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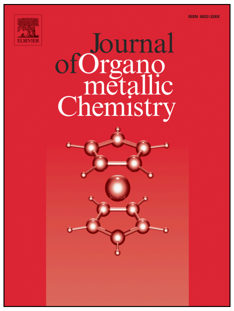

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Stabilization of $[(n\text{Bu}_2\text{SnCl})(\mu\text{-Cl})_2(\text{ClSn}n\text{Bu}_2)]$ within the Solid-State Structure of a Chlorodi-*n*-butyltin(IV) dithiocarbamate

Ericka Santacruz-Juárez, Jorge Cruz-Huerta, Aaron Torres-Huerta, María G. Hernández-Cruz, Victor Barba, Hugo Tlahuext-Romero, Herbert Höpfl[*]

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C.P. 62209, Cuernavaca, México. Tel., Fax: +52 777 3297997. E-mail: hhopfl@uaem.mx.

Abstract

The combination of *bis*-dithiocarbamate ligands derived from *N*,*N'*-dibenzylcyclohexane-*trans*-1,4-diamine with dimethyl- and di-*n*-butyltin(IV) dichloride provided two discrete dinuclear complexes of the composition $[(\text{Me}_2\text{SnCl})_2(\text{bis-dtc})]\cdot 2\text{CHCl}_3$ (**1**) and $[(n\text{Bu}_2\text{SnCl})_2(\text{bis-dtc})]$ (**2**) with bis-dtc = *N*,*N´*-dibenzylcyclohexane-*trans*-1,4-diamine-bisdithiocarbamate. Additionally, single crystals of the composition $[(n\text{Bu}_2\text{SnCl})(\text{mono-dtc})]\cdot[n\text{Bu}_2\text{SnCl}_2]_2$ (**3**) with mono-dtc = *N*,*N´*-dibenzylcyclohexane-*trans*-1,4-diamine-monodithiocarbamate were isolated. Within the crystal structures of the three complexes, a varied number of common (C–H···S, C–H···Cl and N–H···Cl) and less common (S···S, S···Cl, Cl···Cl, Cl···N and Cl···Sn) secondary interactions were observed and analyzed. The supramolecular solid-state organization of $[(\text{Me}_2\text{SnCl})_2(\text{bis-dtc})]\cdot 2\text{CHCl}_3$ revealed the presence of channels, which were filled with chloroform molecules. In the crystal structure of $[(n\text{Bu}_2\text{SnCl})(\text{mono-dtc})]\cdot[n\text{Bu}_2\text{SnCl}_2]_2$, the di-*n*-butyltin dichloride units are arranged in form of a so far unknown dimeric aggregate of the composition $[(n\text{Bu}_2\text{SnCl})(\mu\text{-Cl})_2(\text{ClSn}n\text{Bu}_2)]$. The latter assembly represents thus a rare example for a two-component co-crystalline assembly, in which a relatively large non-solvent molecule with unusual molecular structure is stored and stabilized.

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[*] Corresponding author. Fax: (+52) 777 329 79 97

E-mail address: hhopfl@uaem.mx

Keywords: Organotin complex, di-*n*-butyltin(IV) chloride, dithiocarbamate, supramolecular chemistry, secondary intermolecular interactions, cocrystal.

2. Introduction

Diorganotin(IV) dichlorides, R_2SnCl_2, can be reacted selectively with either one or two stoichiometric equivalents of dithiocarbamate (dtc) ligands to give the corresponding $(R_2SnCl)(dtc)$ and $R_2Sn(dtc)_2$ complexes.[1] Such mononuclear derivatives have been known for many years, and intensively studied due to anti-fungal, anti-bacterial, insecticidal and cytotoxic properties.[2] In materials science they have proven useful for the preparation of tin sulfide nanoparticles and thin films.[3] However, it was only until recently that di-, tri- and polynuclear derivatives have also emerged, which can be attributed to the following reasons. First, organotin halides have potential for anion recognition, particularly for F^-, Cl^- and $RCOO^-$ species.[4-5] Secondly, bis-dtc complexes derived from di- and tritopic ligands can generate macrocyclic and cage-type assemblies. In this context, Beer *et al.*, our own research groups and others have shown that metallosupramolecular assemblies based on sulphur-containing ligands, in particular bis-dithiocarbamate ligands, are an excellent alternative choice for the formation of new and complex supramolecular structures.[6-8]

Among others, supramolecular chemistry deals with the formation of chemical aggregates through the combination of molecular sub-units (building blocks) by non-covalent intermolecular interactions.[9] These include $\pi\cdots\pi$, $C–H\cdots\pi$, $C–H\cdots X$, $C–X\cdots Y$, and $X\cdots Y$ contacts (with X = O, N, S, F, Cl, Br, I; Y = S, Cl, Br, I), which stabilize the molecular organization in the solid state.[10] Previous studies have shown that $C–H\cdots X$ interactions are of singular importance in molecular recognition processes,[11] in stabilizing inclusion complexes,[12] in crystal engineering,[13] among others. Moreover, crystalline assemblies of molecular compounds linked through such non-covalent interactions can contain cavities or channels, in which additional molecules, frequently solvent, are included.[14] Occasionally, guest molecules included in the confined space of an organic or metal-organic skeleton can present unusual structural properties.[15]

Previous reports in the literature have shown that the solid state structures of diorganotin dithiocarbamates are significantly influenced by the steric effects originated from the organic substituents attached to the tin atoms and intermolecular interactions such as C–H···Cl, C–H···S, S···Cl, S···S, Cl···Sn and C-H···π contacts.[5c, 16]

Herein, we report on the preparation and structural characterization of three chlorodiorganotin(IV) *mono*- and *bis*-dithiocarbamate complexes derived from *N,N´*-dibenzylcyclohexane-*trans*-1,4-diamine. The single-crystal X-ray diffraction analysis of the solid state structures revealed a total of six different secondary interactions involving S and Cl atoms. Additionally, one compound co-crystallized with $n\mathrm{Bu_2SnCl_2}$, which was included within the solid state structure in the form of a so far unknown dimeric assembly of the composition $[(n\mathrm{Bu_2SnCl})(\mu\text{-Cl})_2(\mathrm{ClSn}n\mathrm{Bu_2})]$.

2. Experimental section

2.1. General procedures and methods

Commercial starting materials and solvents have been used. $\mathrm{Me_2SnCl_2}$ and $n\mathrm{Bu_2SnCl_2}$ were commercially available and were used without further purification. The synthesis of the secondary amine *N,N´*-dibenzylcyclohexane-*trans*-1,4-diamine was achieved in high yields by condensation of cyclohexane-*trans*-1,4-diamine with benzaldehyde followed by reduction with $\mathrm{NaBH_4}$ in absolute ethanol.[17]

Elemental analyses of samples dried in an Abderhalden equipment have been carried out on an Elementar Vario ELIII instrument. NMR studies were carried out with Varian Gemini 200 and Varian Inova 400 equipments. Standard references were used: TMS (δ^1H = 0; δ^{13}C = 0) and $\mathrm{SnMe_4}$ (δ^{119}Sn = 0). For the correct assignment of the ^{1}H and ^{13}C NMR spectra, COSY, DEPT and HSQC experiments have been carried out. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on a Jeol JMS 700 equipment.

