], heterocycles [12], and various *N*, *O*, or *S* donor ligands [13], particularly dithiocarbamates [14], given that sulfur ligands coordinated to diorganotin moieties were regarded as very stable in comparison to other ligands coordinated by *N* or *O* [15]. Further interest in the

* Corresponding authors. Tel./fax: +52 777 3297997 (H. Morales-Rojas).
E-mail addresses: cga@uaem.mx (C. Godoy-Alcántar), hugom@uaem.mx (H. Morales-Rojas).

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structural features of organotin(IV) dithiocarbamate complexes is based on the wide range of industrial applications such as chemical vapor deposition processes, flame retardants, polymer stabilizers, and non-linear optical materials [16].

Dithiocarbamates as ligands are well known to bind strongly and selectively to many metal ions [17], so in the past few years self-assembly directed by metal–dithiocarbamate coordination have emerged as a useful supramolecular methodology for the preparation of macrocycles [18], cages [19], catenanes [20], and nanoparticles [21,22]. In several of these reports transition metal dithiocarbamate macrocycles displayed anion recognition with the aid of amides or positively-charged motifs in the macrocycle structure. For instance, Beer et al. recently reported an amide functionalized dithiocarbamate ruthenium(II) bis-bipyridyl compound that showed electrochemical sensing of anions such as $H_2PO_4^-$, AcO^-, and BzO^- [23]. The potential of organotin(IV) complexes in metal-directed self-assembly of macrocyclic and supramolecular structures have been exploited mainly by Höpfl et al. employing dicarboxylates and dithiocarbamates as ligands [24]. Solution chemistry of organotin carboxylates and dicarboxylates have been studied extensively [24,25]. In contrast the solution chemisty of organotin dithiocarbamates is much less explored, and to our knowledge, only one report on the use organotin(IV) dithiocarbamate complexes as host for anions is available [26].

A comprehensive exploration of organotin(IV) dithiocarbamate complexes for ion recognition is worthwhile given that Lewis acidity can be modulated by substitution at the organometallic center and also by substitution at the ancillary ligand (*i.e.*, chloride, or dithiocarbamate) [27]. Herein, we report on the ligand-exchange properties of a series of organotin(IV) dithiocarbamates complexes **1**–**6** (Fig. 1) towards a wide number of biologically relevant anions such as carboxylates, dicarboxylates, dihydrogenphosphate, hydrogensulfate, and halides. By taking advantage of the intrinsic chromogenic properties of dithiocarbamate anions and by attaching dithiocarbamate groups to well-known fluorescent moieties such as antracene, these complexes can sense the presence of *O*-donor anions at very low concentrations by displacement of the metal-coordinated dithiocarbamate.

2. Experimental

2.1. General procedures and methods

All reagents were of commercial grade and were used as received. Ph_2SnCl_2, piperazine, pyrrolidine, and 9-(methylaminomethyl)-antracene were commercially available and were used without further purification. *N*-BOC-piperazine was prepared as reported by Lowe and coworkers [28]. The sodium salts of dithiocarbamates were prepared by published literature methods [29]. Similarly, tetrabutylammonium salts of dithiocarbamates were prepared starting from commercial tetrabutylammonium hydroxide solutions in methanol.

IR spectra were recorded in the region 4000–500 cm^{-1} as KBr pellets using Bruker Vector 22 FTIR spectrometer. The ^1H, ^{13}C and ^{119}Sn NMR spectra were obtained at room temperature on a Varian Inova 400 spectrometer, using $CDCl_3$, pyridine-d_5 or CD_2Cl_2 as solvent. The chemical shifts are relative to internal Me_4Si (^1H, ^{13}C) and external tetramethyltin (^{119}Sn). The FAB mass spectra were measured on a 3-nitrobenzyl alcohol matrix in the positive ion mode on a JEOL MStation JMS-700 instrument. The ESI mass spectra were measured in the positive or negative ion mode using a JEOL MStation JMS-700 instrument. Elemental analyses were obtained in an Elemental Vario ELIII TCD instruments using samples previously dried for 2 h under high vacuum. The electronic absorption spectra were recorded at 25 °C on a Hewlett-Packard 8452A diode-array spectrophotometer, and emission spectra were recorded on a Perkin–Elmer LS55 spectrofluorimeter.

2.2. Synthesis of complex bis[chlorodiphenyltin(IV)] piperazinyldithiocarbamate (*1*)

A solution of the disodium salt of the *N′*,*N″*-piperazinyldithiocarbamate (0.5 g, 1.772 mmol) in ethanol (20 mL) was treated with diphenyltin dichloride (1.217 g, 3.544 mmol). The reaction mixture was stirred for 24 h at room temperature. Then was filtered, the resulting powder was recrystallized from a CH_2Cl_2–hexane mixture afforded white solid of **1** (1.39 g, 84%), m.p. 230–32 °C. *Anal.* Calc. for $C_{30}H_{28}Cl_2N_2S_4Sn_2$: C, 42.23; H, 3.31; N, 3.28. Found: C, 41.77;

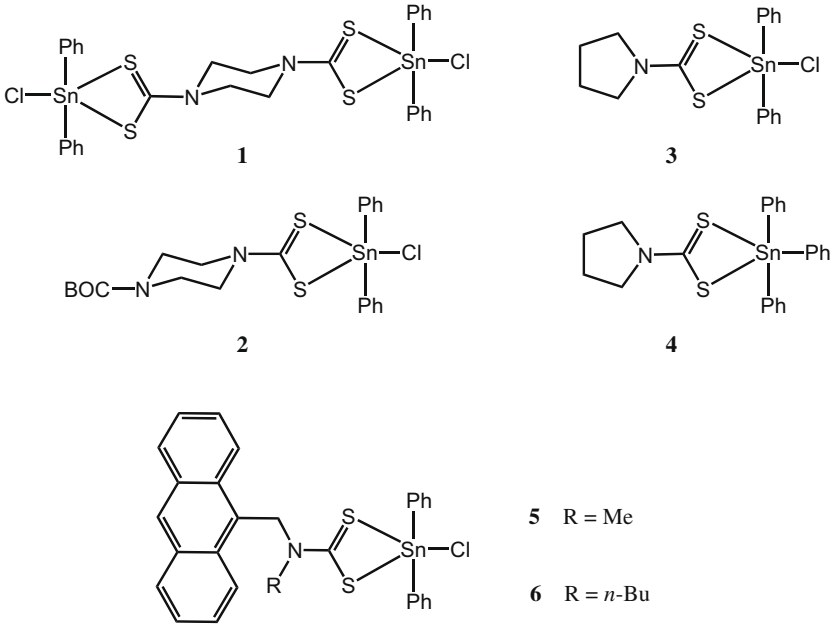


Fig. 1. Chemical structures of dithiocarbamate organotin (IV) complexes.

H, 3.23; N, 3.595%. MS (FAB^+, $CHCl_3$) *m/z*: 817 (8) [M^+−Cl], $C_{30}H_{28}ClN_2S_4Sn_2^+$; 663 (2) $C_{18}H_{18}ClN_2S_4Sn_2^+$; 512 (4) $C_{18}H_{18}ClN_2S_3Sn^+$; 435 (62) $C_{12}H_{13}ClN_2S_3Sn^+$; 391 (30) $C_{11}H_{13}ClN_2S_2Sn^+$; 305 (100) $C_{12}H_{10}SSn^+$; 273 (23) $C_{12}H_{10}Sn^+$. IR (KBr) 3047w, *ν*(C–H); 1493 *ν*(C=N); 1229s $\nu_s(CH_2–N)$; 1000s ν_s(C–S); 911w, (C–N); 693m $\nu_{as,}$(C–S); 446 m *ν*(Sn–S) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 4.09 (8H, s) NC**H**$_2$; 7.46 (12H, m) **H**–Ar; 8.01 (8H, m) **H**–Ar. ^{13}C NMR ($CDCl_3$): *δ* 50.51 (N–**C**H_2); 129.13, 130.66, 135.81 and 141.45 (**C**–Ar); 199.35 (**C**S_2). ^{119}Sn NMR ($CDCl_3$): *δ* −309.19.

2.3. Synthesis of the tetrabutylammonium salt of N′-BOC-piperazinyl-N″-dithiocarbamate (L2-TBA)

An ethanolic solution of *N*-BOC-piperazine (0.56 g, 3 mmol in 10 mL) was treated with an equimolar amount of tetrabutylammonium hydroxide (3 mL of 1 M solution in methanol) in presence of CS_2 (0.18 mL, 1 equiv.). The solution was stirred at room temperature by 6 h, during which turned out yellowish. Solvent was removed by evaporation and the mixture lixiviated with Et_2O (3 × 15 mL) affording a pale green solid (1.19 g, 79%). M.p. 152–153 °C. *Anal*. Calc. for $C_{26}H_{53}N_3O_2S_2$: C, 61.98; H, 10.60; N, 8.34. Found: C, 59.76; H, 10.39; N, 7.99%. IR (KBr) 2964s, 2870s *ν*(C–H); 1671s *ν*(C=O); 1419m *ν*(N–CS_2); 1373s *ν*(C=N); 1249s *ν*(C–O); 1003s $\nu_s(C–S_2)$; 928m, *ν*(C–N) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 0.95 (12H, t) C^{δ}**H**$_3$, 1.40 (17H, m) C^{γ}**H**$_2$ and [C(C**H**$_3)_3$], 1.60 (8H, m) C^{β}**H**$_2$, 3.35 (16H, m) C^{α}**H**$_2$ and NC**H**$_2$, 4.45 (8H, dd) NC**H**$_2$. ^{13}C NMR ($CDCl_3$): *δ* 14.0 **C**$^{\delta}H_3$, 20.08 **C**$^{\gamma}H_2$, 24.51 **C**$^{\beta}H_2$, 28.67 [C(**C**$H_3)_3$], 43.69 (N–**C**H_2), 49.98 (N–**C**H_2), 59.32 **C**$^{\alpha}H_2$, 79.8 [**C**$(CH_3)_3$]; 155.1 (**C**=O), 214.6 (**C**S_2).

