Journal of Organometallic Chemistry 880 (2019) 83–90

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

New hypercoordinated diorganotin(IV) compounds with dithiocarbamato ligands. Synthesis and structural characterization

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ARTICLE INFO

Article history:
Received 29 July 2018
Received in revised form
24 September 2018
Accepted 30 October 2018
Available online 1 November 2018

Keywords:
Hypercoordinated diorganotin(IV) compounds
Solution behavior
Single-crystal X-ray diffraction
Covalent Sn–NCS bonds versus ionic interactions

ABSTRACT

Several homo- and heteroleptic diorganotin(IV) dithiocarbamato halides of type $RR'Sn(S_2CNR''_2)Cl$ [R = R' = Me, R'' = Me (**1**), Et (**2**); R = R' = ^nBu, R'' = Me (**3**), Et (**4**); R = 2-(Me_2NCH_2)C_6H_4, R' = Me, R'' = Me (**5**), Et (**6**)] and pseudo-halides of type $RR'Sn(S_2CNR''_2)(NCS)$ [R = R' = Me, R'' = Me (**7**), Et (**8**); R = R' = ^nBu, R'' = Me (**9**), Et (**10**); R = 2-(Me_2NCH_2)C_6H_4, R' = Me, R'' = Me (**11**), Et (**12**); R' = ^nBu, R'' = Et (**13**), R' = 2-(Me_2NCH_2)C_6H_4, R'' = Me (**14**), Et (**15**)] were prepared by salt metathesis reactions, starting from either $RR'SnCl_2$ or $RR'Sn(NCS)_2$. In all compounds the dithiocarbamato ligand acts as a bidentate moiety. For the compounds **11**–**15**, as well as for the species **5** and **6**, of type $RR'Sn(S_2CNR''_2)Cl$, bearing aromatic groups with pendant arms attached to tin, the NMR spectra gave no clear evidence for a N→Sn coordination in solution at room temperature. The molecular structures determined by single-crystal X-ray diffraction for compounds **12** and **14**, with one or two 2-(Me_2NCH_2)C_6H_4 groups, respectively, revealed the existence of intramolecular N→Sn interactions in solid state. The IR spectra suggest an isothiocyanato behavior of the NCS group in solid state in all cases, while the ^{119}Sn NMR spectra gave no clear evidence for such a behavior in solution, as no ^{14}N-^{119}Sn couplings were observed. The single-crystal X-ray diffraction studies revealed molecular species for **7, 8** and **12**, while **14** is a ionic compound with $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sn(S_2CNMe_2)]^+$ cations and SCN^- anions.

1. Introduction

C,N-chelating ligands of type 2-(Me_2NCH_2)C_6H_4 or 2,6-(Me_2NCH_2)C_6H_3, bearing one or two pendant arms capable for intramolecular N→Sn coordination, were extensively used during last decades in order to stabilize main group metal compounds. While the organotin(II) and the organotin(I) compounds with such groups are limited to [2-(Me_2NCH_2)C_6H_4]$_2$Sn [1], [2,6-(Me_2NCH_2)C_6H_3]SnCl [2] and the distannyne [{2,6-(Me_2NCH_2)C_6H_3}Sn]$_2$, respectively [3], a large variety of hypercoordinated organotin(IV) species of type [2-(Me_2NCH_2)C_6H_4]$_x$$R'_{3-x}$SnY (x = 1–3, R' = alkyl, aryl, Y = anionic ligand) were investigated in detail during last years by several groups [4–19]. It was noted that the strong intramolecular N→Sn interactions result not only in hypercoordinated tin(IV) monomeric species, but also determine an increased catalytic or biological activity in comparison with the derivatives substituted with simple organic groups, *e.g.* Me, ^nBu, Ph, thus making them more suitable for applications in organic synthesis, biology, medicine or materials science. Already in the 1970th, when the first organotin(IV) compounds bearing the 2-(Me_2NCH_2)C_6H_4 group were reported by van Koten, detailed NMR studies related to their solution behavior, with respect to the intramolecular N→Sn interactions, were employed [20–22]. A temperature dependent mechanism, based on several steps and including decoordination, inversion at nitrogen and recoordination to tin, is now well documented [23].

We have reported recently several hypercoordinated tin(IV) compounds with pseudohalogenido ligands, of type [2-(Me_2NCH_2)C_6H_4](R)Sn(NCE)$_2$ (R = ^nBu, Ph, 2-(Me_2NCH_2)C_6H_4, E = S, Se) or [2-(Me_2NCH_2)C_6H_4](R)$_2$Sn(NCE) (R = Me, Ph, E = S, Se) [18]. As a continuation of our studies, we focused our attention on diorganotin(IV) compounds bearing two types of thiolato ligands, *e.g.* a combination of diorganodithiocarbamato and thiocyanato groups. Our intention was to see the influence of the intramolecular N→Sn interaction upon the coordination behavior of the thiolato ligands, both in solution and in solid state. Thus, we report here the synthesis and the solution behavior of several compounds of type [2-

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https://doi.org/10.1016/j.jorganchem.2018.10.030

$(Me_2NCH_2)C_6H_4](R')Sn(S_2CNR''_2)(NCS)$ [R' = Me, R" = Me (**11**), Et (**12**); R' = ^nBu, R" = Et (**13**), R' = 2-$(Me_2NCH_2)C_6H_4$, R" = Me (**14**), Et (**15**)], as well as the starting halides $[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNR''_2)Cl$ [R" = Me (**5**), Et (**6**)]. For comparison, we have, with respect to the organic substituents at tin, investigated the new homoleptic compounds $Me_2Sn(S_2CNR''_2)(NCS)$ [R" = Me (**7**), Et (**8**)] and $^nBu_2Sn(S_2CNR''_2)(NCS)$ [R" = Me (**9**), Et (**10**)], similarly prepared from the starting $Me_2Sn(S_2CNR''_2)Cl$ [R" = Me (**1**), Et (**2**)] and $^nBu_2Sn(S_2CNR''_2)Cl$ [R" = Me (**3**), Et (**4**)]. Our choice for the dithiocarbamato ligands is motivated not only by their structural features (the small bite and the expected chelating behavior), but also by the specific properties of organotin(IV) complexes with such ligands, which made them valuable agents with antifungal and antiproliferative activity, or precursors for nanomateriales [24]. Moreover, we took the advantage of using a combination of organic groups capable for *C,N*-coordination, bidentate diorganodithiocarbamato ligands and thiocyanato groups, to stabilize new diorganotin(IV) cations which are still of interest, due to their expected reactivity and potential in catalysis and bond activation [25].

2. Results and discussion

2.1. Preparation

The diorganotin(IV) complexes **7**–**15** of type $RR'Sn(S_2CNR''_2)(NCS)$ were prepared by salt metathesis reactions, as depicted in Scheme 1, in one or two steps, depending on the diorganotin(IV) starting material. Sodium diorganodithiocarbamates react in a 1:1 M ratio with diorganotin(IV) bis(thiocyanates), thus resulting in the derivatives **13**–**15**. In a different procedure, diorganotin(IV) dichlorides reacted with sodium diorganodithiocarbamates in a 1:1 molar ratio to form compounds **1**–**6** of type $RR'Sn(S_2CNR''_2)Cl$, which were subsequently treated with KSCN to form the $RR'Sn(S_2CNR''_2)(NCS)$ derivatives **7**–**12**.