2.2 Synthesis and spectroscopic characterization

*2.2.1. Preparation of [(Me$_2$SnCl)$_2$(bis-dtc)] (**1**)*

To a solution of *N,N´*-dibenzylcyclohexane-*trans*-1,4-diamine (0.250 g, 0.85 mmol) in 20 mL of absolute ethanol were added two equivalents of potassium hydroxide (0.095 g, 1.70 mmol) and excess of carbon disulfide (1.30 g, 17 mmol). The mixture was stirred for 2 h at room temperature, whereupon dimethyltin dichloride (0.374 g, 1.70 mmol) dissolved in 30 mL of absolute ethanol was added dropwise. After stirring for 12 h at room temperature, the colorless precipitate was collected by filtration and washed with hot hexane. Single-crystals suitable for X-ray crystallography were grown from a 1:1 solvent mixture of dichloromethane and ethanol. Yield: 65% (0.450 g). Mp 242-244 ºC. High-resolution MS (FAB$^+$) for $C_{26}H_{36}ClN_2S_4Sn_2$ [*M-Cl*]$^+$: *m/z* (%) = 778.9898 (61). Error: +51.9 ppm. IR (KBr, cm^{-1}): $\tilde{\nu}_{max}$ = 2943 (w), 1463 ν(C-N$_{dtc}$) (s), 1423 (s), 1355 (m), 1243 (m), 1151 (m), 1079 (w), 1021 (m), 964 ν_{as}(CSS) (m), 906 (w), 787 (m), 736 (m), 695 (m), 554 (m), 457 (w). ^{1}H NMR (200 MHz, CDCl$_3$, TMS, ppm): δ= 1.31 (s, 12 H, Sn-CH$_3$, $^2J_{Sn\text{-}H}$ = 73 Hz), 1.43 (m, 4H, H2a, H3a), 1.95 (m, 4H, H2e, H3e), 4.59 (br, m, 2H, H1, H4), 4.98 (s, 4H, NCH$_2$), 7.17–7.38 (m, 10H, Ph). ^{13}C NMR (50 MHz, CDCl$_3$, TMS, ppm): δ= 10.2 (Sn-CH$_3$), 29.2 (C2, C3), 53.2, 53.7 (N-*CH$_2$*-Ph), 63.7 (C1, C4), 126.4 (C$_m$), 128.0 (C$_p$), 129.0 (C$_o$), 134.7 (C$_i$), 199.6 (CSS). ^{119}Sn NMR (149 MHz, CDCl$_3$, SnMe$_4$, ppm) δ= -188.5. Anal. calcd. (%) for $C_{26}H_{36}Cl_2N_2S_4Sn_2$ (813.16 gmol^{-1}): C, 38.40; H, 4.46; N, 3.44. Found: C, 38.60; H, 4.48; N, 3.68.

*2.2.2. Preparation of [(nBu$_2$SnCl)$_2$(bis-dtc)] (**2**)*

Complex **2** was prepared following the protocol given for compound **1**. Yield: 56% (0.471 g). Mp 289-290 ºC (dec). High resolution MS (FAB$^+$) for $C_{38}H_{60}ClN_2S_4Sn_2$ [*M-Cl*]$^+$: m/z (%) 947.1329 (100). Error: -4.6 ppm. IR (KBr, cm^{-1}): $\tilde{\nu}_{max}$ = 2953 (m), 2925 (w), 2860 (m), 1631 (m), 1461 ν(C-N$_{dtc}$) (s), 1408 (m), 1236 (w), 1156 (m), 1021 (w), 964 ν_{as}(CSS) (w), 870 (w), 734 (w), 694. ^{1}H NMR (200 MHz, CDCl$_3$, TMS, ppm): δ= 0.96 (t, 12H, δ-CH$_3$), 1.39-1.55 (m, 12H, H2a, H3a, γ-CH$_2$), 1.67-2.10 (m, 20H, H2a, H3a, α-CH$_2$, β-CH$_2$), 4.62 (br, m, 2H, H1, H4), 4.99 (s, 4H, NCH$_2$), 7.16–7.38 (m, 10H, Ph). ^{13}C NMR (50 MHz, CDCl$_3$, TMS, ppm): δ= 13.8 (δ–CH$_3$), 26.4 (γ–CH$_2$), 28.0, 29.2 (C2, C3, α-CH$_2$, β–CH$_2$), 53.1 (N-CH_2-Ph), 63.6 (C1, C4), 126.4 (C_m), 128.0 (C_p), 129.0 (C_o), 134.9 (C_i), 200.5 (CSS). ^{119}Sn NMR (149 MHz, $CDCl_3$, $SnMe_4$, ppm): δ = -188.0. Anal. calcd. (%) for $C_{38}H_{60}Cl_2N_2S_4Sn_2$ (981.48 gmol^{-1}): C, 46.50; H, 6.16. Found: C, 46.37; H, 5.69.

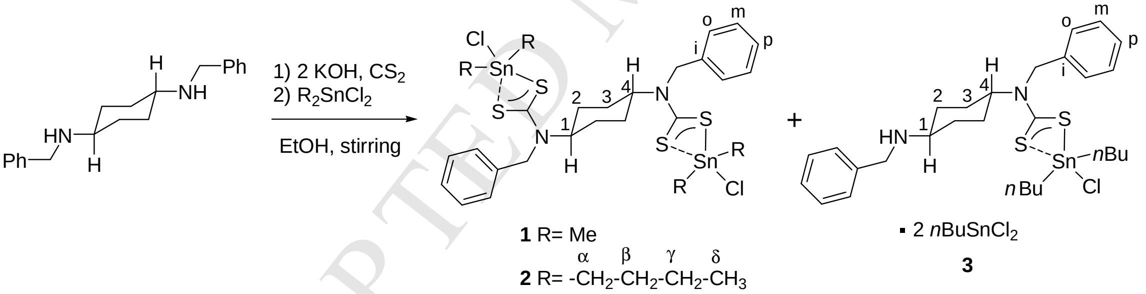
2.2.4. X-ray Crystallography

X-ray diffraction studies were carried out on a BRUKER-AXS APEX diffractometer equipped with a CCD area detector ($\lambda_{\mathrm{MoK\alpha}}$ = 0.71073 Å, monochromator: graphite). Frames were collected at T = 150(2) K (compound **1**) and T = 173(2) K (compounds **2** and **3**) via ω/ϕ-rotation ($\Delta\omega$ = 0.3º) at 10 s per frame. The measured intensities were reduced to F^2 and corrected for absorption with SADABS. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.[18] Non-hydrogen atoms were refined anisotropically, while C–H hydrogen atoms were placed in geometrically calculated positions using a riding model. For compound **3**, N–H hydrogen atoms have been located from iterative examination of difference Fourier maps following least squares refinements of the previous models with $d_{\mathrm{N-H}}$ = 0.86 Å and U_{iso}(H) = 1.5U_{eq}(N). Figures were created with DIAMOND.[19] In compound **1**, the N-benzyl groups and the chloroform solvent molecules were disordered, in the first case over two positions (occupancy factors = 0.49 and 0.51) and in the second case over three positions (occupancy factors = 0.46, 0.48 and 0.06). For the refinement, EADP, DFIX, SIMU, DELU and SAME instructions have been employed. Crystallographic data for the three crystal structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-1002259-1002261. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