2.4. Synthesis of the complex chlorodiphenyltin(IV) N′-BOC-piperazinyl-N″-dithiocarbamate (**2**)

The salt of tetrabutylammonium *N*-BOC-piperazinyldithiocarbamate (1.0 g, 1.98 mmol) in ethanol (10 mL) was treated with diphenyltin dichloride (0.68 g, 1.98 mmol) in one portion as a solid. The reaction mixture was stirred for 6 h at room temperature. Then was filtered, and the resulting powder was recrystallized from a CH_2Cl_2–hexane mixture afforded white-off solid of **2** (0.9 g, 79%), m.p. 167–168 °C. *Anal*. Calc. for $C_{22}H_{27}ClN_2S_4Sn$: C, 46.38; H, 4.78; N, 4.92. Found: C, 45.62; H, 4.56; N, 4.94%. MS (FAB^+) *m/z*: 570 (10) [M^+] $C_{22}H_{27}ClN_2O_2S_2Sn^+$, 535 (100) [$M^+$−Cl], $C_{22}H_{27}N_2S_2Sn^+$; IR (KBr) 3008w, *ν*(C–H); 1734s *ν*(C=O); 1425m *ν*(N–CS_2); 1364s *ν*(C=N); 1221s *ν*(C–O); 1012w $\nu_s(C–S_2)$; 911w, *ν*(C–N) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 1.48 (9H, s) [C($CH_3)_3$], 3.57 (4H, dd) NC**H**$_2$, 3.95 (4H, dd) NC**H**$_2$; 7.47 (6H, m) **H**–Ar; 8.04 (4H, m) **H**–Ar. ^{13}C NMR ($CDCl_3$): *δ* 28.6 [C(**C**$H_3)_3$], 42.9 (N–**C**H_2), 52.2 (N–**C**H_2), 81.3 [**C**$(CH_3)_3$]; 129.9, 135.9, 141.9 (**C**–Ar); 154.3 (**C**=O), 196.9 (**C**S_2). ^{119}Sn NMR ($CDCl_3$): *δ* −313.0

2.5. Synthesis of the complex chlorodiphenyltin(IV) pyrrolidinyldithiocarbamate (**3**)

A solution of the sodium salt of pyrrolidinyldithiocarbamate (0.2 g, 1.18 mmol) in ethanol (20 mL) was treated with diphenyltin dichloride (0.407 g, 1.18 mmol). The reaction mixture was stirred for 24 h at room temperature. Then was filtered, the resulting powder was recrystallized from a CH_2Cl_2–hexane mixture afforded white solid of **3** (0.374 g, 69%). M.p. 143–44 °C. *Anal*. Calc. for $C_{17}H_{18}ClNS_2Sn$: C, 44.91; H, 3.99; N, 3.08. Found: C, 42.44; H, 3.08; N, 3.79%. MS (FAB^+) *m/z*: 420 (100) [M^+−Cl], $C_{17}H_{18}NS_2Sn^+$; 378 (50) [M^+−Ph] $C_{11}H_{13}ClNS_2Sn^+$; IR (KBr) 3050w, 2943w *ν*(C–H); 1503 *ν*(C=N); 1153m $\nu_s(CH_2–N)$, 1066w ν_s(C–S); 945w, (C–N); 694w $\nu_{as,}$(C–S); 448m *ν*(Sn–S) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 2.01 (4H, m) NC**H**$_2$; 3.69 (4H, m); 7.44 (6H, m) **H**–Ar; 8.08 (4H, m) **H**–Ar. ^{13}C NMR ($CDCl_3$): *δ* 27.0 (N–CH_2**C**H_2), 55.4 (N–**C**H_2CH_2); 128.9, 130.3, 135.9 and 142.2 (**C**–Ar); 192.1 (**C**S_2). ^{119}Sn NMR ($CDCl_3$): *δ* −311.1.

2.6. Synthesis of the complex triphenyltin(IV) pyrrolidinyldithiocarbamate (**4**)

This compound was prepared in similar fashion to **3**, using the sodium salt of pyrrolidinyldithiocarbamate (0.2 g, 1.18 mmol) and triphenyltin chloride (0.456 g, 1.18 mmol) to give a white solid (0.535 g, 91%). M.p. 147 °C. *Anal.* Calc. for $C_{23}H_{23}NS_2Sn$: C, 55.66; H, 4.67; N, 2.82. Found: C, 55.31; H, 4.54; N, 3.24%. MS (FAB^+) *m/z*: 497 (5) [M^+], $C_{23}H_{23}NS_2Sn^+$; 420 (30) [M^+−Ph] $C_{17}H_{18}NS_2Sn^+$; IR (KBr) 3055w, 2947w *ν*(C–H); 1476s *ν*(C=N); 1439m, 1330m $\nu_s(CH_2–N)$; 1163m, 1066m, 999m, 950m ν_s(C–S); 911w, (C–N); 695w $\nu_{as,}$(C–S); 449m *ν*(Sn–S) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 2.01 (4H, m) NC**H**$_2$; 3.72 (4H, m); 7.37 (9H, m) **H**–Ar; 7.71 (8H, m) **H**–Ar. ^{13}C NMR ($CDCl_3$): *δ* 27.0 (N–CH_2**C**H_2); 55.3 (N–**C**H_2CH_2); 128.6, 129.2, 136.9 and 142.2 (**C**–Ar); 196.4 (**C**S_2). ^{119}Sn NMR ($CDCl_3$): *δ* −175.1.

2.7. Synthesis of complex chlorodiphenyltin(IV) 9-(methylaminomethyl)-antracenyl dithiocarbamate (**5**)

A solution of 9-(methylaminomethyl)-antracene (0.5 g, 2.26 mmol) in ethanol (20 mL) was treated with tetrabutylammonium hydroxide (2.27 mL, 1.0 M solution in methanol, 1 equiv.) and CS_2 (0.14 mL, 2.26 mmol). The reaction mixture was stirred for 18 h at room temperature. Diphenyltin dichloride (0.76 g, 2.26 mmol) was added after this time. A solid was formed after 2 h, the mixture was filtered, affording a yellow powder of **5** (1.07 g, 78.7%). M.p. 251–53 °C. *Anal.* Calc. for $C_{29}H_{24}ClNS_2Sn$: C, 57.59; H, 4.00; N, 2.32. Found: C, 55.89; H, 3.79; N, 2.48%. MS (FAB^+) *m/z*: 570 (10) [M^+−Cl], $C_{29}H_{24}NS_2Sn^+$; IR (KBr) 3055w, *ν*(C–H); 1489 *ν*(C=N); 1392s $\nu_s(CH_2–N)$; 1072s ν_s(C–S); 980w, (C–N); 889w 731s, 562w $\nu_{as,}$(C–S); 449m *ν*(Sn–S) cm^{-1}. ^1H NMR (pyridine-d_5): *δ* 2.78 (3H, s) NC**H**$_3$, 6.09 (2H, s) NC**H**$_2$; 7.46 (12H, m) **H**–Ar; 8.01 (8H, m) **H**-Ar. ^{13}C NMR (pyridine-d_5): *δ* 40.6 (N–**C**H_3); 54.0 (N–**C**H_2); signals for aromatics appeared from 125 to 136 ppm overlapping with solvent; 196.04 (**C**S_2). ^{119}Sn NMR (pyridine-d_5): *δ* −328.02.

2.8. Synthesis of chlorodiphenyltin(IV) 9-(butylaminomethyl)-antracenyl dithiocarbamate (**6**)

To a solution of 9-formylanthracene in ethanol (0.5 g, 2.42 mol in 20 mL) butylamine (0.177 g, 2.42 mmol) was added, and the mixture was stirred under reflux by 4 h. After this time formation of the imine was complete. The ethanolic solution was treated with excess $NaBH_4$ (0.183 g, 4.84 mmol) under stirring at 0 °C, then the mixture was stirred to room temperature by 8 h. To the reaction mixture 1 mL of water was added to eliminate excess of $NaBH_4$. The resultant solution mixture was concentrated to a yellow oil, partitioned in water and dichloromethane, and from the organic phase 9-(butylaminomethyl)-anthracene was obtained as a yellow oil.

The latter product (0.5 g, 2.26 mmol) was dissolved in 20 mL of ethanol and treated with sodium hydroxide solution (2.5 mL, 2.42 mmol, 1 equiv.) and CS_2 (0.15 mL, 2.26 mmol). The reaction mixture was stirred for 18 h at room temperature. Diphenyltin dichloride (0.832 g, 2.24 mmol) was added after this time. The solid formed after 2 h was filtered affording a yellow powder of **6** (0.77 g, 49.4%). M.p. 150–152 °C. *Anal.* Calc. for $C_{32}H_{30}ClNS_2Sn$: C, 59.41; H, 4.67; N, 2.17. Found: C, 59.68; H, 4.65; N, 2.46%. MS (FAB^+) *m/z*: 612 (10) [M^+−Cl], $C_{32}H_{30}NS_2Sn^+$; IR (KBr) 3050w, 2958w, 2866w *ν*(C–H); 1484s *ν*(C=N); 1428s $\nu_s(CH_2–N)$; 1225m, 1172m, 1101m ν_s(C–S); 988w, (C–N); 886w 732s, $\nu_{as,}$(C–S); 446w

ν(Sn–S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.44 (3H, q) NC**H**$_3$, 0.8 (2H, m), 1.3 (2H, m), 3.2 (2H, m), 5.99 (2H, s) NC**H**$_2$; 7.46–7.61 (10H, m) **H**–Ar; 8.1–8.3 (8H, m) **H**–Ar, 8.6 (1H, s) **H**–Ar. ^{13}C NMR ($CDCl_3$): δ 13.3 **C**H_3, 19.9 **C**$^{\gamma}H_2$, 29.7 **C**$^{\beta}H_2$, 51.9 **C**$^{\alpha}H_3$; 52.89 (N–**C**H_2-Arom); 123.3, 124.1, 125.4, 125.6, 127.8, 129.0, 129.5, 129.7, 130.1, 130.4, 131.4, 131.5, 135.9, 142.3 (**C**–Ar); 195.9 (**C**S_2). ^{119}Sn NMR ($CDCl_3$): δ −313.8.