We have to note that our attempts to isolate diorganotin(IV) complexes of type $RR'Sn(NCS)Cl$ failed due to the Schlenk equilibrium established between $RR'Sn(NCS)Cl$ and the redistribution products $RR'Sn(NCS)_2$ and $RR'SnCl_2$, as we have reported previously [18].

The compounds were isolated as colorless solids, except the ^nBu substituted derivatives **9** and **10**, which are oils. All compounds were investigated by NMR spectroscopy and mass spectrometry. The solid species were characterized by IR spectroscopy as well, and for compounds **7**, **8**, **12** and **14** the crystal and molecular structures were determined by single crystal X-ray diffraction.

2.2. Spectroscopic characterization

The ^1H and ^{13}C NMR spectra display the expected resonances for the organic groups present in their structure. The methyl and the n-butyl groups show equivalence in solution in the disubstituted $Me_2Sn(IV)$ and $^nBu_2Sn(IV)$ moieties, respectively. A special attention we gave to the compounds bearing aryl groups with pendant arms capable for intramolecular N→Sn coordination in solution.

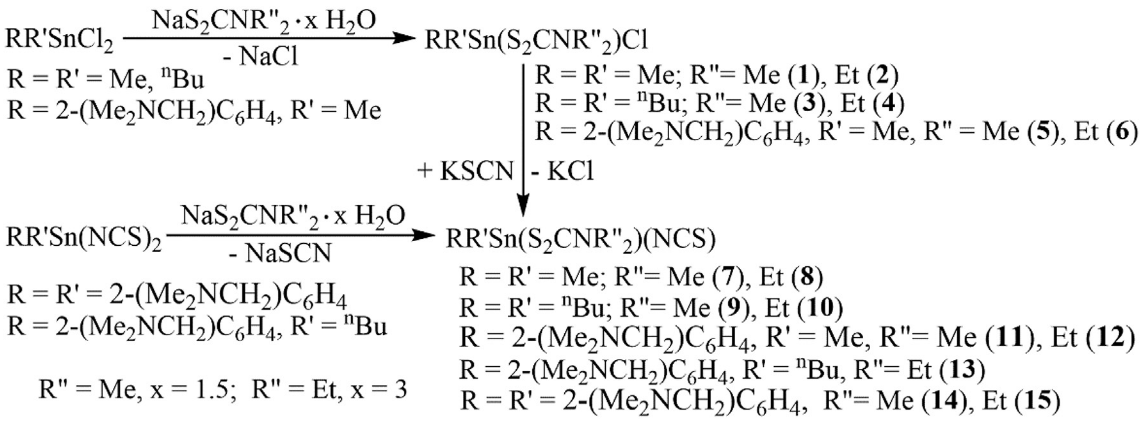
Compounds **14** and **15**, bearing two organic groups with pendant arms, display at room temperature broad resonances for the $N(CH_3)_2$ and the CH_2N protons, respectively, in the two equivalent 2-$(Me_2NCH_2)C_6H_4$ groups, thus suggesting a dynamic behavior in solution. For compound **14** we employed variable temperature ^1H NMR experiments which revealed the intramolecular N→Sn coordination in solution for the pendant arms in both groups ($\delta = 2.25$ and 2.42 ppm for the non-equivalent $N(CH_3)_2$ groups and δ_A 3.78 and δ_B 4.01 ppm, for the CH_AH_BN protons, $^2J_{HH} = 14.3$ Hz). Free enthalpies of 13.72 and 14.54 kcal/mol were calculated for the dynamic processes suffered by the $N(CH_3)_2$ groups and the CH_2N protons at a coalescence temperature of 10 °C and 30 °C, respectively (see ESI, Fig. S1).

For the Me_2NCH_2 groups in compounds **11**–**13** only sharp singlet resonances were observed in the aliphatic region at room temperature, thus suggesting that these groups are either not coordinated to tin, or they are involved in a fluxional process which comprises decoordination, inversion at nitrogen and recoordination to tin [23], even faster than in the case of compounds **14** and **15**.

The ^1H and the ^{13}C NMR resonances of the organic groups attached to tin are accompanied by $^1H–^{117/119}Sn$ and $^{13}C–^{117/119}Sn$ satellites, respectively (ESI, Fig. S2). Based on the $^1H–^{119}Sn$ and $^{13}C–^{119}Sn$ coupling constants we calculated the C–Sn–C angle (Table 1) [26].

Based on these calculations we proposed an appropriate coordination geometry in solution for the investigated compounds, *i.e.* a distorted trigonal bipyramidal geometry for the compounds with two methyl or two n-butyl groups attached to tin, both of them placed in equatorial positions. For compounds **7** and **8** the calculated C–Sn–C angle in solution is close to the values found in solid state by single crystal X-ray diffraction (see Table 1).

The methyl and the ethyl groups in the dithiocarbamato ligands



Scheme 1.
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Table 1
C–Sn–C angles [deg.] calculated for compounds **7**–**10** from their $^{2}J(^{119}Sn-^{1}H)$ and $^{1}J(^{119}Sn-^{13}C)$ coupling constants found in their solution ($CDCl_3$) NMR spectra.

Compound	^{1}H		^{13}C		X-ray
	$^{2}J(^{119}Sn-^{1}H)$ [Hz]	C–Sn–C [deg.][a]	$^{1}J(^{119}Sn-^{13}C)$ [Hz]	C–Sn–C [deg.][b,c]	C–Sn–C [deg.]
$Me_2Sn(S_2CNMe_2)(NCS)$ (**7**)	77.5	123.5	582.3	127.8, 132.9	128.6(2)
$Me_2Sn(S_2CNEt_2)(NCS)$ (**8**)	74.6	121.2	576.0	127.2, 132.3	130.04(19)
$Bu_2Sn(S_2CNMe_2)(NCS)$ (**9**)	–		523.2	122.6, 127.0	
$Bu_2Sn(S_2CNEt_2)(NCS)$ (**10**)	–		524.3	122.7, 127.1	

[a] $\theta = 0.0105|^{2}J|^{2} - 0.799|^{2}J| + 122.4$ [26a].
[b] $^{1}J = 11.4\theta - 875$ [26b].
[c] $^{1}J = 9.99\theta - 746$ [26c].

are equivalent in each compound at room temperature and they show one set of characteristic resonances, both in the ^{1}H and the ^{13}C NMR spectra, thus suggesting a bidentate behavior of these ligands in solution. The SCN ligands display singlet ^{13}C resonances at δ values in the range 138–145 ppm in compounds **7**–**15**.