3. Results and Discussion

3.1. Preparation and Spectroscopic Characterization

Reaction of *trans*-1,4-cyclohexanediamine with benzaldehyde followed by reduction with $NaBH_4$ in absolute ethanol resulted in the secondary amine *N,N´*-dibenzylcyclohexane-*trans*-1,4-diamine in high yields (> 95%). For the formation of the coordinating dtc ligands, the *N,N´*-disubstituted diamine was then combined with two equivalents of potassium hydroxide and an excess of carbon disulfide (10-fold). After stirring for two hours, either dimethyl- or di-*n*-butyltin dichloride dissolved in 20 mL of absolute ethanol was added dropwise. After 12 hours, a white precipitate had formed, which was filtered and washed with hot *n*-hexane (Scheme 1). Compound **3** was obtained in a small amount as crystalline by-product during the preparation of compound **2**. The chlorodiorganotin bis-dithiocarbamate complexes **1**-**2** were characterized by elemental analysis, IR spectroscopy, NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy, FAB$^+$ mass spectrometry and single-crystal X-ray diffraction analysis. Selected spectroscopic and mass spectrometric data are summarized in Table 1.



Scheme 1. Preparation of the chlorodiorganotin (IV) dithiocarbamate complexes **1-3**.

Table 1. Selected IR (cm^{-1}) and NMR (ppm) spectroscopic data for compounds **1-2**.

Compound	υ(N-CSS)	υ_{as}(CSS)	δ^{13}C(CS$_2$)	δ^{119}Sn
1	1463	964	199.6	-188.5
2	1461	964	200.5	-188.0

The IR spectra of compounds **1** and **2** showed bands for the stretching vibration of the N–CS_2 bonds in the range of 1461-1463 cm^{-1}, which are intermediate between the values observed for C–N single and C=N double bonds. The asymmetric vibrations of the CS_2 groups appeared at 964 cm^{-1}, in agreement with the values reported previously for a series of different organotin dithiocarbamates.[7, 20]

As previously established for related compounds, in the ^1H and ^{13}C NMR spectra of **1-2** (recorded in $CDCl_3$) the signals of the NCH_2Ph methylene and $NCHR_2$ methine groups are significantly low-field shifted when compared to the starting bis-amine.[7-8] In the ^1H NMR spectra, the variations of the chemical shifts were approximately $\Delta\delta = 1.2$ ppm for the NCH_2Ph functions and $\Delta\delta = 2.1$ ppm for the $NCHR_2$ hydrogen atoms of the cyclohexylene ring. Of these, the low-field shift of the axially oriented $NCHR_2$ hydrogen atoms is unusually large, but can be explained by the presence of a short intramolecular C–H···S contact, as established by the single-crystal X-ray diffraction analyses (vide infra). In the ^{13}C NMR spectra, the variations were approximately $\Delta\delta = 2$ ppm for the NCH_2Ph functions and $\Delta\delta = 7$ ppm for the $NCHR_2$ carbon atoms. The ^{13}C NMR spectra gave also signals in the range from $\delta = 199.6$ to 200.5 ppm, which are characteristic for NCS_2 groups coordinated to tin atoms.[7,21] ^{119}Sn NMR data were recorded in $CDCl_3$ and the chemical shifts for compounds **1** ($\delta = -188.5$ ppm) and **2** ($\delta = -188.0$ ppm) indicate that the tin atoms are embedded in five-coordinate coordination geometries.[22] For the structurally related complexes $(nBu_2SnCl)(S_2CNEt_2)$ and $(Me_2SnCl)(S_2CNEt_2)$ similar shift displacements have been reported.[23]

The molecular structures of compounds **1**-**2** were finally established by high-resolution mass spectrometry. The corresponding mass spectra gave peaks at m/z = 778.9898 and 947.1329, respectively, which correspond to the $[M–Cl]^+$ fragments. In both cases the experimental isotope pattern matches the simulated pattern (Figure S1). The loss of the chlorine atoms from chlorodimethyl and chlorodi-*n*-butyltin dithiocarbamates is commonly observed and has been previously reported.[7c,7g, 16, 24]

3.2. Single-crystal X-ray diffraction analysis

Complexes **1-2** were also characterized by single-crystal X-ray diffraction analysis. Additionally, during the recrystallization of compound **2** from a 1:1 (v/v) dichloromethane-ethanol mixture a small portion of crystals having the composition [(Bu_2SnCl)(mono-dtc)][$n$$Bu_2SnCl_2$]$_2$ (**3**) were distinguished under the microscope due to their different color (**2**, light yellow; **3**, colorless). Crystals for compound **1** were grown from a 1:1 (v/v) solvent mixture of chloroform and ethanol. Relevant crystallographic data are summarized in Table 2. Selected intra- and intermolecular geometric parameters for the corresponding crystal structures are given in Tables 3-5.

Table 2. Selected crystallographic data for compounds **1-3**

Crystal data[a]	**1**	**2**	**3**
Formula	$C_{26}H_{36}Cl_2N_2$ $S_4Sn_2\cdot 2CHCl_3$	$C_{38}H_{60}Cl_2N_2S_4Sn_2$	$C_{29}H_{43}ClN_2S_2Sn\cdot 2nBu_2SnCl_2$
M.p. (°C)	242-244	289-290 (dec.)	110-112
MW (g mol^{-1})	1051.82	981.40	1245.54
Crystal system	Monoclinic	Trigonal	Triclinic
Space group	*C2/c*	$P3_22_1$	*P-1*
Temp. (K)	150(2)	173 (2)	173(2)
a (Å)	17.6156(14)	16.7228(11)	9.7551(6)
b (Å)	11.0285(9)	16.7228(11)	15.4575(9)
c (Å)	21.7555(18)	14.2267(13)	19.3268(12)
β (°)	103.092(1)	90	101.600(1)
V (Å^3)	4116.7(6)	3445.5(4)	2831.1 (3)
Z	4	3	2
μ (mm^{-1})	1.959	1.412	1.652
ρ_{calcd} (g cm^{-3})	1.697	1.419	1.461
R[b, c]	0.0339	0.0521	0.0512
R_w[d, e]	0.0859	0.1239	0.1392
GOF	1.043	1.031	1.074

[a] $\lambda_{MoK\alpha}$ = 0.71073 Å, [b] $F_o > 4\sigma(F_o)$. [c] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [d] All data. [e] $R_w = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$.