2.9. X-ray crystallography

Suitable crystals of **1**, **3** and **6** were obtained from DCM–hexane (for **1**) and acetonitrile solutions. X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{Mo\ K\alpha}$ = 0.71073 Å, monochromator: graphite). Frames were collected at T = 293 and 100 K via ω/ϕ-rotation at 10 s per frame (SMART) [30a]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [30b]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [30c,d]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. For compound **1** the piperazine ring is disordered over two positions. SAME, SIMU and DELU instructions have been used to model the disorder. Molecular structure was illustrated by the SHELXTL-NT software package [30d].

2.10. Solution phase experiments

2.10.1. Preparation of tetrabutylammonium dicarboxylate salts

Tetrabutylammonium dicarboxylate salts were preparared *in situ* by mixing 987 μL of dicarboxylic acid (1×10^{-2} M) in acetonitrile with 13 μL of tetrabutylammonium hydroxide solution (40% in methanol) affording a final concentration of the salt *c.a.* 1×10^{-2} M. Stock solutions were prepared freshly to carry out titration experiments.

2.10.2. UV–Vis titrations

UV–Vis titrations were measured at 25 °C in acetonitrile. Aliquots of the corresponding tetrabutylammonium anion stock solution (1×10^{-2} M) were added to the organotin(IV) dithiocarbamate complex solution (*i.e.*, 3.3×10^{-5} M for **1**, 6.6×10^{-5} M for **2**, and 7.0×10^{-5} M for **3–6**), and the spectrum was recorded after each addition. The spectral changes in absorbance were monitored within the range λ = 200–400 nm. Final concentrations of added salt in the cuvette were within 8×10^{-6} to 4×10^{-4} M.

2.10.3. Fluorimetric titrations

Fluorimetric titrations were measured at 25 °C in acetonitrile. Aliquots of the corresponding tetrabutylammonium anion stock solution (1×10^{-4} M) were added to the diorganotin(IV) dithiocarbamate complex solution (*i.e.*, 1×10^{-7} M for **5**). The emission spectra was recorded after each addition, and the changes in fluorescence intensity were monitored at λ_{em} = 380–600 nm using λ_{ex} = 368 nm. Final concentrations of added salt in the cell were within 4×10^{-8} to 4.4×10^{-7} M. The experimental data were fitted using non-linear least-squares regression for 1:1 binding isotherm with Microcal Origin 5.

3. Results and discussion

3.1. Preparation and spectroscopic characterization of complexes 1–6

The coordination chemistry of dithiocarbamates is well known, and often secondary amines are used as starting materials for the ligand preparation, as these give more stable complexes [17]. The organotin(IV) derivatives **1–6** were prepared by direct reaction of the diphenyltin dichloride or triphenyltin chloride and the corresponding salt of the dithiocarbamate. All compounds were characterized by elemental analysis, mass spectrometry, FTIR, and multinuclear NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy, as well as single-crystal X-ray diffraction for compounds **1**, **3** and **6**. X-ray structure for **4** was previously reported [31].

From the IR spectra of compounds **1–6** (Table 1) valuable structural information could be obtained since metal-coordinated dithiocarbamates generally show strong to moderate characteristic vibrations. It is accepted that metal–dithiocarbamate compounds exhibit three main regions of interest; the "thioureide" band appears in the range 1450–1580 cm^{-1} due to N–CSS stretching vibrations. Other set of bands are observed in the range of 950–1050 cm^{-1} for the asymmetric ν_{as}(SCS) vibration and at approximately 450–700 cm^{-1} for the symmetric ν_s(SCS) vibration [32]. In complexes **1–6** the N–CSS bonds in the dithiocarbamate functions vibrate within 1425–1503 cm^{-1} indicating an increase in the carbon-nitrogen double bond character. The ν_{as}(SCS) vibrations could be identified in the region of 999–1101 cm^{-1}, always as a single band which indicates mostly a symmetrical bonding according to Bonati and Ugo criterion [33]; vibrations belonging to the *N*-alkyl and *SCS* have similar frequencies, and often coupling is observed, thus bands within 693–988 cm^{-1} were assigned to these groups. Finally, bands associated with ν(Sn–S) vibrations appeared in the region of 446–449 cm^{-1} in similar fashion to other organotin(IV) compounds [14,24f–h].

The ^1H NMR spectra for diphenyltin compounds **1–3**, **5**, and **6** exhibit the expected pattern in the aromatic region for the phenyl groups on the tin atoms in which coupling Sn–C is observed; these compounds also showed an upfield shift for the methylene groups located alpha to the nitrogen atom on the dithiocarbamate complex in comparison to the free amine precursor. Selected values for ^1H, ^{13}C and ^{119}Sn NMR spectroscopic data are included in Table 2. In particular complex **1** displayed a single signal in 4.09 ppm for

Table 1
Selected data for vibrational frequencies for complexes **1–6**.

Vibration (cm^{-1})	**1**	**2**[a]	**3**[b]	**4**[b]	**5**[b]	**6**[c]
$\nu(C_{aryl}–H)$	3047w	3008w	3050w	3055w	3055w	3050w
ν(N–CSS)	1493s	1425s	1503s	1476s	1489s	1484s
$\nu_s(N–C_{alkyl})$	1229s	1364m	1153m	1163m	1392m	1225m
ν_{as}(SCS)	1000s	1012s	1066w	999m	1072m	1101m
$\nu_{as}(N–C_{alkyl})$	911w	910w	945w	950m	980w	988w
ν_s(SCS)	693m	730w	735m	728m	731m	732m
ν(Sn–S)	446m	449m	448m	449m	449w	446w

[a] Also showed the typical vibrations for ν(C=O) and ν(C–O) at 1734 s and 1221 s cm^{-1}, respectively.
[b] These compounds also showed vibrations for the alkyl chain at 2943 and 2947 cm^{-1}.
[c] Also showed vibrations for butyl chain at 2958 and 2866 cm^{-1}.

Table 2
Selected ^1H, ^{13}C and ^{119}Sn NMR spectroscopic data for compounds **1–6**.[a]

Compound	^1H NMR $\delta(CH_2NCSS)$	^{13}C NMR $\delta(CH_2NCSS)$	^{13}C NMR δ(CSS)	^{119}Sn NMR
1	4.09	50.5	199.3	−309
L2-TBA	4.40	49.9	217.3	–
2	3.95	52.2	196.9	−313
3	3.72	55.4	192.1	−311
4	3.69	55.3	196.4	−175
5[b]	6.09	54.0	196.0	−328
6	5.99	51.9	195.9	−313

[a] In $CDCl_3$.
[b] In Pyridine-d_6.

Table 3
Crystallographic data for compounds **1**, **3** and **6**.

Crystal data	**1**[a]	**3**[b]	**6**[a]
Formula	$C_{30}H_{28}C_{12}N_2S_4Sn_2$	$C_{17}H_{18}ClNS_2Sn$	$C_{32}H_{30}ClNS_2Sn$
Crystal size (mm^3)	0.23 × 0.19 × 0.09	0.57 × 0.45 × 0.34	0.54 × 0.32 × 0.17
Molecular weight ($g\ mol^{-1}$)	853.06	454.58	646.83
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*n*
Cell parameters			
a (Å)	10.0927(12)	12.6949(14)	13.553(2)
b (Å)	13.0211(16)	10.3570(12)	14.847(3)
c (Å)	25.681(3)	14.0426(16)	14.715(3)
α (°)	90	90	90
β (°)	95.962(2)	105.297(2)	106.234(2)
γ (°)	90	90	90
V ($Å^3$)	3356.7(7)	1780.9(3)	2843.0(8)
Z	4	4	4
μ (mm^{-1})	1.919	1.814	1.511
ρ_{calc} ($g\ cm^{-3}$)	1.688	1.695	1.731
Data collection			
θ Limits (°)	1.59 < θ < 25.00	2.48 < θ < 25.00	1.81 < θ < 25.00
hkl Limits	11, 12; −12, 15; −30, 27	−15, 14; −12, 12; −16, 13	−14, 16; −17, 17; −17, 17
Number of collected reflections	16 672	9607	20 823
Number of independent reflections (R_{int})	5914 (0.0496)	3127 (0.0352)	5004 (0.0260)
Number of observed reflections[c]	4361	2984	4798
Refinement			
R[c,d]	0.0912	0.0306	0.0352
R_w[e,f]	0.2002	0.0785	0.0856
Number of variables	470	199	335
Goodness-of-fit (GOF)	1.259	0.953	1.228
$\Delta\rho_{min}$ ($e\ Å^{-3}$)	−0.743	−0.417	−0.334
$\Delta\rho_{max}$ ($e\ Å^{-3}$)	1.419	0.934	0.618

[a] Data collection at $T = 293$ K.
[b] Data collection at $T = 100$ K.
[c] $I > 2\sigma(I)$.
[d] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$.
[e] All data.
[f] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

the methylene groups CH_2–N, that reveal the equivalence of these protons, due a the interconversión between equal populations of the two chair conformations of the piperazine ring. This is also supported by the signal observed in the ^{13}C NMR at δ 50.51 ppm assigned to the carbon atoms of the piperazine ring. The ^{13}C NMR signals for dithiocarbamate functions in these complexes fall in the region at δ 192.1–199.3 ppm, located upfield to the corresponding free dithiocarbamate ligands [34].