All compounds give singlet ^{119}Sn resonances, in contrast with the situation found in compounds of type $[2-(Me_2NCH_2)C_6H_4](R)_2Sn(NCS)$ (R = Me) or $[2-(Me_2NCH_2)C_6H_4](R)Sn(NCS)_2$ (R = ^{n}Bu, Ph), where the ^{119}Sn resonances appeared as triplets or quintets, depending on the number of NCS groups attached to tin, thus clearly suggesting an isothiocyanato behavior of this ligand [18]. Anyway, in the case of our compounds we have no clear evidence for a certain thiocyanato or isothiocyanato behavior of the SCN ligand in solution. ^{119}Sn NMR is a particulary sensitive probe for assigning the coordination environment about tin and a large range of tin complexes were investigated over time in order to establish a general trend for the dependency of the coordination number and the chemical shift of the ^{119}Sn NMR resonance [27]. It was noticed that five-coordinate dithiocarbamato complexes usually give ^{119}Sn resonances in the range $-150 \div -250$ ppm, while the increase in the coordination number results in an up-field shift of the corresponding resonance, *e.g.* in the range $-300 \div -500$ ppm for six-coordinated species [28].

The FT-IR spectra of the compounds bearing SCN^{-} ligands display very strong υ(CN) bands around 2050 cm^{-1} and υ(CS) bands in the range 754–798 cm^{-1}, thus supporting an isothiocyanato behavior of this ligand [29] in solid state, as we observed for compounds **7**, **8** and **12** by single-crystal X-ray diffraction as well. The dithiocarbamato ligands act as bidentate moieties in all compounds. Bands of strong or medium intensity in the range 1240–1550 cm^{-1}, suggesting C-N bonds of a strength intermediate between single C–N (1250–1360 cm^{-1}) and double C=N (1640–1690 cm^{-1}) bonds, are present in all FT IR spectra, in accordance with partial delocalization of π electrons over the dithiocarbamato skeleton. In addition, bands of strong or medium intensity, characteristic for $\nu(CS_2)_{as}$ and $\nu(CS_2)_{s}$ are present at about 1250 cm^{-1} and 990 cm^{-1} in the spectra of the investigated compounds [30].

The ESI+ mass spectra present for all compounds only one peak corresponding to the cation $[M - Cl]^{+}$ for compounds **1**–**6** and $[M-NCS]^{+}$ for compounds **7**–**15**.

2.3. Single-crystal X-ray diffraction studies

The molecular structures of compounds **7**, **8**, **12** and **14** exhibit several common features, with respect to the coordination pattern of the thiolato ligands. The dithiocarbamato units act as *S,S*-chelating, monometallic biconective moieties, with planar SnS_2CNC_2 skeletons, while the SCN group behaves as an isothiocyanato ligand.

2.3.1. Crystal and molecular structure of $Me_2Sn(S_2CNMe_2)(NCS)$ (**7**) and $Me_2Sn(S_2CNEt_2)(NCS)$ (**8**)

The compounds have very similar molecular structures, so that the ellipsoids representation of **8** is depicted in Fig. 1, while that one of **7** is given in ESI, Fig. S3. Selected interatomic distances and angles are listed in Table 2 for both compounds.

The tin atom has a highly distorted trigonal bipyramidal coordination geometry, with the NCS ligand placed *trans* to the S2 atom in the dithiocarbamato moiety (N2–Sn1–S2 152.63(12)° in **7** and 152.11(11)° in **8**, respectively). While the Sn–S interatomic distances are different, thus resulting in an unsymmetrical bidentate coordination, the two carbon - sulfur interatomic distances in each *S,S*-dithiocarbamato moiety are of similar strength and they correspond to intermediate values between single C–S and double C=S bonds, similarly with the situation found in $Me_2Sn(S_2CNMe_2)Cl$ [31], $Me_2Sn(S_2CNEt_2)Cl$ [32] or $Ph_2Sn(S_2CNMe_2)Cl$ [33]. The molecules are associated in polymeric chains by bridging NCS groups. The NCS···Sn interaction in **7** is just at the limit of the sum of the van der Waals radii of the two elements (4.02 Å cf. $\Sigma r_{vdW}(S,Sn)$ 4.05 Å [34]), while in **8** the NCS···Sn interatomic distance (3.88 Å) is quite well below this value. The polymeric association for both compounds are given in ESI, Figs. S4 and S5.

2.3.2. Crystal and molecular structure of $[2-(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNEt_2)(NCS)$ (**12**) and $[\{2-(Me_2NCH_2)C_6H_4\}_2Sn(S_2CNMe_2)]^{+}[SCN]^{-}$ (**14**)

The ellipsoids representation of **12** is given in Fig. 2, while that one of **14** is depicted in Fig. 3. Selected interatomic distances and angles are listed in Table 3.

In compounds **12** and **14**, bearing one and two, respectively, 2-

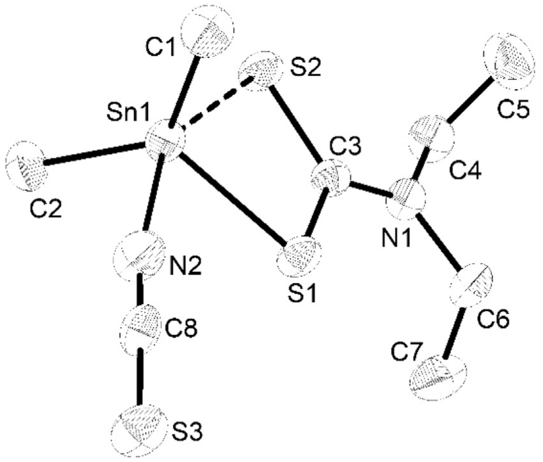


Fig. 1. Thermal ellipsoids representation at 30% probability of **8**. Hydrogen atoms were omitted for clarity.

Table 2
Selected interatomic distances [Å] and angles [deg.] in compounds $Me_2Sn(S_2CNMe_2)(NCS)$ (**7**) and $Me_2Sn(S_2CNEt_2)(NCS)$ (**8**).

	7	8
Sn(1)–C(1)	2.109(5)	2.104(4)
Sn(1)–C(2)	2.141(5)	2.110(4)
Sn(1)–S(1)	2.4596(13)	2.4666(10)
Sn(1)–S(2)	2.6688(13)	2.6594(11)
Sn(1)–N(2)	2.212(4)	2.243(4)
C(3)–S(1)	1.737(4)	1.739(3)
C(3)–S(2)	1.710(4)	1.724(4)
C(3)–N(1)	1.325(5)	1.306(4)
C(6)/C(8)–S(3)	1.595(5)	1.599(5)
C(6)/C(8)–N(2)	1.156(5)	1.168(5)
C(1)–Sn(1)–C(2)	128.6(2)	130.04(19)
C(1)-Sn(1)-S(1)	117.21(15)	114.89(15)
C(1)-Sn(1)-S(2)	98.99(17)	99.07(14)
C(2)-Sn(1)-S(1)	114.22(14)	115.07(14)
C(2)-Sn(1)-S(2)	98.66(18)	97.26(13)
S(1)-Sn(1)-S(2)	69.90(4)	70.05(3)
S(1)-Sn(1)-N(2)	82.80(13)	82.08(11)
S(2)-Sn(1)-N(2)	152.63(12)	152.11(11)
C(1)-Sn(1)-N(2)	91.6(2)	93.25(19)
C(2)-Sn(1)-N(2)	94.2(2)	93.68(17)
S(3)-C(6)/C(8)-N(2)	177.2(5)	178.5(4)