*Analysis of the molecular geometries of **1-3***

The X-ray crystallographic studies revealed that compound **1** had crystallized in form of a chloroform solvate of the composition [(Me_2SnCl)$_2$(*bis*-dtc)]·$2CHCl_3$. As expected, the molecular structure corresponds to a discrete dinuclear molecule, in which according to the τ –parameter the coordination geometries around the tin atoms are intermediate between ideal trigonal-bipyramidal and square-pyramidal coordination polyhedra (τ = 0.45).[25] The molecules possess crystallographic inversion symmetry which orients the benzyl groups *anti* with respect to the central cyclohexylene ring of the ligand (Figure 1a). Within the coordination polyhedron of the metal center, the carbon atoms of the CH_3-Sn groups and one of the sulfur atoms (S1) from the dtc group occupy approximate equatorial positions, giving bond angles around the tin center in the range of 115.10(19)° to 127.81(19)° (Table 2). The latter value corresponds to the C-Sn-C bond angle, which is in good agreement with the bond angle calculated according to Lockhart’s equation[26] from the $^2J(^{119}Sn-^1H)$ coupling constant in solution (123 °). The remaining sulfur atom (S2) and the chlorine substituent occupy approximate axial positions; however, the S2-Sn-Cl bond angle of 155.07(3)° deviates significantly from the ideal value for a trigonal bipyramide, which can be attributed to the formation of the four-membered CS_2Sn chelate ring with a S1-Sn-S2 bond angle of only 69.74(3)°. According to Bent´s rule, the axial Sn-S2 bond is significantly longer than the equatorial Sn-S1 bond, thus giving an anisobidentate coordination mode with Sn-S bond distances of 2.4733(9) Å for Sn-S1 and 2.6530(10) Å for Sn-S2, respectively. The bonding asymmetry of the dtc ligand is also reflected in the C-S bond lengths, which are significantly different from each other, 1.745(4) Å for C1-S1 and 1.711(4) Å for C1-S2. Within the dtc function, the C-N_{dtc} bond length of 1.331(5) Å indicates a substantial delocalization of π–electron density.[27] In agreement with the ^1H NMR data, which showed an unusual low-field shift for the $NCHR_2$ hydrogen atoms upon the dtc-formation, there is a short intramolecular C–H···S contact formed between the hydrogen and one of the dtc-sulphur atoms (H2···S1, 2.49 Å; Σr_{vdw} (H, S) = 3.00 Å). Interestingly, this contact is observed in all three molecular structures examined herein (**2**, H2···S1, 2.42 Å; **3**, H2···S2, 2.45 Å; Table S1). A somewhat longer contact is also observed for the NCH_2Ph hydrogen atoms (**1**, H5B···S2, 2.55 Å; **2**, H5B···S2, 2.58 Å; **3**, H8A···S1, 2.55 Å; Table S1).

The crystal structure of compound **2** has the composition $[(Bu_2SnCl)_2(bis\text{-}dtc)]$. As for the dimethyltin analogue **1**, a discrete dinuclear molecular structure is observed with the difference that the molecules possess now crystallographic C_2-symmetry, in which the benzyl groups as an overall entity are *anti*-oriented with respect to the central cyclohexylene ring of the ligand, but, contrary to compound **1**, the phenyl rings are *syn*-oriented (Figure 1b). The τ-parameter indicates that the metal coordination polyhedron in this case approaches more the square-pyramidal than the trigonal-bipyramidal geometry (τ = 0.39). The Sn-S1 and Sn-S2 bond distances are 2.4626(15) and 2.7677(19) Å, respectively, indicating a substantially longer Sn-S2 bond in comparison to **1**, which is in agreement with the presence of the more voluminous Sn-*n*-butyl groups. Accordingly, the C-Sn-C bond angle increases from 127.81(19)° for **1** to 128.8(3)° for **2**. The coordination characteristics found for compounds **1** and **2** are common for chlorodiorganotin dithiocarbamates and are comparable to those previously described for a series of chlorodimethyltin, chlorodiethyltin, chlorodi-*t*-butyltin and chlorodiphenyltin dithiocarbamates.[1b,5b,5c,24]

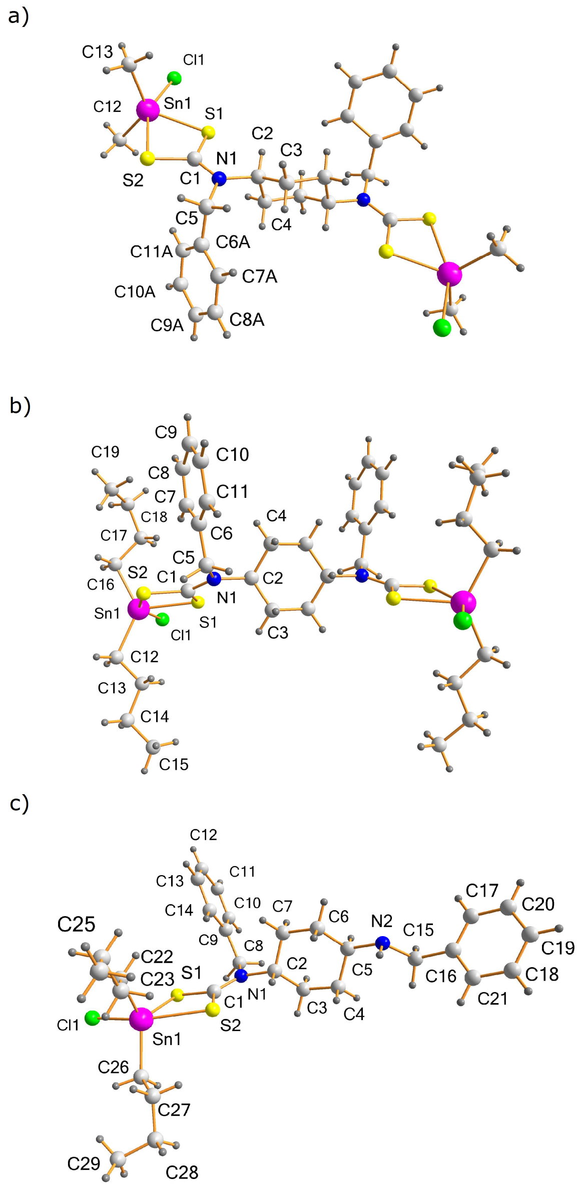


Figure 1. Perspective views of the molecular structures of the chlorodiorganotin dithiocarbamates **1**-**3**: a) $[(Me_2SnCl)_2($*bis*-dtc$)]$; b) $[(n\text{Bu}_2SnCl)_2($*bis*-dtc$)]$; c) $[(n\text{Bu}_2SnCl)($*mono*-dtc$)]$.

Table 3: Selected bond lengths [Å] and angles [°] for the molecular structures of compounds **1**-**3**.

Compound	**1**	**2**	**3**
Bond lengths			
Sn-C	2.115(4)	2.125(10)	2.106(8)
	2.117(4)	2.132(8)	2.134(6)
Sn-S1	2.4733(9)	2.4626(15)	2.4576(17)
Sn-S2	2.6530(10)	2.7677(19)	2.7263(17)
Sn-Cl	2.5224(10)	2.493(2)	2.4850(18)
C1-S1	1.745(4)	1.757(7)	1.751(6)
C1-S2	1.711(4)	1.701(6)	1.701(6)
C1-N1	1.331(5)	1.320(8)	1.328(8)
Bond Angles			
C-Sn-C	127.81(19)	128.8(3)	126.8(3)
C-Sn-S(1)	115.10(12)	113.4(2)	117.5(3)
	116.67(14)	116.6(2)	114.21(19)
C-Sn-Cl	94.31(12)	98.6(3)	95.2(2)
	95.88(14)	96.9(3)	99.08(19)
S(1)-Sn-Cl	85.34(3)	84.09(6)	86.94(6)
C-Sn-S(2)	95.88(12)	93.3(3)	95.5(3)
	95.70(14)	94.9(2)	91.48(18)
S(1)-Sn-S(2)	69.74(3)	68.31(5)	69.07(5)
Cl-Sn-S(2)	155.07(3)	152.39(6)	156.01(6)