The ^{119}Sn NMR chemical shift values for diphenylchloride tin(IV) compounds were found in the range −309 to −328 ppm (Table 2), indicating that in solution the tin atoms maintained a pentacoordinated geometry observed in X-ray structures (*vide infra*), and in very good agreement with the shift displacements measured for chlorodiphenyltin *N*,*N*-diethyldithiocarbamate, $[Ph_2Sn(Et_2dtc)Cl]$ ($\delta = -327$ ppm in CD_2Cl_2 [35], $\delta = -325/-340$ ppm in $CDCl_3$ and $\delta = -311$ ppm in the solid-state [36]).

3.2. X-ray crystallographic study

Compounds **1**, **3**, and **6** gave single-crystals that were suitable for X-ray diffraction analysis. The most relevant crystallographic data and selected geometric parameters are summarized in Tables 3 and 4 (see also Supplementary Tables S1–S3 in support information). In compound **1** the unit cell contains two independent molecules with different chair conformation of the piperazine ring. The molecular structure of one of the conformers is shown in Fig. 2. The molecular structure of mononuclear diphenyltin(IV) compounds **3** and **6** is shown in Fig. 3.

The tin centers in these complexes are five-coordinated having the dithiocarbamate groups with an anisobidentate chelating coordination mode. The short Sn–S bond lengths fall in the range of 2.444(6) Å (for **1**) to 2.4808 Å (for **6**), which are comparable with the values reported for other diphenyltin(IV) dithiocarbamates like $Ph_2Sn(S_2CNEt_2)Cl$ (2.4449(13) Å) and $Ph_2Sn(S_2CNpiperidyl)Cl$ (2.4737(7) Å) [35,37]. The Sn–S bond distance approximately *trans* to the chloride substituent is longer, for instance in compound **1** the bond lengths were 2.944(2) Å and 2.826(11) Å for Sn(1)–S(2) and Sn(2)–S(4), respectively, which are similar to other reported dinuclear diorganotin(IV) structures such as $[PhSn(S_2CNEt_2)(S)(CH_2CH_2CH_2)SnPh(S_2CNEt_2)]$ with values ranging from 2.894(2) to 2.9573(18) Å [38].

The $Sn–S_{coord}$ bond distance in compounds **3** and **6** were 2.6766(9) and 2.6748(10) Å, which are similar to other reported values for mononuclear diorganotin(IV) complexes like $Ph_2SnCl(S_2CNEt_2)$ (2.716 Å) [35,39]. The carbon-sulfur bond lengths of approximately 1.74 and 1.71 Å in these complexes are also indicative of the asymmetric coordination of the sulfur atoms with single and double bonds, respectively.

The coordination geometry around of tin atoms in these compounds can be described as a distorted trigonal bipyramid. The two carbon atoms of phenyl groups and one of the sulfur atoms of the dithiocarbamate group occupying the equatorial positions for each tin atom. The second sulfur atom of each dithiocarbamate group and the chlorine atom occupying the axial positions with angles $Cl–Sn–S_{coord}$ of 153.5(5)° and 154.7(2)° for **1**, 156.18(3) and 154.72(3) for **3** and **6**, respectively, which are comparable with the typical trigonal bipyramid in related dithiocarbamate compounds [35,39,40].

In compound **1**, two different sets of nitrogen–carbon bonds are observed, the single N–C in the range 1.448–1.478 Å in the hetero-

Table 4
Selected bond lengths (Å), and bond angles (°) of compounds **1**, **3**, and **6**.

	1[a]	**3**	**6**
Bond lengths (Å)			
Sn–C	2.087(12)	2.136(3)	2.132(3)
	2.125(11)	2.142(3)	2.136(3)
	2.110(12)		
	2.102(11)		
Sn–Cl	2.441(3)	2.4678(9)	2.4557(10)
	2.441(3)		
Sn···S	2.944(2)	2.6766(9)	2.6748(10)
	2.826(11)		
Sn–S	2.457(6)	2.4549(9)	2.4808(9)
	2.444(6)		
C–S	1.740(16)	1.722(3)	1.744(3)
	1.706(16)	1.742(3)	1.716(3)
	1.728(16)		
	1.697(13)		
$C–N_{dtc}$	1.340(2)	1.303(4)	1.316(4)
	1.321(17)		
Bond angles (°)			
C–Sn–C	119.9(5)	118.61(12)	120.32(12)
	119.1(5)		
C–Sn–Cl	97.4(3)	94.49(9)	95.85(10)
	98.7(3)	98.31(10)	97.32(9)
	98.4(3)		
	96.7(3)		
S–Sn–S	67.7(8)	70.37(3)	69.08(3)
	66.2(2)		
$Cl–Sn···S_{coord}$	153.5(5)	156.18(3)	154.72(3)
	154.7(2)		
$Cl–Sn–S_{cov}$	87.0(3)	86.85(3)	86.84(3)
	87.0(3)		
S–C–S	119.8(5)	117.54(19)	115.58(18)
	119.3(3)		

[a] There are two independent molecules with different chair conformation of the piperazine ring.

cycle of the bis-dithiocarbamate ligand are significantly longer than the exocyclic in 1.34 and 1.321 Å for N(1)–C(1) and N(2)–C(6) suggesting a partial double bond character. In the mononuclear compounds **3** and **6**, this double character is more evident having even shorter nitrogen-carbon bonds with values of 1.303(4) and 1.316(4), respectively. These data are consistent with the IR data shown in Table 1 (*vide supra*). The sp^2 hybridization of the nitrogen atoms is also supported by the angles nitrogen ∑(C–N–C) 360°.

3.3. Solution phase behavior of compounds 1 and 2 in the presence of anions

Initially anion binding experiments were carried out with bis(chlorodiphenyltin(IV)) complex **1** using as potential guest the following anions: chloride, acetate (AcO^-), and dicarboxylates of general formula $^-OOC\text{-}(CH_2)_n\text{-}COO^-$ (n = 2–8) as tetrabutylammonium salts in acetonitrile solutions. Complex **1** holds two organotin centers separated by 11.446 Å, suitable to possibly bind some of the dicarboxylates anions in cooperative fashion. The use of a polar organic solvent like acetonitrile instead of chloroform or dichloromethane is preferred due to the higher stability of the solutions and better reproducibility.

Complex **1** showed an electronic absorption spectra in acetonitrile at 25 °C with characteristic bands for π–π* transitions in the UV region and absorption coefficients of ϵ_{252} = 38600 M^{-1} cm^{-1}, and ϵ_{286} = 13200 M^{-1} cm^{-1}. The spectrum was stable for several days at room temperature. Fig. 4 shows the changes in the absorption spectra during the titration of complex **1** (3.5×10^{-5} M) with different amounts of chloride, acetate, and glutarate in CH_3CN.

Qualitatively the spectral changes occurring in response to an increasing concentration of the anion are different in each case. For instance, a decrease in the absorption bands located at λ_{max} 252 and 286 nm was observed upon the addition of chloride (Fig. 4a), conversely the addition of acetate caused a decrease in the absorption bands of complex **1** along with the appearance of two new absorption bands in the region of λ_{max} 274 and 308 nm (see Fig. 4b). In the latter case an isosbestic point is clearly seen. Titrations of complex **1** with glutarate dianion and other dicarboxylates (Supplementary Fig. S1) also caused the appearance of new absorptions bands at longer wavelengths similar to the titration with acetate, however, the spectral changes were not as smooth and the isobestic was not observed (see Fig. 4c for glutarate).

A comparison of the changes in the molar absorption coefficient at λ = 300 nm during titration of compound **1** with chloride, acetate, malonate, glutarate, and succinate is shown in Fig. 5. Only in the presence of the carboxylate anions the bands at longer wavelengths raised concomitant to the addition of the anion. Note that there are differences in the curves displayed by acetate and dicarboxylates anions, for instance, dicarboxylates such as malonate, succinate or glutarate started a steep increase of the absorption coefficient at about 1 molar equivalent of the added anion

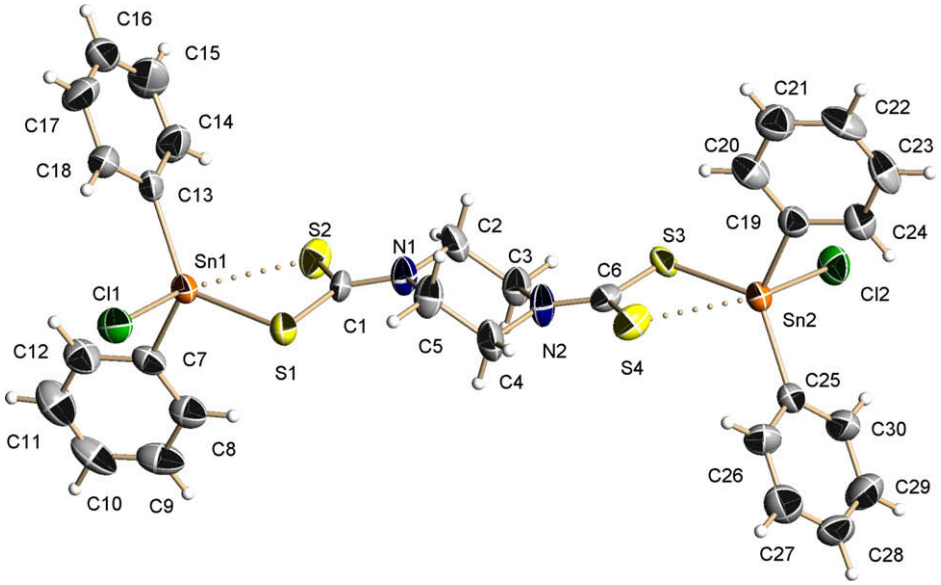


Fig. 2. Molecular structure of dinuclear compound **1**. Ellipsoids are shown at the 50% probability level.