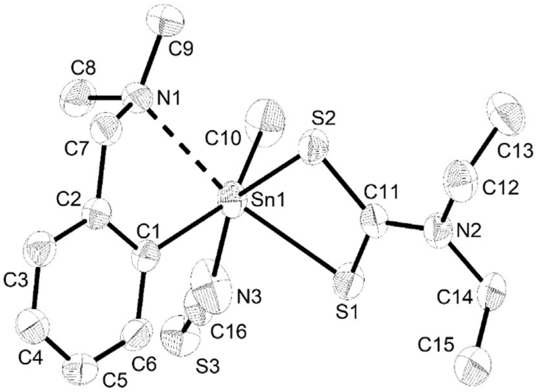


Fig. 2. Thermal ellipsoids representation at 30% probability of $A_{Sn}S_{N1}$-**12**. Hydrogen atoms were omitted for clarity.

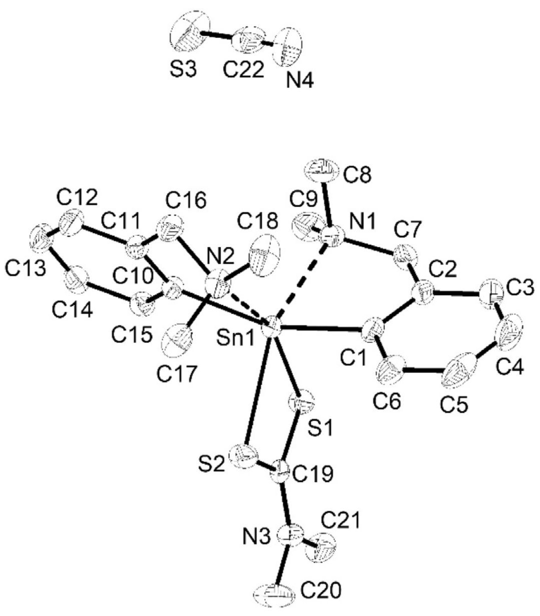


Fig. 3. Thermal ellipsoids representation at 30% probability of $A_{Sn}S_{N1},R_{N2}$-**14**. Hydrogen atoms were omitted for clarity.

Table 3
Selected interatomic distances [Å] and angles [deg.] in compounds $[2-(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNEt_2)(NCS)$ (**12**) and $[\{2-(Me_2NCH_2)C_6H_4\}_2Sn(S_2CNMe_2)]^+[SCN]^-$ (**14**).

	12		14
Sn(1)–C(1)	2.121(3)	Sn(1)–C(1)	2.135(4)
Sn(1)–C(10)	2.129(4)	Sn(1)–C(10)	2.139(3)
Sn(1)–N(1)	2.554(3)	Sn(1)–N(1)	2.401(3)
Sn(1)–S(1)	2.5359(10)	Sn(1)–S(1)	2.5708(10)
Sn(1)–S(2)	2.6317(10)	Sn(1)–S(2)	2.5928(10)
Sn(1)–N(3)	2.310(4)	Sn(1)–N(2)	2.489(3)
C(11)–S(1)	1.733(4)	C(19)–S(1)	1.723(4)
C(11)–S(2)	1.725(4)	C(19)–S(2)	1.714(4)
C(11)–N(2)	1.318(4)	C(19)–N(3)	1.318(4)
C(16)–S(3)	1.583(4)	C(22)–S(3)	1.649(7)
C(16)–N(3)	1.150(5)	C(22)–N(4)	1.054(6)
C(1)–Sn(1)–C(10)	149.60(16)	C(1)–Sn(1)–C(10)	159.60(14)
C(1)-Sn(1)-S(1)	103.96(9)	C(1)-Sn(1)-S(1)	96.18(10)
C(1)-Sn(1)-S(2)	99.86(9)	C(1)-Sn(1)-S(2)	95.26(11)
C(10)-Sn(1)-S(1)	104.31(13)	C(10)-Sn(1)-S(1)	100.13(10)
C(10)-Sn(1)-S(2)	100.24(15)	C(10)-Sn(1)-S(2)	101.76(10)
S(1)-Sn(1)-S(2)	69.61(3)	S(1)-Sn(1)-S(2)	69.98(3)
C(1)-Sn(1)-N(1)	73.69(11)	C(1)-Sn(1)-N(1)	77.15(13)
C(1)-Sn(1)-N(3)	86.58(13)	C(1)-Sn(1)-N(2)	92.62(12)
C(10)-Sn(1)-N(1)	85.89(15)	C(10)-Sn(1)-N(1)	91.99(12)
C(10)-Sn(1)-N(3)	86.64(18)	C(10)-Sn(1)-N(2)	75.05(12)
S(1)-Sn(1)-N(1)	153.15(7)	S(1)-Sn(1)-N(1)	85.33(8)
S(1)-Sn(1)-N(3)	81.71(12)	S(1)-Sn(1)-N(2)	162.76(8)
S(2)-Sn(1)-N(1)	84.28(7)	S(2)-Sn(1)-N(1)	153.38(8)
S(2)-Sn(1)-N(3)	151.32(12)	S(2)-Sn(1)-N(2)	94.51(8)
N(1)-Sn(1)-N(3)	124.18(13)	N(1)-Sn(1)-N(2)	111.13(11)
S(3)-C(16)-N(3)	177.9(4)	S(3)-C(22)-N(4)	177.5(5)

$(Me_2NCH_2)C_6H_4$ groups the nitrogen atoms in the pendant arms are strongly coordinated to tin, thus giving rise to five membered NC_3Sn chelate rings, which are not planar, but folded on the imaginary Sn···CH_2 axes. The intramolecular N→Sn interaction induces planar chirality to metal and thus the compounds crystallize as racemic mixtures of R_N and S_N isomers, with regard to each *C,N*-chelate ring [35]. Moreover, in these two compounds the tin atom becomes chiral itself and the two molecular structures can be discussed in terms of Λ/Δ or, more general, C/A enantiomers as well [36].

In compound **12** the isothiocyanato ligand is covalently attached to metal and the Sn–S interatomic distances in the bidentate diethyldithiocarbamato ligand are only slightly different. The coordination geometry about tin is distorted octahedral (N1–Sn1–S1 153.15(7)°), with a strong N→Sn intramolecular interaction (2.554(3) Å). Taking into account both the planar chirality in the SnC_3N ring and the chirality at the tin(IV) atom, a racemic mixture of $C_{Sn}R_{N1}$ and $A_{Sn}S_{N1}$ isomers should be considered in the crystal of **12**.