As already mentioned, the crystals isolated for compound **3** had the composition [(nBu$_2$SnCl)(mono-dtc)][nBu$_2$SnCl$_2$]$_2$, indicating that the chlorodi-*n*-butyltin dithiocarbamate co-crystallized with two equivalents of the starting nBu$_2$SnCl$_2$. The molecular structure of [(nBu$_2$SnCl)(*mono*-dtc)] showed the expected mononuclear composition with a coordination geometry around the tin atom very similar to that observed for the dinuclear analogue **2** (τ = 0.49, Figure 1c, Table 3). On the contrary, the molecular structure of the di-*n*-butyltin dichloride entity embedded within the crystal structure of this compound is rather different from that observed in neat nBu$_2$SnCl$_2$.[28] Figure 2 shows that the nBu$_2$SnCl$_2$ units are arranged in form of dimeric aggregates of the composition [(nBu$_2$SnCl)(μ-Cl)$_2$(ClSnnBu$_2$)] with Sn-Cl bond distances (Table 4) close to the sum of the corresponding covalent radii (Sn, 1.39(4) Å; Cl, 1.02(4) Å). Some years ago, Tiekink *et al.* performed a comprehensive analysis of Sn···Cl interactions in a series of diorganotin dichlorides and found that this type of interaction is quite common for derivatives carrying small to medium-sized organic substituents at the tin metal center.[29] Nevertheless, in all structures analyzed in this report, the Sn···Cl distances were secondary interactions with values varying from 3.308(1) to 3.976(3) Å, and, therefore, significantly larger than the Sn-Cl bond lengths found for [*n*Bu_2SnCl_2]$_2$ in compound **3**. Furthermore, and contrary to what is expected, two of the bridging Sn-Cl bonds are significantly shorter (Sn2-Cl3, 2.4212(16); Sn3-Cl3, 2.4197(16) Å) than the remaining terminal and bridging Sn-Cl bonds (Sn2-Cl2, 2.4744(16); Sn3-Cl4, 2.6588(16); Sn2-Cl5, 2.8777(18); Sn3-Cl5, 2.5961(18) Å).

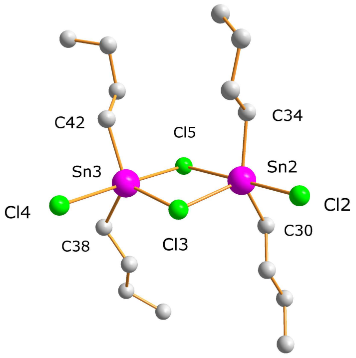


Figure 2. Perspective view of the dimeric aggregate formed between the *n*Bu_2SnCl_2 components in the crystal structure of [(*n*Bu_2SnCl)(mono-dtc)][*n*Bu_2SnCl_2]$_2$.

In the crystal structure of **3**, the [*n*Bu_2SnCl_2]$_2$ dimers are asymmetric, but the molecular structure approaches mirror plane symmetry. The coordination geometries of the two tin centers are both distorted trigonal-bipyramidal with slight differences regarding bond lengths and angles (Table 4). The corresponding τ-values are 0.71 for Sn2 and 0.79 for Sn3. The equatorial positions of the coordination polyhedra are occupied by the organic substituents and the bridging chlorine atom having the shortest Sn-Cl bond (Cl3), with bond angles ranging from 111.1(2) to 135.8(2) ° (Table 4). The axial positions are occupied by the terminal and the remaining bridging chlorine atom Cl5 with bond angles close to 180° (Cl2-Sn2-Cl5, 178.62(5); Cl4-Sn3-Cl5, 177.75(5) °). Within the four-membered Sn_2Cl_2 ring, the Cl-Sn-Cl and Sn-Cl-Sn bond angles are significantly different from each other. Of these, the largest bond angle corresponds to the Sn-Cl-Sn bond formed with chlorine Cl3, Sn2-Cl3-Sn3 = 99.41(6) °, that occupies one of the equatorial positions in the coordination polyhedra surrounding Sn2 and Sn3. The Sn-Cl-Sn bond angle formed with the axially oriented Cl5 bridge is smaller by approximately 15 °, Sn2-Cl5-Sn3 = 84.67(5) °.

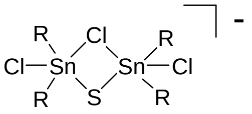
The values of the Cl-Sn-Cl bond angles are less different from each other, Cl3-Sn2-Cl5 = 83.72(5) and Cl3-Sn3-Cl5 = 90.11(5) °. In neat $n\mathrm{Bu_2SnCl_2}$, the molecular geometry of the tin atom is distorted octahedral due to weak secondary Sn···Cl contacts with bond distances of 3.514(5) and 3.544(5) Å, giving rise to 1D chains of the composition $[(n\mathrm{Bu_2Sn}(\mu\text{-}\mathrm{Cl})_2]_n$.[28]

Table 4. Selected bond lengths [Å] and bond angles [°] for the molecular structure of $[(n\mathrm{Bu_2SnCl})(\mu\text{-}\mathrm{Cl})_2(\mathrm{ClSn}n\mathrm{Bu_2})]$ embedded in the crystal structure of $[(\mathrm{Bu_2SnCl})(\text{mono-dtc})][n\mathrm{Bu_2SnCl_2}]_2$.

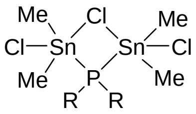
Bond lengths		*Bond angles*	
Sn2-C34	2.127(6)	C34-Sn2-C30	135.8(3)
Sn2-C30	2.135(6)	C34-Sn2-Cl3	111.1(2)
Sn2-Cl3	2.4212(16)	C30-Sn2-Cl3	111.6(2)
Sn2-Cl2	2.4744(16)	C34-Sn2-Cl2	94.0(2)
Sn2-Cl5	2.8777(18)	C30-Sn2-Cl2	93.6(2)
		Cl3-Sn2-Cl2	94.95(6)
		C34-Sn2-Cl5	86.8(2)
		C30-Sn2-Cl5	86.6(2)
		Cl3-Sn2-Cl5	83.72(5)
		Cl2-Sn2-Cl5	178.62(5)
Sn3-C38	2.130(8)	C38-Sn3-C42	130.3(4)
Sn3-C42	2.163(9)	C38-Sn3-Cl3	114.8(2)
Sn3-Cl3	2.4197(16)	C42-Sn3-Cl3	114.4(3)
Sn3-Cl5	2.5961(18)	C38-Sn3-Cl5	93.7(2)
Sn3-Cl4	2.6588(16)	C42-Sn3-Cl5	92.1(4)
		Cl3-Sn3-Cl5	90.11(5)
		C38-Sn3-Cl4	87.4(2)
		C42-Sn3-Cl4	88.6(4)
		Cl3-Sn3-Cl4	87.65(5)
		Cl5-Sn3-Cl4	177.75(5)
		Sn3-Cl3-Sn2	99.41(6)
		Sn3-Cl5-Sn2	84.67(5)

Although arrangements with a central four-membered cyclic $\mathrm{M_2Cl_2}$ core are quite common in coordination chemistry, for organotin complexes they are unusual. A revision of the Cambridge Structural Database (CSD version 5.35)[30] reveals that there is no entry so far for a double clorine-bridged five-coordinate organotin (IV) species, but there are four entries for five-coordinate organotin complexes containing a single-bridged chlorine atom