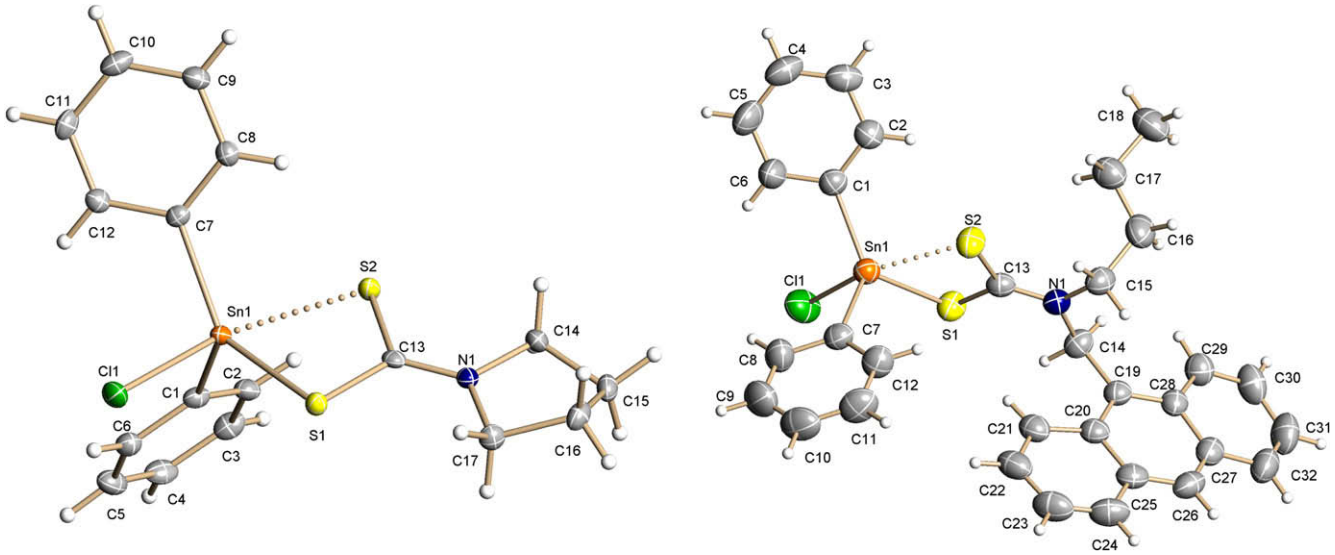


Fig. 3. Molecular structures of mononuclear compounds **3** (left) and **6** (right). Ellipsoids are shown at the 50% probability level.

whereas addition of acetate increases absorption after two molar equivalents. Other *O* donor monoanions like $H_2PO_4^-$ also showed curves similar to acetate (Supplementary Fig. S1).

In these experiments the absorption band at 300 nm reached saturation when excess of the anion salt was added, however, while for acetate about 12 molar equivalents of the anion were required, dicarboxylates such as malonate, succinate or glutarate displayed a maximum at about 4 molar equivalents, leveling off at the same absorption coefficient as in the titration with acetate (see Fig. 5). Attempts to fit the experimental titration plots to the formation of a 1:1 or 1:2 host–guest complexes failed, indicating that a more complicated process was taking place. Note also that the behavior of dicarboxylates is particularly odd because their curves go through a maximum.

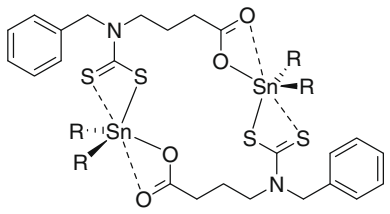
In order to assign the absorption bands appearing at longer wavelengths during the experiments described above, UV–Vis and ^{1}H NMR titration experiments were performed using chlorodiphenyltin(IV) complex **2**, in which only one organotin(IV) center is present.[1] Changes of the absorption coefficient at 301 nm during titration of complex **2** with acetate, succinate and glutarate as TBA salts in acetonitrile solutions are depicted in Fig. 6. In general these curves showed a similar behavior for carboxylate anions with complex **2** as in titrations of complex **1**. A pure sample of the tetrabutylammonium *N*-BOC-piperazinyl-1-carbodithioate salt (*i.e.*, **L2-TBA**) was also prepared, dissolved in acetonitrile and examined by UV–Vis spectroscopy. The maximum of the absorption bands fully agree with those observed during the titration experiments with complex **2** (ϵ_{268} = 12100 M^{-1} cm^{-1}, ϵ_{300} = 12500 M^{-1} cm^{-1} in acetonitrile), indicating that the dithiocarbamate groups are indeed being dissociated by the carboxylate ions from the tin coordination sphere [41].

Further support was obtained from ^{1}H NMR titration experiments between AcOTBA and complex **2** in a deuterated acetonitrile solution. Fig. 7 shows the ^{1}H NMR signals for complex **2** in the absence of acetate and in the presence of about one and two molar equivalents of the salt. For comparison the spectrum of the corresponding dithiocarbamate salt **L2-TBA** and AcOTBA were also included.

After 1 molar equivalent of acetate anion had been added to complex **2**, only slight chemical shift displacements occurred for the ^{1}H NMR signals corresponding to the piperazinyl moiety CH_2–CS_2 or CH_2–*N*-BOC, however, the aromatic protons bound to the tin(IV) center were shifted to higher fields. Upon the addition of a second equivalent of the acetate, the CH_2–CS_2 signals shifted towards lower fields nearly to the region corresponding to the free dithiocarbamate anion. The signals corresponding to CH_2–*N*-BOC also suffered a displacement to higher fields.

Above observations were in full agreement with the changes in the ^{13}C and ^{119}Sn NMR spectrum for these mixtures summarized in Table 5 and the reaction sequence proposed in the Scheme 1.

^{13}C NMR signal for *CSS* originally located at δ 195.45 ppm for complex **2** is displaced to lower fields (199.38 ppm) in the presence of one molar equivalent of acetate, thus indicating the formation of an intermediate complex **2a** (see Scheme 1), in which dithiocarbamate group is still coordinated to the tin center and only chloride is displaced; addition of a second molar equivalent of acetate anion caused a greater shift to 218 ppm, a region usually assigned to the free dithiocarbamate anion (for instance, ligand **L2** shows δ 217.3 in CD_3CN see Table 2). The intermediate species **2a** is more likely to be a neutral complex where one acetate has substituted chloride in a stepwise fashion changing tin(IV) coordination geometry from pentacoordinated to an hexacoordinated complex. This coordination geometry has been previously seen with macrocycles derived from γ-amino-acid dithiocarbamates and diorganotin(IV) centers as depicted below for **7** and **8** [26].



7 R= Ph

8 R= *n*-Bu

Furthermore, the ^{119}Sn NMR signal for the equimolar mixture of **2** and AcOTBA appeared at δ −374.8 (see Table 5 below), in very good agreement with the chemical shift displacement found for diphenyltin(IV) macrocycle **7** (δ −371.6 ppm in $CDCl_3$) that contains both carboxylate and dithiocarbamate groups coordinated to the tin center.

[1] Low solubility of complex **1** in acetonitrile hampered its use at higher concentrations required for NMR experiments.

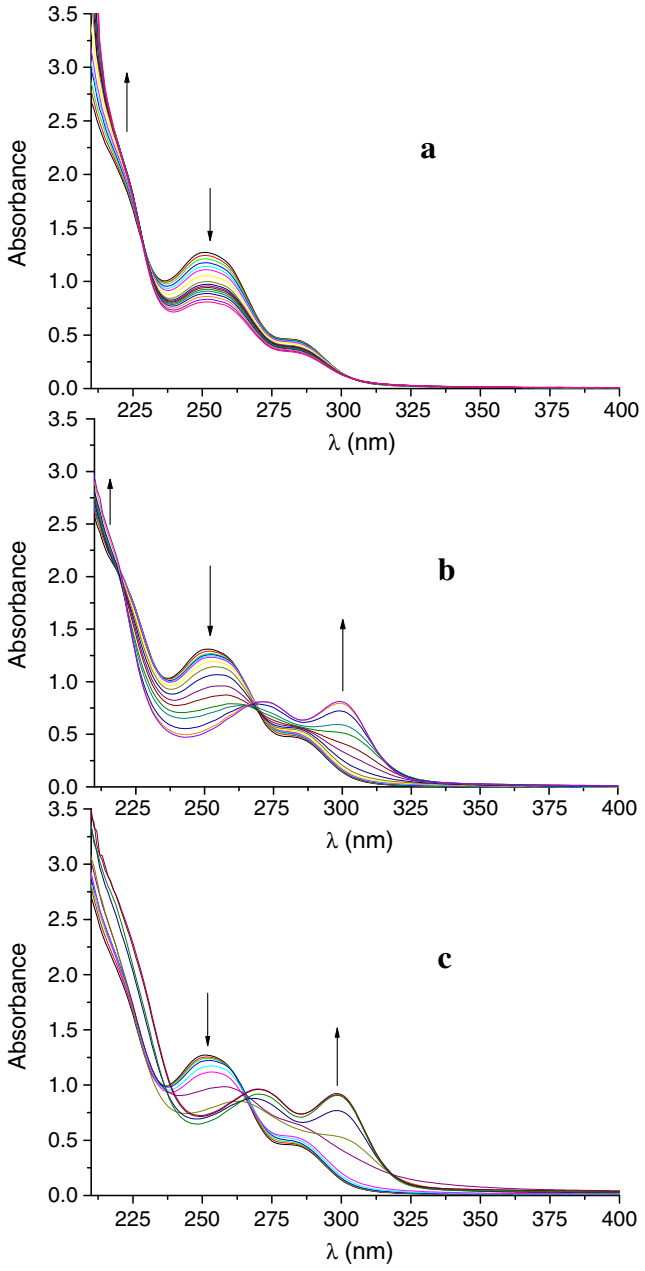


Fig. 4. Changes in the absorption spectra during the titration of **1** (3.5×10^{-5} M) with different quantities of (a) chloride (0–5.0×10^{-4} M), (b) acetate (0–4.7×10^{-4} M) and (c) glutarate (0–2.1×10^{-4} M) as TBA salts in CH_3CN. The arrows indicate the spectral changes occurring in response to an increasing concentration of anion.