Compound **14** is an ionic species, with $[\{2-(Me_2NCH_2)C_6H_4\}_2Sn(S_2CNMe_2)]^+$ cations and $[SCN]^-$ anions. The tin atom in the cation has a distorted octahedral coordination geometry realized by the two *C,N*-chelating organic groups and the isobidentate dithiocyanato ligand. As a consequence of the N→Sn intramolecular coordination in both $2-(Me_2NCH_2)C_6H_4$ groups (N1···Sn1 2.401(3) and N2···Sn1 2.489(3) Å vs. $\Sigma r_{vdW}(N,Sn)$ 3.54 Å), and the chirality induced to the tin atom, the compound crystalizes as a racemic mixture of $A_{Sn}S_{N1},R_{N2}$ and $C_{Sn}R_{N1},S_{N2}$ isomers.

Weak π [CH_{Me}···C_g(C10-C15)] interactions (2.87 and 2.99 Å) generate polymeric chains of cations in the crystal of **14**. Weak SCN···H interactions, involving one CH proton in the C10-C15 aromatic ring were also identified in the crystal of **14** (see ESI, Fig. S6).

While the Sn–NCS fragment is almost linear in **7**, in **8** and **12** it is slightly folded about the nitrogen atom (Sn–N–C 175.84° in **7**, 162.96° in **8** and 155.75° in **12**).

3. Conclusions

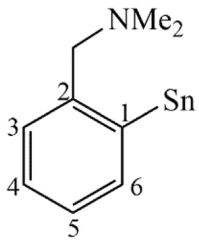
Our studies upon several homo- and heteroleptic, with respect to the organic groups attached to tin, diorganotin(IV) compounds bearing two or one 2-(Me_2NCH_2)C_6H_4 groups and mixt thiolato ligands, *e.g.* $R''_2NCS_2^-$ (R'' = Me, Et) and NCS^-/SCN^- moieties, revealed a bidentate coordination behavior of the dithiocarbamato ligands in all cases. At room temperature, the ^1H NMR spectra suggested a dynamic behavior in solution for the homoleptic compounds **14** and **15** with regard to the intramolecular N→Sn coordination, showing broad resonances for the CH_2N and the $N(CH_3)_2$ protons in the two 2-(Me_2NCH_2)C_6H_4 groups, while for the heteroleptic compounds **5**, **6**, **11**–**13** the sharp resonances corresponding to the $(CH_3)_2NCH_2$ protons gave no indices for the intramolecular N→Sn coordination in solution. Low temperature ^1H NMR spectra of **14** confirmed the intramolecular N→Sn coordination in the two equivalent 2-(Me_2NCH_2)C_6H_4 groups.

We found no clear evidence for an isothiocyanato behavior of the SCN^- ligand in solution, as all compounds gave singlet ^{119}Sn resonances. In solid state we observed an ionic structure for the homoleptic species $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sn(S_2CNMe_2)]^+[SCN]^-$ (**14**), while in $[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNEt_2)(NCS)$ (**12**) the NCS^- ligand is covalently attached to tin in an isothiocyanato fation. The IR spectra suggested Sn–NCS bonds in solid state in compounds **7**–**13**. Both in **12** and **14**, a *C,N* coordination pattern was observed for the 2-(Me_2NCH_2)C_6H_4 groups, thus resulting in distorted octahedral coordination geometries about tin.

4. Experimental

4.1. Materials and procedures

Starting materials were prepared according to literature procedures: $[2\text{-}(Me_2NCH_2)C_6H_4](R')SnCl_2$ (R' = [2-(Me_2NCH_2)C_6H_4] [16], ^{n}Bu [14]). Only disparate data regarding the synthesis of the starting $Me_2Sn(S_2CNR''_2)Cl$ (R'' = Me, Et) [28,37] and $^nBu_2Sn(S_2CNR''_2)Cl$ (R'' = Et) [28] and their spectroscopic characterization were reported previously, thus we decided to insert in the Supplementary information of this paper our own experimental results regarding compounds **1**–**4**. All the other materials were commercially available: KSCN, $NaS_2CNMe_2{\cdot}xH_2O$, $NaS_2CNEt_2{\cdot}3H_2O$. Elemental analyses were performed on a Flash EA 1112 analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 on a BRUKER DRX 400 or a Bruker Avance 600 MHz instrument. The chemical shifts, δ, are reported in ppm relative to the residual peak of solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.16 ppm; CH_2Cl_2: ^1H 5.33, ^{13}C 54.24 ppm). ^1H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HSQC and HMBC), according to the numbering scheme shown in Scheme 2. The ^{119}Sn NMR spectra were obtained on a BRUKER DRX 400 equipment, using Me_4Sn as external standard. The NMR data were processed using the MestReNova software [38]. Infrared spectra were recorded on a BioRad FTS-165 machine as KBr pellets. ESI + mass spectra were performed on a LTQ Orbitrap - XL instrument equipped with a standard ESI/APCI source.



Scheme 2.

4.2. Synthesis of $[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNMe_2)Cl$ (**5**)

A solution of $NaS_2CNMe_2{\cdot}1.5\ H_2O$ (0.505 g, 2.95 mmol) in methanol (15 mL) was added dropwise, under stirring, to a solution of $[2\text{-}(Me_2NCH_2)C_6H_4](Me)SnCl_2$ (1.00 g, 2.95 mmol) in CH_2Cl_2 (15 mL) and stirring was continued overnight. The solvent was removed in vacuum and CH_2Cl_2 (25 mL) was added to the reaction mixture. NaCl was separated by filtration and after removing the solvent from the remained clear solution, the title compound resulted as a colorless microcrystalline solid. The product was washed with n-hexane (3 × 5 mL) and dried under reduced pressure. Yield: 1.1 g (88%). M.p. 142 °C. Anal. Found: C, 36.58; H, 5.11; N, 6.59; S, 15.22%. Calc. for $C_{13}H_{21}ClN_2S_2Sn$ (Mw = 423.61): C, 36.86; H, 5.00; N, 6.61; S, 15.14%; ^1H NMR ($CDCl_3$, 400 MHz, 20 °C): $\delta = 1.59$ (s, 3H, $SnCH_3$, $^2J_{SnH}$ 96.1 Hz), 2.45 (s, br., 6H, $CH_2N(CH_3)_2$), 3.36 (s, 6H, $S_2CN(CH_3)_2$), 3.81 (s, br., 2H $CH_2N(CH_3)_2$), 7.10 (d, 1H, C_6H_4, H_3, $^3J_{HH} = 7.4$, $^4J_{SnH} = 44.7$ Hz), 7.24–7.42 (m, 2H, C_6H_4, $H_{4,5}$), 8.15 (d., 1H, C_6H_4, H_6, $^3J_{SnH} = 96.5$ Hz). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz, 20 °C): $\delta = -267.5$(s). MS (ESI+, MeOH), *m/z* (%): 389.02 (100) $[M - Cl]^+$. FT-IR (υ, cm^{-1}): 787s, 982s, 1154m, 1243s, 1396s, 1539s.