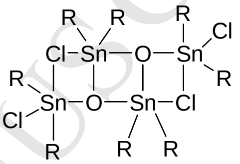
(FUJQEG, JAHQAK, SEJCEP and SEYFUX). There is a limited number of six-coordinate diorganotin (IV) compounds containing a Sn_2Cl_2 ring (BENFOP, DERTUP, FUPTEP, KUVGOX, VAXCON, WIGLIH, YATLIQ), and there are five entries for double heteroatom-bridged structures with five-coordinate organotin atoms of the compositions $[(R_2SnCl)(\mu\text{-Cl})(\mu\text{-S})(ClSnR_2)]^-$ (with R = Me and *t*Bu)[31] and $[(Me_2SnCl)(\mu\text{-Cl})(\mu\text{-}PR_2)(ClSnMe_2)]$ (with R = *i*Pr, *t*Bu).[32] On the contrary, diorganotin complexes containing Sn_2OCl rings are quite frequent, most of them being bis(tetraorganodistannoxane) derivatives.[33]



R = Me, *t*Bu



R = *i*Pr, *t*Bu



R = Me, Et, *i*Pr, *n*Bu, CH_2Ph

Overall, this structural discussion shows that the formation of inclusion compounds or co-crystals provides an interesting strategy for the stabilization and characterization of unusual molecular and coordination geometries of metal complexes, providing in such a way insight into the structural variations such complexes may suffer even in solution due to solvent coordination or the formation of intermolecular aggregates. Reports in this direction exist, but are still relatively scarce.[15]

*Analysis of the supramolecular structures of **1-3***

Within the crystal lattice of compound **1**, two crystallographically independent intermolecular interactions were observed, which are both involving the Sn–Cl chlorine atom. First, a C–H···Cl contact with a C_{arom}–H hydrogen atom of the benzyl group and, second, a S···Cl type interaction with the S2 sulfur atom from the dtc group. As seen from Table S1, the distances for both interactions are shorter than the corresponding sum of the van der Waals radii [Σr_{vdw} (H, Cl) = 2.95 Å; Σr_{vdw} (S, Cl) = 3.55 Å] (Figure 3a). The presence of these secondary interactions generates 2D layers parallel to the *bc* plane. In the third dimension, these layers are stacked in such a way that channels are generated along *c*, which house the disordered chloroform molecules. Within these channels, the solvent molecules are linked through Cl···Cl contacts into infinite 1D chains (Figure 3b); however, in this case the disorder prevents an accurate determination of the geometric parameters for this interaction.

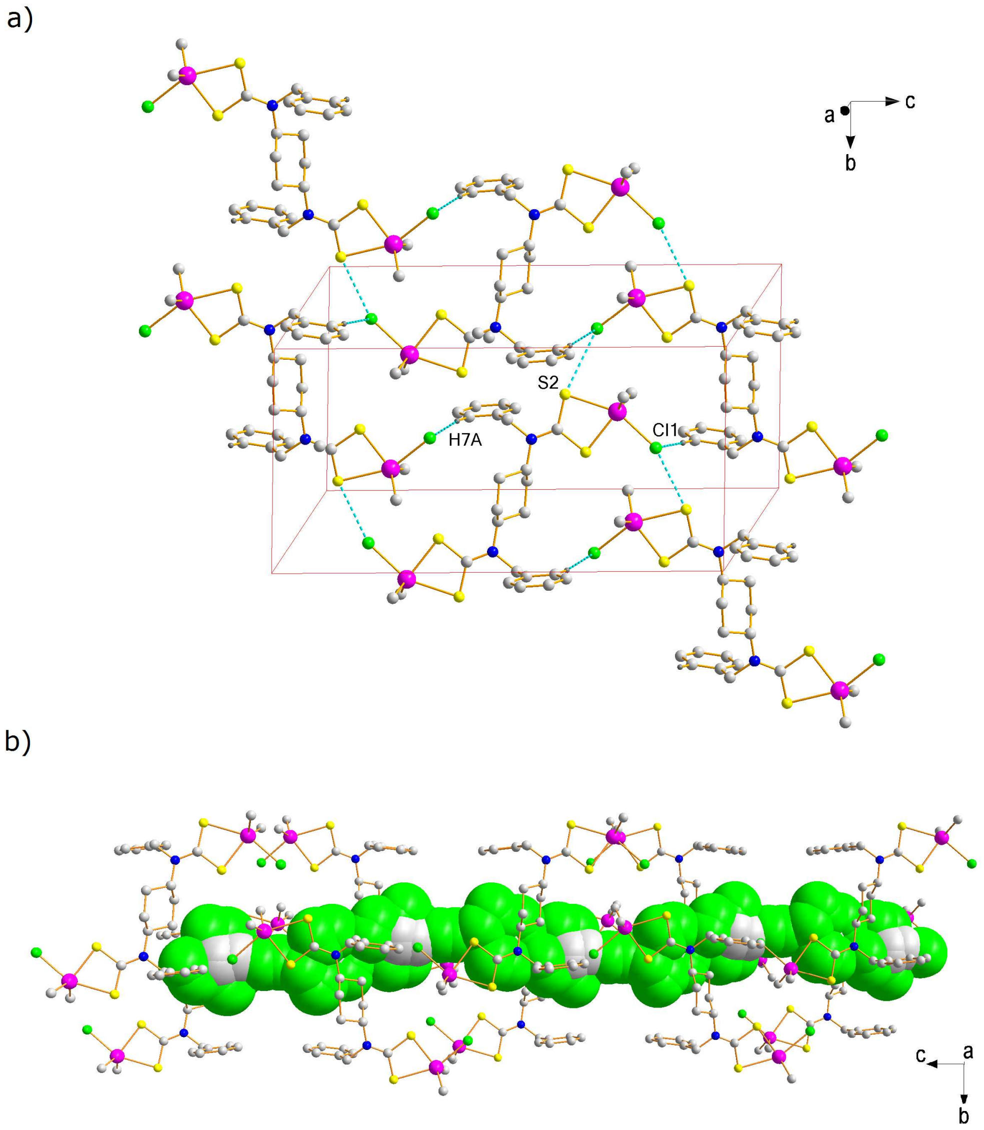


Figure 3. Fragments of the crystal structure of compound **1**, showing a) the intermolecular C–H···Cl and S···Cl interactions formed between the dinuclear complex molecules, and b) a lateral perspective view of one of the channels containing 1D chains of the disordered chloroform molecules. Note: Hydrogen atoms not involved in intermolecular interactions have been omitted for clarity.

In compound **2**, the dominant supramolecular interactions are S···S and C–H···X (X= Cl, S) contacts within the crystal lattice. Of these, the S···S interactions have a separation distance of 3.261(2) Å [Σr_{vdw} (S, S) = 3.60 Å] and generate 1D chains along *c*, which are further linked by two crystallographically independent C–H···X (X= Cl, S) contacts to give an overall 3D network (Figure 4).