Evidence that the mechanisms proposed in Scheme 1 may also be valid for compound **1** was obtained from mass spectrometry. In a mixture of **1** (0.01 M) and excess of AcOTBA, peaks corresponding to the species $Ph_2Sn(AcO)_2$ (*m/z* 392, FAB^+) were observed. Similarly, in a mixture of **2** (0.01 M) and excess of AcOTBA peaks of **L2** anion were observed (*m/z* 262, FAB^-).

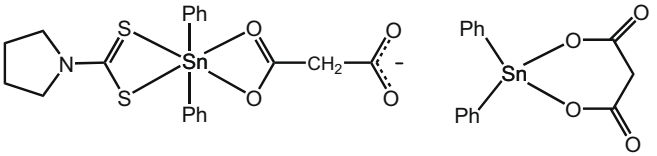
3.4. Compounds 3 and 4 in the presence of anions

The ligand-exchange process of the organotin(IV) complexes **1** and **2** in the presence of carboxylate anions is explained by the stepwise reactions occurring at the tin center as indicated in Scheme 1, and apparently there is no influence of other structural features in these complexes. Thus, the expectation of stable organotin(IV) dithiocarbamate complexes involved in anion recognition was not fulfilled because dithiocarbamate ligands did not remain within the coordination sphere in the presence of carboxylate anions; nevertheless, the process of binding a *new ligand* is directly indicated by the appearance of the absorption bands at longer wavelengths (*i.e.*, 300 nm), corresponding to the free dithiocarbamate ligand. Certainly, free dithiocarbamate can be detected by other means like ^1H NMR, however, the intrinsic chromogenic properties of dithiocarbamate anion can be viewed as advantageous because it becomes a reporter of the binding event and also allows for a direct comparison of the binding ability of different anions for the organotin(IV) moiety in solution.

To this aim, we studied in further detail more simple di- and triorganotin(IV) complexes **3** and **4** derived from pyrrolidine (for their synthesis see Section 2). Titrations of these compounds were monitored by following spectral changes in the UV region, in particular, the increase of the band located at 294–295 nm. A comparison of the changes in the molar absorption coefficient at 294 nm during titration of compound **3** with several anions including halides (chloride, fluoride, and bromide), carboxylates (acetate, malonate, glutarate, and succinate) and other *O* donor ligands ($H_2PO_4^-$, HSO_4^-) is shown in Fig. 8. Three types of behaviors can be distinguished: (i) dicarboxylates (malonate, succinate, and glutarate) rapidly increased the intensity of the absorption at anion/complex concentration ratios lower than two and displayed a *transient* maximum in the observed $\Delta\epsilon_{294}$; (ii) AcO^-, $H_2PO_4^-$ and F^- also increased the absorption at 294 nm but in a more steady fashion, and (iii) Cl^-, Br^-, and HSO_4^- did not show any enhancement of the absorption within the concentration range explored (i.e., about ten times excess anion over **3**).

The general trends of the results with chlorodiphenyltin(IV) complex **3** are similar to those obtained previously with complexes **1** and **2**, however titration plots of monoanions with **3** allowed to further note that anions like acetate, dihydrogenphosphate, and fluoride – all able to fully displace the dithiocarbamate group- showed differences in their titrations curves (Supplementary Fig. S2), pointing out that the interplay of affinities between the incoming anion and the coordinated ligand for the diphenyltin(IV) moiety is of great importance. In this regard, hydrogen sulfate, chloride and bromide anions displayed lesser affinity than dithiocarbamates for diphenyltin(IV).

The mechanism that operates in the cleavage of **3** by carboxylates must be to some extent similar to the proposed in Scheme 1 for complex **2** in the presence of acetate anion. In a mixture of complex **3** (1.3×10^{-2} M) and malonate (0.33 M as TBA salt) in acetonitrile, it was possible to observe the intermediate species **3a** (*m/z* 521, FAB^-) indicating that displacement of chloride occurred before the exchange of the dithiocarbamate group. In the same mixture it was also observed a diphenyltin(IV) product with *m/z* 256 (FAB^+). The only feasible structure matching this result is **3b** (below), which pointed out to an intramolecular displacement of the dithiocarbamate group by the remaining free carboxylate in the coordinated malonate. It is reasonable to expect that this kind of mechanism also holds for other small dicarboxylates like succinate and glutarate but not for the larger members of this group.



3a **3b**

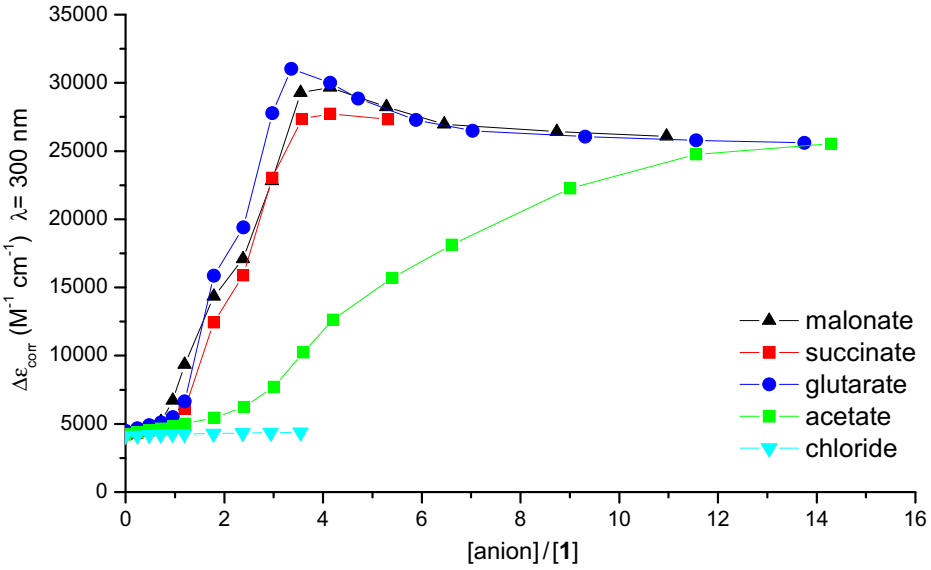


Fig. 5. Changes of absorption coefficient at 300 nm during the titration of **1** (3.5×10^{-5} M) with different quantities of (a) chloride (0–5.0×10^{-4} M), (b) acetate (0–4.7×10^{-4} M), (c) dicarboxylates like malonate, succinate and glutarate (0–2.1×10^{-4} M) as TBA salts in CH_3CN.

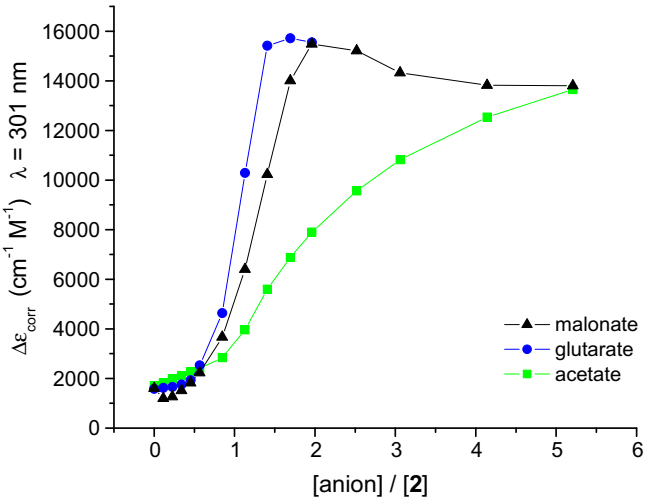


Fig. 6. Changes of absorption spectra during the titration of **2** (6.6×10^{-5} M) with different quantities of (a) acetate (0–4.7×10^{-4} M), (b) malonate (0–3.6×10^{-4} M), and (c) glutarate (0–3.6×10^{-4} M) as TBA salts in CH_3CN.

For the sake of comparison, UV–Vis titrations with complex **4** and the same set of anions used with **3** were studied and the results are depicted in Fig. 9. Note that complex **4** bears only one exchangeable ligand in its structure (*i.e.*, *N*-pyrrolidinyldithiocarbamate), and therefore it was expected that titration curves show different features than those observed for **3** (see Fig. 8). Dicarboxylates increased quite steeply the absorption at this wavelength in comparison to AcO^-, F^- and $H_2PO_4^-$, however, the *transient* maximum observed with complex **3** was not longer present, indicating that in this case there is a direct displacement of the dithiocarbamate by the incoming anion. Absorption coefficient at 295 nm saturate at the same value at the end of the titrations plots for all anions that were able to displace the dithiocarbamate group. Anionic species such as Br^-, and HSO_4^- did not significantly change the absorption even at a large excess of the anion over **4,** and there was only a slight increase with Cl^-. These data show that even simple triorganotin dithiocarbamates may display selective ligand-exchange. Titration data for complex **4** with AcO^- and F^- were adequately fitted to a 1:1 binding model obtaining the following constants of 460 ± 34 M^{-1} and 8572 ± 716 M^{-1}, for F^- and AcO^-, respectively. However, titration with dihydrogenphosphate showed a different curvature and do not fit well to a 1:1 binding model.

The ligand-exchange behavior of these acyclic organotin(IV) complexes studied here (**1**–**6**) is markedly different to the observed in the cases of macrocyclic compounds **7** and **8** [26]. In these macrocycles acetate bound weakly (about 15 M^{-1} in chloroform solution), and they were stable at equimolar host–guest concentrations. Ligand-exchange of the dithiocarbamate functionality happened under a high excess of the acetate anion over **8** (~200-fold), indicating that **8** is less prone to decomposition than any of the acyclic complexes.