*$[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNEt_2)Cl$ (**6**)*, was prepared similarly with **5**, from $[2\text{-}(Me_2NCH_2)C_6H_4](Me)SnCl_2$ (1.00 g, 2.95 mmol) and $NaS_2CNEt_2{\cdot}3H_2O$ (0.667 g, 2.95 mmol), as a colorless solid. Yield: 1.16 g (87.2%). M.p. 142 °C. Anal. Found: C, 39.95; H, 5.62; N, 6.27; S, 14.88%. Calc. for $C_{15}H_{25}ClN_2S_2Sn$ (Mw = 451.66): C, 39.89; H, 5.58; N, 6.20; S, 14.20%. ^1H NMR ($CDCl_3$, 600 MHz, 20 °C): $\delta = 1.31$ (t, 6H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH} = 7.1$ Hz), 1.62 (s, 3H, $SnCH_3$, $^2J_{SnH} = 99.2$ Hz), 2.47 (s, $CH_2N(CH_3)_2$), 3.79 (s, 2H, $CH_2N(CH_3)_2$), 3.82 (q, 4H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH} = 7.0$ Hz), 7.11 (d, 1H, C_6H_4, H_3, $^3J_{HH} = 6.4$, $^4J_{SnH} = 43.8$ Hz), 7.29–7.43 (m, 2H, C_6H_4, $H_{4,5}$), 8.18 (d, 1H, C_6H_4, H_6, $^3J_{HH} = 7.2$, $^3J_{SnH} = 104.1$ Hz). ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): $\delta = 12.02$ (s, $S_2CN(CH_2CH_3)_2$), 18.08 (s, $SnCH_3$), 45.03 (s, $CH_2N(CH_3)_2$), 48.94 (s, $S_2CN(CH_2CH_3)_2$), 63.18 (s, $CH_2N(CH_3)_2$), 126.84 (s, C_6H_4, C_3), 128.48 (s, C_6H_4, C_5), 129.29 (s, C_6H_4, C_4), 134.91 (s, C_6H_4, C_6), 139.85 (s, C_6H_4, C_2), 146.67 (s, C_6H_4, C_1), 199.01 (s, $S_2CN(CH_2CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz, 20 °C): $\delta = -266.3$(s). MS (ESI+, MeOH), *m/z* (%): 417.05 (100) $[M - Cl]^+$. FT-IR (υ, cm^{-1}): 789m, 992m, 1087m, 1211s, 1283s, 1302s, 1443s, 1514s.

4.3. Synthesis of $Me_2Sn(S_2CNMe_2)(NCS)$ (**7**)

KSCN (0.148 g, 1.53 mmol) in methanol was added to a solution of $Me_2Sn(S_2CNMe_2)Cl$ (0.465 g, 1.53 mmol) in dichloromethane and the reaction mixture was left with stirring for 12 h. The solvent was removed in vacuum and CH_2Cl_2 (25 mL) was added to the reaction mixture. NaCl was separated by filtration and after removing the solvent from the remained clear solution, the title compound resulted as a colorless microcrystalline solid. The product was washed with n-hexane (3 × 5 mL) and dried under reduced pressure. M.p. 149 °C. Yield: 0.473 g (94.6%). Anal. Found: C, 22.11; H, 3.77; N, 8.63; S, 29.83%. Calc. for $C_6H_{12}N_2S_3Sn$ (Mw = 327.07): C, 22.03; H, 3.70; N, 8.57; S, 29.41%; ^{1}H NMR ($CDCl_3$, 600 MHz, 20 °C): δ = 1.17 (s, 6H, $SnCH_3$, $^2J_{SnH}$ 77.5 Hz), 3.40 (s, 12H, $S_2CN(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): δ = 6.81 (s, $SnCH_3$, $^1J_{SnC}$ 582.3 Hz), 45.47 (s, $S_2CN(CH_3)_2$), 139.55 (s, br., SCN), 196.58 (s, $S_2CN(CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz, 20 °C): δ = −270.1(s). MS (ESI+, MeOH), *m/z* (%):269.9428 (*vs.* 269.9428, theoretical) (100) $[M{-}NCS]^+$. FT-IR (υ, cm^{-1}): 781m, 985m, 1169m, 1254m, 1395s, 1550s, 2065vs.

Compounds **8**–**12** were prepared similarly:

*$Me_2Sn(S_2CNEt_2)(NCS)$ (**8**)*: from $Me_2Sn(S_2CNEt_2)Cl$ (0.469 g; 1.41 mmol) and KSCN (0.137 g; 1.41 mmol), as a colorless solid. M.p. 142 °C. Yield: 0.445 g (89.0%). Anal. Found: C, 27.15; H, 4.66; N, 7.83; S, 27.34%. Calc. for $C_8H_{16}N_2S_3Sn$ (Mw = 355.12): C, 27.06; H, 4.54; N, 7.89; S, 27.08%; ^{1}H NMR ($CDCl_3$, 600 MHz, 20 °C): δ= 1.16 (s, 6H, $SnCH_3$, $^2J_{SnH}$ 74.6 Hz), 1.33 (t, 6H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH}$ = 7.3 Hz), 3.74 (q, 4H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): δ = 6.82 (s, $SnCH_3$, $^1J_{SnC}$ 576 Hz), 12.06 (s, $S_2CN(CH_2CH_3)_2$), 50.55 (s, $S_2CN(CH_2CH_3)_2$), 139.60 (s, SCN), 194.85 (s, $S_2CN(CH_2CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.21 MHz, 20 °C): δ = −264.1(s). MS (ESI+, MeOH), *m/z* (%): 297.9738 (*vs.* 297.9741, theoretical) (100) $[M{-}NCS]^+$. FT-IR (υ, cm^{-1}): 783 m, 1207 m, 1292 m, 1443 m, 1510s, 2040vs.

*$^nBu_2Sn(S_2CNMe_2)(NCS)$ (**9**)*: from $Bu_2Sn(S_2CNMe_2)Cl$ (0.472 g, 1.26 mmol) and KSCN (0.122 g; 1.26 mmol), in methanol (25 mL), as a colorless oil. Yield: 0.417 g (80.5%). ^{1}H NMR ($CDCl_3$, 600 MHz, 20 °C): δ = 0.77–1.03 (m, 6H, $SnCH_2CH_2CH_2CH_3$), 1.17–1.51 (m, 4H, $SnCH_2CH_2CH_2CH_3$), 1.55–2.07 (m, 8H, $SnCH_2CH_2CH_2CH_3$), 3.37 (s, $S_2CN(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): δ = 13.77 (s, $SnCH_2CH_2CH_2CH_3$), 26.32 (s, $SnCH_2CH_2CH_2CH_3$, $^2J_{SnC}$ 97.1 Hz), 26.51 (s, $SnCH_2CH_2CH_2CH_3$, $^1J_{SnC}$ 523.2 Hz), 27.79 (s, $SnCH_2CH_2CH_2CH_3$, $^3J_{SnC}$ 34.3 Hz), 45.47 (s, $S_2CN(CH_2CH_3)_2$); 139.95 (s, SCN), 196.95 (s, $S_2CN(CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz, 20 °C): δ = −272.0(s). MS (ESI+, MeOH), *m/z* (%): 354.0366 (*vs.* 354.0367, theoretical) (100) $[M-\ NCS]^+$.