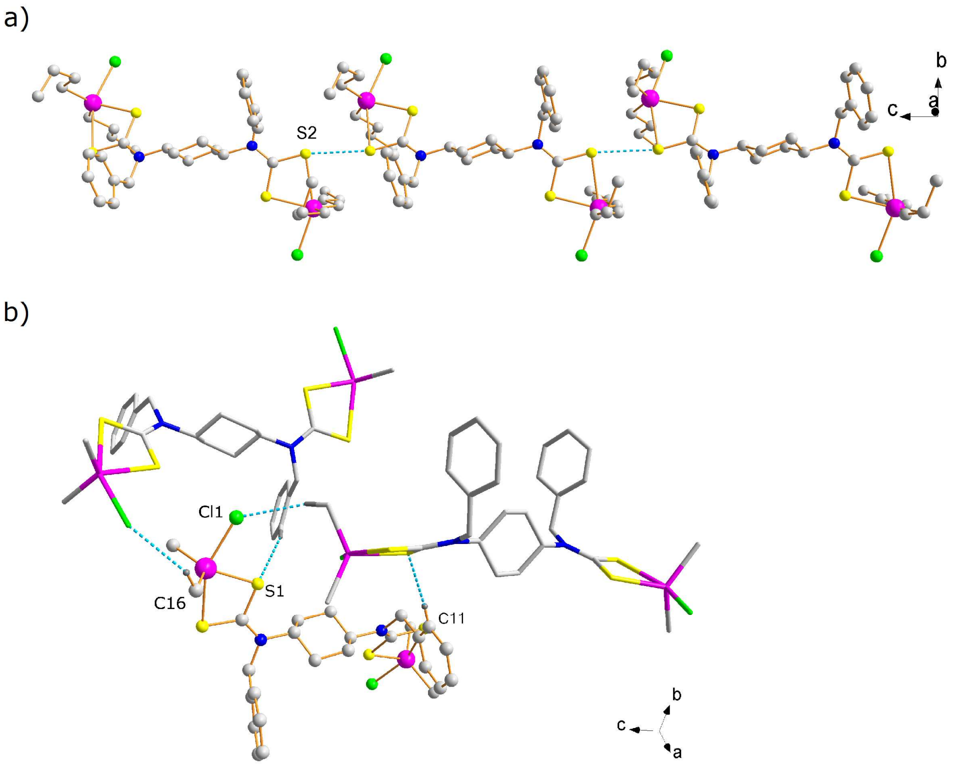


Figure 4. Fragments of the crystal structure of compound **2**, showing a) the 1D chains formed through S···S contacts, and b) the intermolecular C–H···S and C–H···Cl interactions formed between the dinuclear complex molecules. Note: Parts of the *n*-butyl groups and hydrogen atoms not involved in intermolecular contacts have been omitted for clarity.

The supramolecular arrangement of compound **3** is particularly interesting, mainly for two reasons. First, the diversity of secondary interactions generates cavities in the crystal lattice, and, second, this crystal structure is an unusual example of a two-component solid state structure, in which large non-solvent molecules are included. This arrangement can be attributed to the presence of only one dithiocarbamate group, generating an asymmetric molecule that maintains an amine group and enables N–H···Cl interactions with neighboring molecules. Interestingly, in this case the diorganotin dithiocarbamates are linked to each other only through relatively weak C–H···S and C–H···π contacts (C8-H8A···S1 and C22-H22B···C14, Table S1), while a larger number of interactions of the N–H···Cl, C–H···Cl and N···Cl type are formed with the second component of the crystal structure (Figure 5a, Table S1). This indicates that [(*n*Bu$_2$SnCl)(mono-dtc)][*n*Bu$_2$SnCl$_2$]$_2$ is rather a co-crystal than an inclusion complex. This is an important observation when considering that the global organization of the molecular components within the crystal lattice seems to indicate the presence of the latter structure type with channels along *a* (Figure 5b). However, the four [(*n*Bu$_2$SnCl)(mono-dtc)] molecules that surround a total of four di-*n*-butyltin dichloride molecules are not directly connected to each other. As already mentioned, the di-*n*-butyltin dichloride molecules are arranged in form of dimeric entities of the composition [(*n*Bu$_2$SnCl)(μ-Cl)$_2$(ClSn*n*Bu$_2$)]. Interestingly, within the cavities formed by each four [(Bu$_2$SnCl)(mono-dtc)] units, the [*n*Bu$_2$SnCl$_2$]$_2$ dimers are located close to each other thus resembling a bis(tetraorganodistannoxane) type arrangement; however, the Sn···Cl distances of 3.7476(19) Å approach the upper limit established for Sn···Cl interactions (4.0 Å).[29] Therefore, it is suggested that the approximation is indeed induced by two C-H···Cl contacts (Figure 5a).

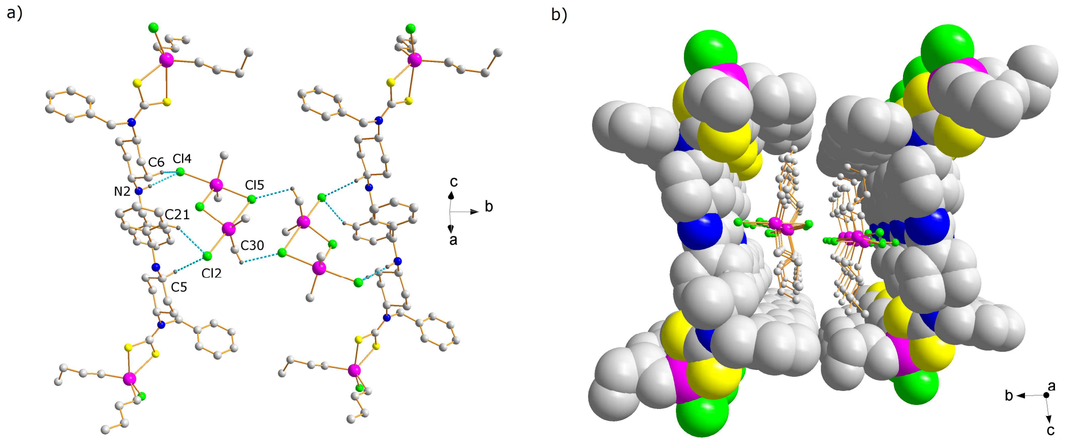


Figure 5. Fragments of the crystal structure of compound **3**, showing a) the intermolecular N–H···Cl and C–H···Cl interactions formed between the molecular components, and b) a perspective view of the supramolecular organization along *a*. Note: Parts of the *n*-butyl

groups and hydrogen atoms not involved in intermolecular contacts have been omitted for clarity.

4. Conclusions

This work described discrete mono- and dinuclear dimethyl- and dibutyltin chloride complexes derived from *mono*- and *bis*-dithiocarbamate ligands and analyzed the supramolecular arrangements generated by C–H···Cl, C–H···S, N–H···Cl and S···S, S···Cl, Cl···Cl, Cl···N and Cl···Sn intermolecular interactions. Interestingly, one compound co-crystallized with di-*n*-butyltin dichloride molecules giving a so far unknown dimeric aggregate with a central Sn_2Cl_2 core, in which the Sn-Cl distances are close to the sum of the covalent radii of tin and chlorine. Thus, the results presented in this article contribute to the understanding of the factors responsible for the supramolecular organization of organotin derivatives in the solid state. It should also be noticed that the non-covalent interactions described in this contribution are of relevance not only in chemistry, but also in related fields such as biochemistry, pharmaceutical chemistry, medicine and materials science.

Supplementary Material

High resolution FAB^+ mass spectra for compounds **1** and **2** (Figure S1) and geometric parameters for relevant intra- and intermolecular interactions in the crystal structures of compounds **1**-**3** (Table S1).