3.5. Compounds *5* and *6* in the presence of anions

Among optical probes and sensors, those displaying fluorescence signaling are usually preferred given the enhanced detection limit and sensibility in comparison to measuring the absorbance in solution [42]. Neither diorganotin(IV) complexes nor dithiocarbamate anions displayed intrinsic fluorescence or phosphorescence, therefore we seek to add this feature by employing a well-known fluorescence moiety such as antracene linked to the dithiocarbamate ligand. There are several examples in which 9-(aminomethyl)anthracenyl unit is used in conjunction to chelating ligands to detect both anions and cations [43,44]. Typically fluorescence of the anthracenyl moiety is quenched by the benzylic nitrogens due to PET. Fluorescence enhancement is then detected as an indication of a binding event or protonation on the amine site. In this regard, a related ligand containing anthracenyl and dithiocarbamate groups linked by a piperazine moiety reported a threefold quenching of fluorescence of the free ligand upon complexation to a Cu(II) center [44].

Chlorodiphenyltin(IV) complex **5** was prepared starting from commercial 9-(methylaminomethyl)-anthracene. In similar fashion, complex **6** was synthesized starting from 9-(methylaminobutyl)-anthracene (for synthetic details see Section 2). The absorption spectra in acetonitrile for complex **5** and **6** displayed three well-defined bands in the region 340–390 nm in addition to the UV bands

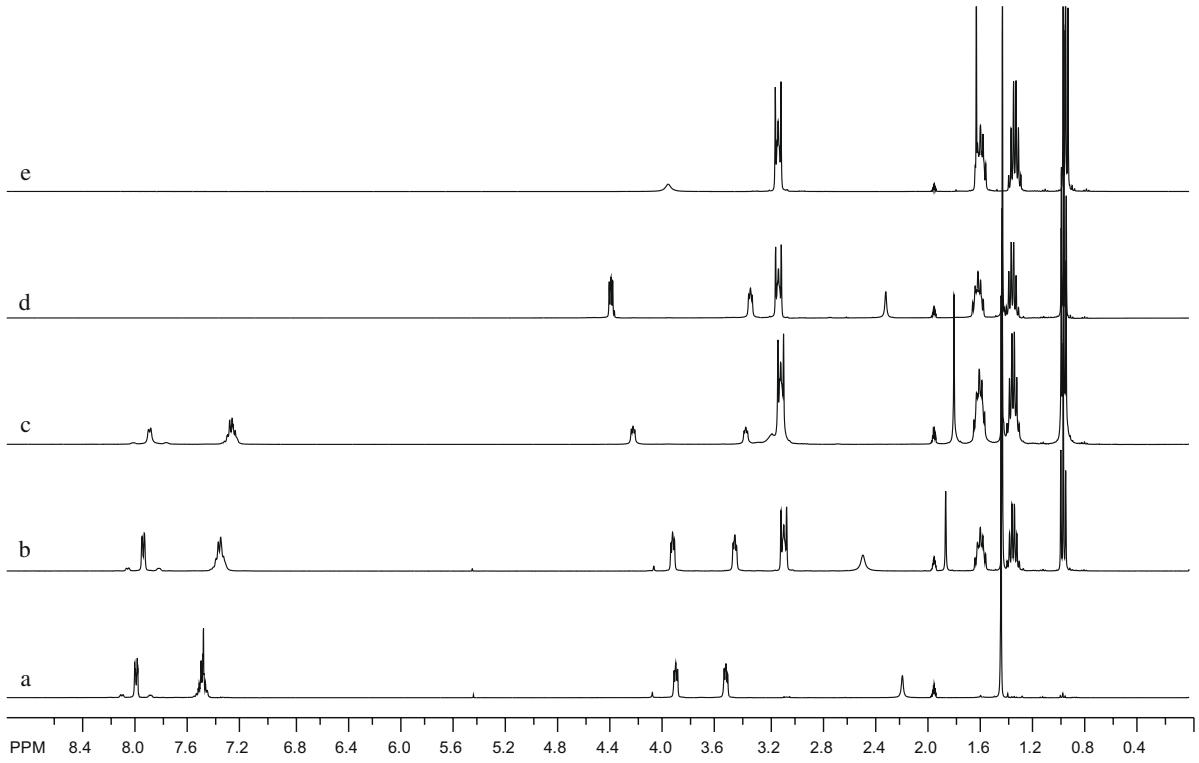


Fig. 7. ^{1}H NMR spectra for **2** upon addition of AcOTBA in CD_3CN. (a) Complex **2**; (b) **2** +1 molar equiv. AcOTBA; (c) **2** +2 molar equiv. AcOTBA; (d) **L2-TBA** salt, (e) AcOTBA salt.

Table 5
^{13}C and ^{119}Sn NMR chemical shifts observed during titration of **2** with AcOTBA in CD_3CN.

Entry	Mixture	^{13}C (CSS, ppm)	^{119}Sn (ppm)
1	**2** (8.8×10^{-2} M)	195.45	−321.35
2	**2** (8.8×10^{-2} M) + AcOTBA ~ 1 equiv.	199.38	−374.81[b]
3	**2** (8.8×10^{-2} M) + AcOTBA ~ 2 equiv.	218.82[a]	−489.66

[a] For comparison, chemical shift of **L2-TBA** salt is observed at 217.3 ppm in CD_3CN, see Table 2.

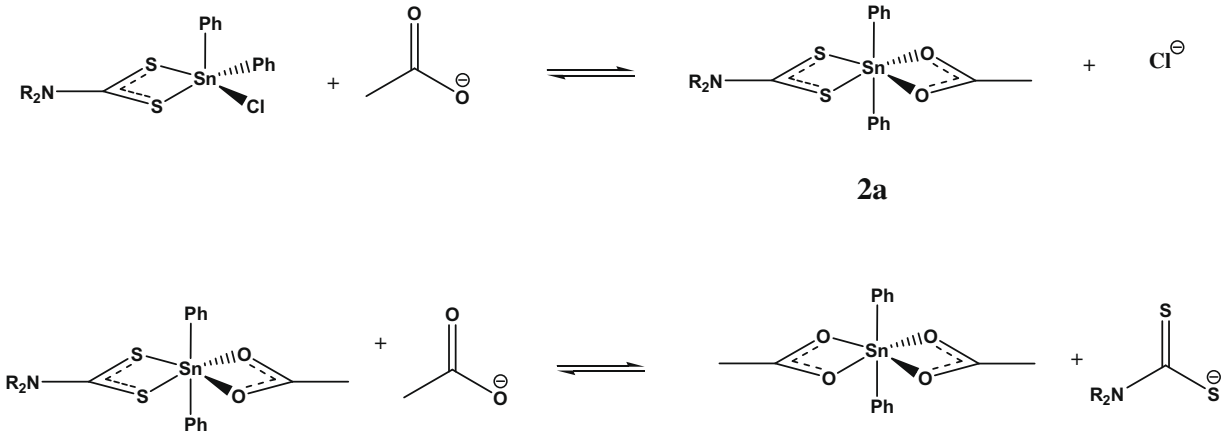
[b] Diphenyltin(IV) macrocycle derived from γ-aminoacid dithiocarbamate in which Sn is coordinated to one carboxylate and one dithiocarbamate units in hexacoordinate fashion showed signal at −371.6 ppm (in $CDCl_3$) [26].

corresponding to the diphenyltin(IV) group. Excitation at λ_{exc} 368 nm produced an emission spectrum containing well-defined and structured bands centered at 417 nm. Other spectroscopic features were similar between these complexes, however complex **6** possessed a much better solubility in acetonitrile than **5**.

As before titrations of compounds **5** and **6** were carried out employing the same set of anions tested with **3** and **4**, monitoring the spectral changes in the UV region at 299 nm. Fig. 10 (and Supplementary Fig. S3 for complex **5**) shows a comparison of the changes observed in ϵ_{299} during the titration of **6** in the presence of anions.

The trends observed here were the same as with **3**, however the behavior of the dicarboxylates malonate and succinate is particularly remarkable because $\Delta\epsilon_{299}$ goes through a well-defined maximum at about 1 molar equivalent of added ligand. At similar concentrations the observed changes with monoanions such as AcO^-, F^- or $H_2PO_4^-$ are very small.

The presence of this maximum in the titration curves has been observed with every chlorodiphenyltin(IV) complex studied in this



Scheme 1. Stepwise ligand substitution for complex **2** occurring in the presence of acetate anion.

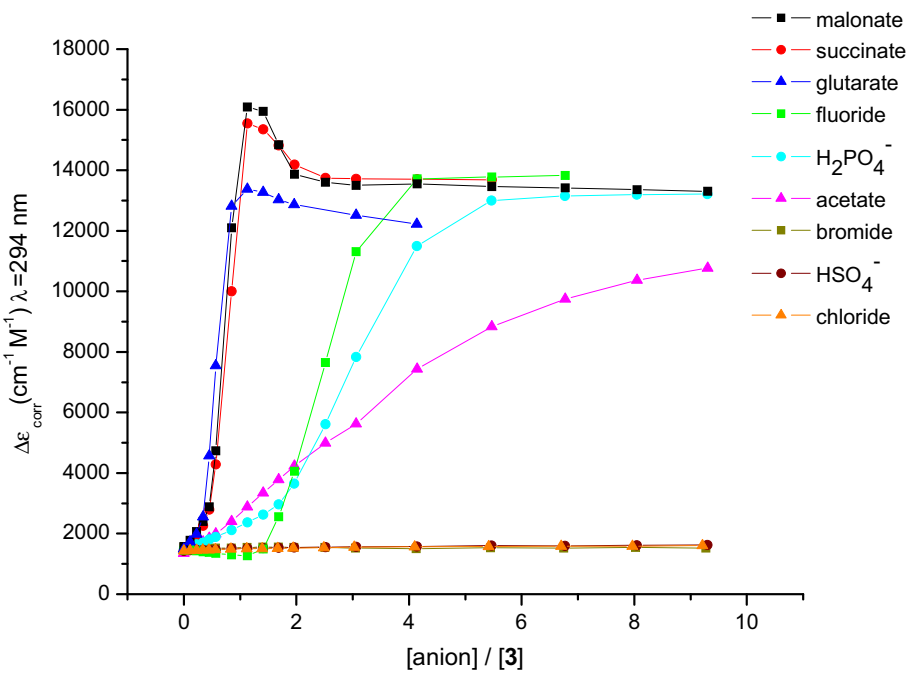


Fig. 8. Changes of absorption coefficient at 294 nm during the titration of **3** (7×10^{-5} M) with different anions including halides (chloride, fluoride, bromide), carboxylates (acetate, malonate, glutarate, and succinate) and other O donor ligands ($H_2PO_4^-$, HSO_4^-) as TBA salts in CH_3CN.