*$^nBu_2Sn(S_2CNEt_2)(NCS)$ (**10**)*: from $Bu_2Sn(S_2CNEt_2)Cl$ (0.475 g; 1.14 mmol) and KSCN (0.111 g; 1.14 mmol), as a colorless oil. Yield: 0.387 g (77.3%). ^{1}H NMR ($CDCl_3$, 600 MHz, 20 °C): δ = 0.90 (t, 6H, $SnCH_2CH_2CH_2CH_3$, $^3J_{HH}$ 7.6 Hz), 1.28 (t, 6H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH}$ 6.8 Hz), 1.32–1.46 (m, 4H, $SnCH_2CH_2CH_2CH_3$), 1.57–1.93 (m, 8H, $SnCH_2CH_2CH_2CH_3$), 3.71 (q, 4H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH}$ 6.9 Hz); ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): δ = 11.98 (s, $S_2CN(CH_2CH_3)_2$), 13.60 (s, $SnCH_2CH_2CH_2CH_3$), 26.14 (s, $SnCH_2CH_2CH_2CH_3$, $^2J_{SnC}$ 94.1 Hz), 26.28 (s, br., $SnCH_2CH_2CH_2CH_3$, $^1J_{SnC}$ 524.3 Hz), 27.7 (s, $SnCH_2CH_2CH_2CH_3$, $^3J_{SnC}$ 35.9 Hz), 50.15 (s, $S_2CN(CH_2CH_3)_2$); 139.69 (s, SCN), 194.75 (s, $S_2CN(CH_2CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz, 20 °C): δ = −265.9(s). MS (ESI+, MeOH), *m/z* (%): 382.0683 (*vs.* 382.0680, theoretical) (100) $[M{-}NCS]^+$.

*$[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNMe_2)(NCS)$ (**11**)*: from $[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNMe_2)Cl$ (0.474 g, 1.12 mmol) and KSCN (0.109 g, 1.12 mmol), as a colorless solid. The title compound was recrystallized from a CH_2Cl_2/n-hexane mixture to give a microcrystalline product. Yield: 0.411 g (82.3%). M.p. 137 °C. Anal. Found: C, 37.54; H, 4.72; N, 8.31; S, 18.77%. Calc. for $C_{14}H_{21}N_3S_3Sn$ (Mw = 446.23): C, 37.68; H, 4.74; N, 8.14; S, 18.63%; ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ = 1.44 (s, 3H, $SnCH_3$, $^2J_{SnH}$ = 107.8 Hz), 2.41 (s, 6H, CH_2NCH_3), 3.36 (s, 6H, $S_2CN(CH_3)_2$), 3.74 (s, 2H, CH_2NCH_3), 7.11 (d, 1H, C_6H_4, H_3, $^3J_{HH}$ = 7.6 Hz), 7.28 (t, 1H, C_6H_4, $H_{4/5}$ $^3J_{HH}$ = 7.3 Hz), 7.34 (br., 1H, C_6H_4, H_4), 7.39 (br., 1H, C_6H_4, H_5), 8.08 (br., 1H, C_6H_4, H_6, $^3J_{SnH}$ = 120.5 Hz). ^{13}C NMR ($CDCl_3$, 75.45 MHz, 20 °C): δ = 14.6 (s, $SnCH_3$, $^1J_{SnC}$ = 884.6 Hz), 44.86 (s, $S_2CN(CH_3)_2$), 45.07 (s, CH_2NCH_3), 63.29 (s, CH_2NCH_3), 127.22 (s, C_6H_4, C_3), 128.74 (s, C_6H_4, C_5, $^3J_{SnC}$ = 103.9 Hz), 129.07 (s, br., C_6H_4, C_4), 135.44 (s, C_6H_4, C_6), 135.52 (s, C_6H_4, C_2), 138.31 (s, C_6H_4, SCN), 140.32 (s, C_6H_4, C_1), 202.96 (s, $S_2CN(CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, 20 °C): δ = −432.6(s). MS (ESI+, MeOH), *m/z* (%): 389.01 (100) $[M-\ NCS]^+\ ]^+$. FT-IR (υ, cm^{-1}): 768s, 987s, 1154m, 1213m, 1263m, 1345w, 1442s, 1537s, 2052vs.

*$[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNEt_2)(NCS)$ (**12**)*: from $[2\text{-}(Me_2NCH_2)C_6H_4](Me)Sn(S_2CNEt_2)Cl$ (0.542 g, 1.2 mmol) and KSCN (0.117 g, 1.2 mmol), in dichloromethane, as a colorless solid. Yield: 0.458 g (80.5%). M.p. 133 °C. Anal. Found: C, 40.74; H, 5.23; N, 8.91; S, 20.54%. Calc. for $C_{16}H_{25}N_3S_3Sn$ (Mw = 474.29): C, 40.52; H, 5.31; N, 8.86; S, 20.28%; ^{1}H NMR ($CDCl_3$, 600 MHz, 20 °C): δ = 1.29 (br., 6H, $S_2CN(CH_2CH_3)_2$), 1.45 (s, 3H, $SnCH_3$, $^2J_{SnH}$ = 103.2 Hz), 2.39 (s, $CH_2N(CH_3)_2$), 3.73 (br., 4H, $S_2CN(CH_2CH_3)_2$), 3.75 (s, 2H, $CH_2N(CH_3)_2$), 7.12 (d, 1H, C_6H_4, H_3, $^3J_{HH}$ = 7.5, $^4J_{SnH}$ = 45.5 Hz), 7.30–7.45 (m, 2H, C_6H_4, $H_{4,5}$), 8.08 (d, 1H, C_6H_4, H_6, $^3J_{HH}$ = 6.8, $^3J_{SnH}$ = 102.6 Hz). ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): δ = 12.03 (s, $S_2CN(CH_2CH_3)_2$), 14.49 (s, $SnCH_3$, $^1J_{SnC}$ = 867.4 Hz), 45.05 (s, $CH_2N(CH_3)_2$), 49.66 (s, $S_2CN(CH_2CH_3)_2$), 63.35 (s, $CH_2N(CH_3)_2$), 127.16 (s, C_6H_4, C_3, $^3J_{SnC}$ = 92.7 Hz), 128.76 (s, C_6H_4, C_5, $^3J_{SnC}$ = 102.3 Hz), 129.82 (s, C_6H_4, C_5), 135.64 (s, C_6H_4, C_6), 137.86 (s, C_6H_4, C_2), 140.42 (s, C_6H_4, C_1), 144.06 (SCN), 198.02 (s, $S_2CN(CH_2CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.21 MHz, 20 °C): δ = −427.3(s). MS (ESI+, MeOH), *m/z* (%): 417.05 (100) $[M-\ SCN]^+$ FT-IR (υ, cm^{-1}): 763s, 992s, 1157m, 1213m, 1266m, 1348w, 1444s, 1538s, 2049vs.