Acknowledgements

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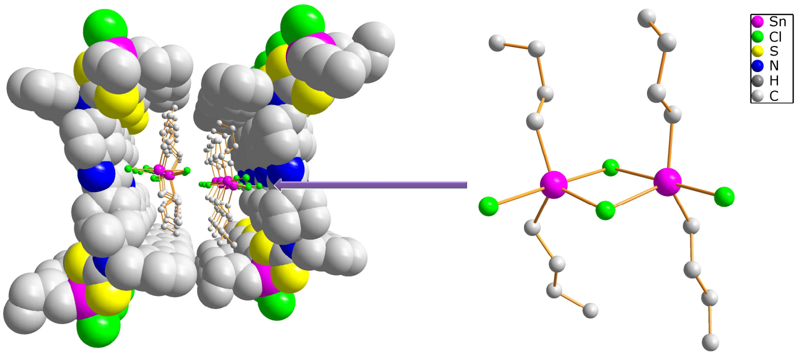
Synopsis and Graphical Abstract

The single-crystal X-ray diffraction analysis of three chlorodiorganotin dithiocarbamates revealed the presence of a variety of intermolecular interactions including C–H···S, C–H···Cl, N–H···Cl, S···S, S···Cl, Cl···Cl, Cl···N and Cl···Sn contacts, which can stabilize supramolecular co-crystalline assemblies containing unusual molecular aggregates such as the $[n\mathrm{Bu}_2\mathrm{SnCl}_2]$ dimer.



Highlights

1. Chlorodiorganotin dithiocarbamates have been prepared.
2. S···S, S···Cl, Cl···Cl, Cl···N and Cl···Sn contacts were found in the solid state.
3. Unusual dimers of the composition $[(n\mathrm{Bu}_2\mathrm{SnCl})(\mu\text{-Cl})_2(\mathrm{ClSn}n\mathrm{Bu}_2)]$ are described.
4. The latter are stored in form of a co-crystalline assembly.

Supplementary Material

Stabilization of [(nBu$_2$SnCl)(μ-Cl)$_2$(ClSnnBu$_2$)] within the Solid-State Structure of a Chlorodi-*n*-butyltin(IV) dithiocarbamate

Ericka Santacruz-Juárez, Jorge Cruz-Huerta, Aaron Torres-Huerta, María G. Hernández-Cruz, Victor Barba, Hugo Tlahuext-Romero, Herbert Höpfl[*]

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001,
C.P. 62209, Cuernavaca, México. Tel., Fax: +52 777 3297997. E-mail: hhopfl@uaem.mx.

Figure S1.	High resolution FAB$^+$ mass spectra for compounds a) **1** and b) **2**, indicating the presence of the corresponding [M–Cl]$^+$ fragment. For comparison, the simulated isotope patterns are also given.
Table S1.	Geometric parameters for relevant intra- and intermolecular interactions in the crystal structures of compounds **1**-**3**.

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[*] Corresponding author. Fax: (+52) 777 329 79 97

E-mail address: hhopfl@uaem.mx

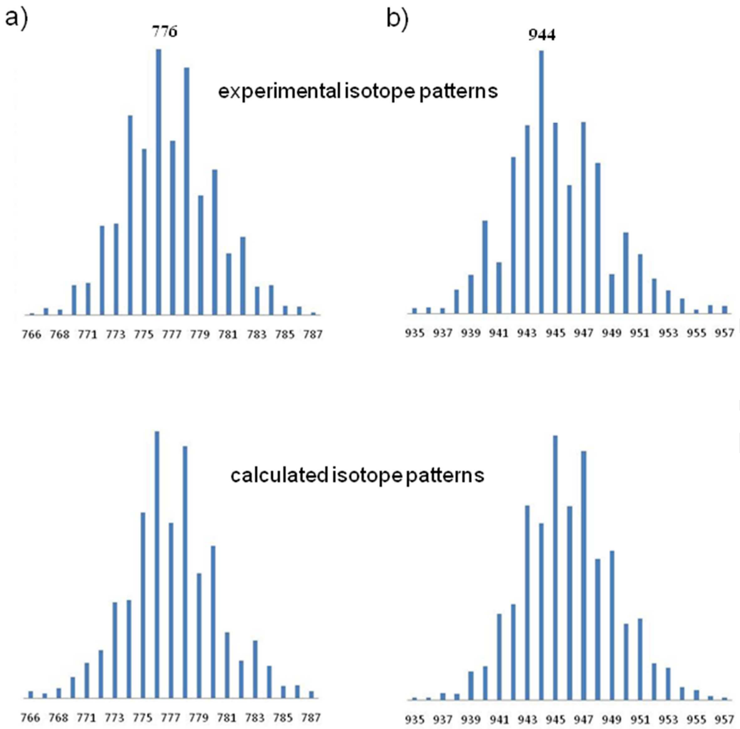

Figure S1. High resolution FAB$^+$ mass spectra for compounds a) **1** and b) **2**, indicating the presence of the corresponding [M–Cl]$^+$ fragment. For comparison, the simulated isotope patterns are also given.

Table S1. Geometric parameters for relevant intra- and intermolecular interactions in the crystal structures of compounds **1-3**

Interaction	D–H	H···A	D···A	D–H···A	Symmetry codes
1					
C2-H2···S1	1.00	2.49	2.972(4)	109	x, y, z
C5-H5B···S2	0.99	2.55	3.032(4)	110	x, y, z
S2···Cl1	--	--	3.5086(14)	--	3/2-x, y+1/2, 3/2-z
C7A-H7B···Cl1	0.95	2.74	3.679(3)	171	x, 1-y, 1/2+z
2					
C2-H2···S1	1.00	2.42	2.973(7)	114	x, y, z
C5-H5B···S2	0.99	2.58	3.028(8)	107	x, y, z
S2···S2	--	--	3.261(2)	--	x-y, -y, 5/3-z
C16-H16A···Cl1	0.99	2.93	3.840(10)	153	-x+y+1, 1-x, 1/3+z
C11-H11···S1	0.95	2.90	3.795(9)	157	1-x,1-x+y, 5/3-z
3					
C2-H2···S2	1.00	2.45	3.047(7)	118	x, y, z
C8-H8A···S1	0.99	2.55	2.949(7)	104	x, y, z
N2-H2’···Cl4	0.84	2.28	3.122(6)	177	x, y, z
N2···Cl2	--	--	3.283(6)	--	1-x, -y, 1-z
N2···Cl4	--	--	3.220(5)	--	-x, -y, 1-z
C5-H5···Cl2	1.00	2.89	3.485(6)	118	1-x, -y, 1-z
C6-H6A···Cl4	0.99	2.89	3.678(7)	137	x, y, z
C8-H8A···S1	0.99	2.93	3.875(6)	160	1-x, -y, 2-z
C21-H21···Cl2	0.95	2.90	3.736(8)	148	1-x, -y, 1-z
C22-H22B···Cl4	0.99	2.84	3.731(10)	150	-x, -y, 2-z
C30-H30B···Cl5	0.99	2.94	3.408(7)	110	1-x, 1-y, 1-z
C38-H38B···Cl2	0.99	2.85	3.696(9)	144	x-1, y, z
Sn2···Cl5	--	--	3.7476(19)	--	-x+1, -y+1, 1-z