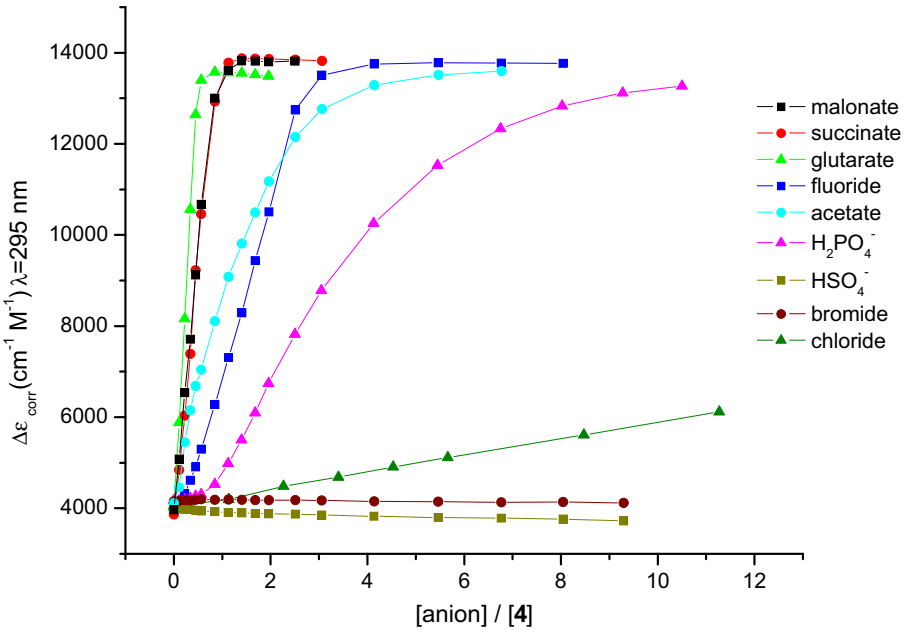


Fig. 9. Changes of absorption coefficient at 295 nm during the titration of **4** (7×10^{-5} M) with different anions including halides (chloride, fluoride, and bromide), carboxylates (acetate, malonate, glutarate, and succinate) and other *O* donor ligands ($H_2PO_4^-$, HSO_4^-) as TBA salts in CH_3CN.

work (**1**, **2**, **3**, **5** and **6**) in their interaction with malonate and succinate, and to a less extent with glutarate, indicating that the mechanism of ligand exchange in the presence of small dicarboxylates (*i.e.*, malonate and succinate) is different than the one depicted in Scheme 1 for compound **2** with acetate. Only for complex **4**, which lacks of the chloride coordinated ligand, titration curves did not show any maximum in the presence of small dicarboxylates. According to our previous results the bands with absorption maxima located about 294–300 nm correspond to free dithiocarbamate ligand and therefore, we would expect approximately the same value of absorption coefficient at the end of titration plots when all bound dithiocarbamate ligand had been released, as it was observed in the case of monoanions AcO^-, F^-, and $H_2PO_4^-$ (see Fig. 10). A closer examination of the absorption spectra in the titration of complex **6** (or complexes **2** and **3**) with acetate and malonate did not shed light on the molecular basis for this behavior. Perhaps differences in the mechanism of cleaving the dithiocarbamate group by acetate that may follow an stepwise displacement of chloride and dithiocarbamate groups, respectively, and by small dicarboxylates, which may follow an intramolecular displacement of the dithiocarbamate group, accounts for the appearance of the maximum in the titrations of chlorodiphenyl-

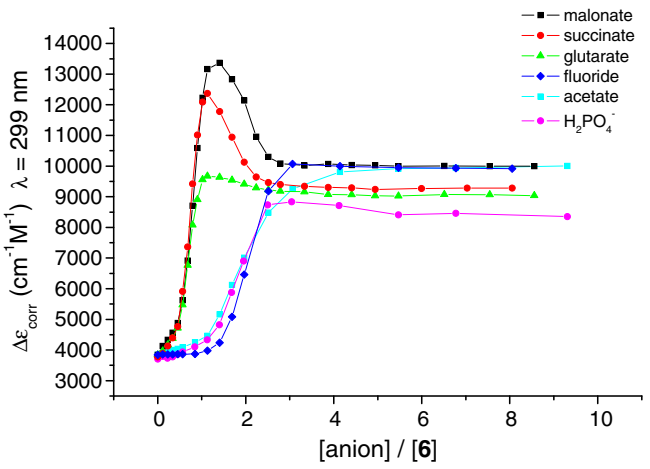


Fig. 10. Changes of absorption coefficient at 299 nm during the titration of **6** (7×10^{-5} M) with different anions including carboxylates (acetate, malonate, glutarate, and succinate), $H_2PO_4^-$, and F^- as TBA salts in CH_3CN.

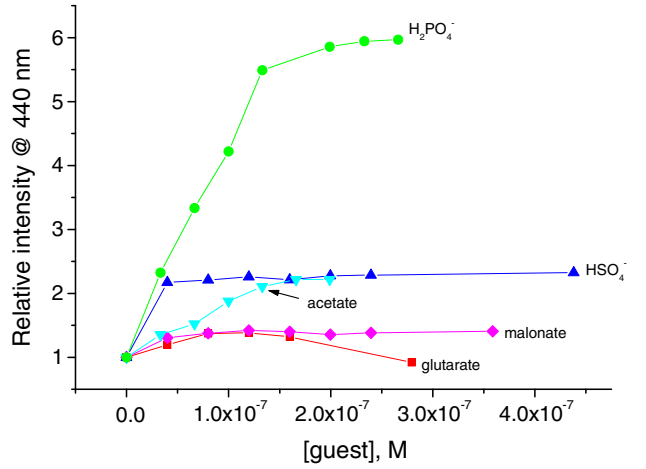


Fig. 11. Changes in fluorescence intensity at 440 nm (λ_{exc} 368 nm) during the titration of **5** (1×10^{-7} M) with different anions including acetate, malonate, glutarate, $H_2PO_4^-$, and HSO_4^- as TBA salts in CH_3CN.

tin(IV) complexes. In line with this scheme, dicarboxylate anions with larger spacer groups like adipate, suberate, or azelate, did not show any maximum in their titration plots (see Supplementary Fig. S1) suggesting that intramolecular displacement is not possible in these cases.

Fluorescence titrations were carried out in acetonitrile solutions with complexes **5** and **6** in the presence of several anions. In the case of **6**, addition of acetate, malonate, glutarate, dihydrogenphosphate, and hydrogensulfate only showed a minor enhancement or quenching of the anthracenyl fluorescence at 400 nm. Conversely, complex **5** presented a selective response to the presence of anions. Fig. 11 shows the changes in fluorescence relative intensity at 440 nm (λ_{exc} 368 nm) for complex **5** during titration with different amounts of anions. In some cases only a modest increase was obtained (*i.e.*, twofold for acetate and hidrogensulfate), but for dihydrogenphosphate an emission intensity increment up to sixfold was obtained.

4. Conclusions

Underscoring the potential lability of organotin(IV) dithiocarbamate compounds in solution is of high importance given the great deal of attention they have earned in the context of biological activity and therapeutic applications [9,14,15]. Thus, the solution stability of chlorodiphenyltin(IV) dithiocarbamate complexes examined here demonstrated that these complexes in the presence of *O* donors anions like as acetate, dicarboxylates of general formula $^-OOC\text{-}(CH_2)_n\text{-}COO^-$ ($n = 2$–8), dihydrogenphosphate, and fluoride, were prone to readily exchange their coordinated ligands in stepwise fashion by first displacing chloride, and then follow by the dithiocarbamate group under excess of the incoming anion. This ligand-exchange reaction could be nicely monitored by tracing changes in the UV absorption region for the free dithiocarbamate (*i.e.*, 294–300 nm), which becomes a chromogenic reporter of the binding. By attaching an anthracenyl moiety to the dithiocarbamate ligand it was observed a more selective displacement of dihydrogenphosphate anion over other *O* donor ligands.

From UV–Vis titration experiments it was found that dicarboxylates with small spacers like malonate and succinate, acted differently in the exchange of the dithiocarbamate group, perhaps by following an intramolecular displacement of the coordinated ligand. Also, it was noted that the extent of dithiocarbamate exchange in these complexes depended directly on the nature of the anion, and on their relative affinity for the diorganotin(IV) moiety following a stability trend such as: dicarboxylates > *O* donor monoanions ≈ fluoride > other halides and HSO_4^-. When only dithiocarbamate is present such as in triphenyltin(IV) complex **4**, a similar trend in displacement of the dithiocarbamate was also observed indicating that that even simple triorganotin(IV) dithiocarbamates may display selective ligand-exchange.

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Appendix A. Supplementary data

CCDC 684317, 734761 and 734760 contain the supplementary crystallographic data for **1, 3** and **6**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.09.010.

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