4.4. Synthesis of $[2\text{-}(Me_2NCH_2)C_6H_4](Bu)Sn(S_2CNEt_2)(NCS)$ (**13**)

A solution of Et_2NCS_2Na x $3H_2O$ (0.259 g, 1.15 mmol) in MeOH was added to a solutiom of $[2\text{-}(Me_2NCH_2)C_6H_4](Bu)Sn(NCS)_2$ (0.492 g, 1.15 mmol) in CH_2Cl_2. The mixture was stirred for 3 h at room temperature, than the solvents were removed in vacuum. The remained oily product was treated with CH_2Cl_2 and NaSCN was removed by filtration. Evaporation of dichloromethane under reduced pressure afforded the title product as an oily material. Yield: (0.409 g, 68.8%). ^{1}H NMR ($CDCl_3$, 600 MHz, 20 °C): δ = 1.00 (t, 3H, $SnCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 6.3 Hz), 1.28 (t, 6H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH}$ = 6.5 Hz), 1.46–1.54 (m, 2H, $SnCH_2CH_2CH_2CH_3$), 1.94 (m, 2H, $SnCH_2CH_2CH_2CH_3$), 2.39 (s, 6H, $CH_2N(CH_3)_2$), 2.43–2.51 (m, 2H, $SnCH_2CH_2CH_2CH_3$), 3.71 (s, 2H, $CH_2N(CH_3)_2$), 3.75 (q, 4H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 7.12 (d, 1H, C_6H_4, H_3, $^3J_{HH}$ = 6.3, $^4J_{SnH}$ = 35.0 Hz), 7.34 (t, 1H, C_6H_4, H_4, $^3J_{HH}$ = 7.5 Hz), 7.40 (t, 1H, C_6H_4, H_5, $^3J_{HH}$ = 7.3 Hz), 8.10 (d, 1H, C_6H_4, H_6, $^3J_{HH}$ = 6.3, $^3J_{SnH}$ = 95.3 Hz); ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): δ = 12.09 (s, $S_2CN(CH_2CH_3)_2$), 13.96 (s, $SnCH_2CH_2CH_2CH_3$), 26.34 (s, $SnCH_2CH_2CH_2CH_3$), 28.35 (s, $SnCH_2CH_2CH_2CH_3$, $^2J_{SnC}$ = 41.6 Hz), 31.70 (s, $SnCH_2CH_2CH_2CH_3$, $^1J_{SnC}$ = 846 Hz), 45.74 (s, $CH_2N(CH_3)_2$), 50.02 (s, $S_2CN(CH_2CH_3)_2$, 63.79 (s, $CH_2N(CH_3)_2$), 127.40 (s, C_6H_4, C_3), 128.94 (s, C_6H_4, C_5), 129.96 (s, C_6H_4, C_4), 136.24 (s, C_6H_4, C_6), 140.73 (s, C_6H_4, C_2), 144.71 (s, C_6H_4, C_1 + SCN), 198.11 (s, $S_2CN(CH_2CH_3)_2$, ^{119}Sn NMR ($CDCl_3$, 149.21 MHz, 20 °C): δ = −414.87(s). MS (ESI+, MeOH), *m/z* (%): 459.0943 (*vs.* 459.0945, theoretical) (100) $[M-\ NCS]^+$.

Compounds **14** and **15** were prepared similarly:

*$[2\text{-}(Me_2NCH_2)C_6H_4]_2Sn(S_2CNMe_2)(NCS)$ (**14**)*: from Me_2NCS_2Na x 1.5 H_2O (0.149 g, 0.88 mmol) and $[2\text{-}(Me_2NCH_2)C_6H_4]_2Sn(NCS)_2$ (0.443 g, 0.88 mmol), as a colorless solid. Yield: 0.413 g, 83.0%. M.p. 196 °C. Anal. Found: C, 46.70; H, 5.29; N, 10.01; S, 17.35%. Calc. for $C_{22}H_{30}N_4S_3Sn$ (Mw = 565.40): C, 46.74; H, 5.35; N, 9.91; S, 17.01%; ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ = 2.32 (s, br., 12H, $CH_2N(CH_3)_2$),

3.46 (s, 6H, $S_2CN(CH_3)_2$), 3.90 (AB spin system, br., with δ_A 3.81 and δ_B 3.98, 4H, $CH_2N(CH_3)_2$), 7.30–7.45 (m, 2H, C_6H_4, H_3, $^4J_{SnH} = 44.4$ Hz), 7.49–7.60 (m, 4H, C_6H_4, $H_{4,5}$), 7.99–8.30 (m, 2H, C_6H_4, H_6, $^3J_{SnH} = 105.3$ Hz). ^1H NMR ($CDCl_3$, 400 MHz, −15 °C): $\delta = 2.25$ (s, 6H, $CH_2N(CH_3)_2$), 2.42 (s, 6H, $CH_2N(CH_3)_2$), 3.43 (s, 6H, $S_2CN(CH_3)_2$), 3.90 (AB spin system with δ_A 3.78 and δ_B 4.01, 4H, $CH_2N(CH_3)_2$, $^2J_{HH} = 14.3$ Hz), 7.31–7.44 (m, 2H, C_6H_4, H_3, $^4J_{SnH} = 42.4$ Hz), 7.50–7.58 (m, 4H, C_6H_4, $H_{4,5}$), 7.99–8.28 (m, 2H, C_6H_4, H_6, $^3J_{SnH} = 104.8$ Hz). ^1H NMR ($CDCl_3$, 400 MHz, +30 °C): $\delta = 2.33$ (s, 12H, $CH_2N(CH_3)_2$), 3.47 (s, 6H, $S_2CN(CH_3)_2$), 3.91 (s, 4H, $CH_2N(CH_3)_2$), 7.31–7.46 (m, 2H, C_6H_4, H_3, $^4J_{SnH} = 41.9$ Hz), 7.50–7.61 (m, 4H, C_6H_4, $H_{4,5}$), 8.01–8.32 (m, 2H, C_6H_4, H_6, $^3J_{SnH} = 103.9$ Hz). ^{13}C NMR ($CDCl_3$, 100.61 MHz, 20 °C): $\delta = 45.57$ (s, $S_2CN(CH_3)_2$), 47.05 (s, br., $CH_2N(CH_3)_2$), 64.06 (s, $CH_2N(CH_3)_2$), 128.65 (s, C_6H_4, C_3), 129.46 (s, C_6H_4, C_4), 131.59 (s, C_6H_4, C_5), 134.24 (s, C_6H_4, C_6), 139.05 (s, C_6H_4, C_2), 140.33 (s, C_6H_4, C_1), 144.95 (s, SCN) 195.97 (s, $S_2CN(CH_3)_2$), ^{119}Sn NMR ($CDCl_3$, 149.2 MHz, 20 °C): $\delta = -367.2$(s). MS (ESI+, MeOH), *m/z* (%): 508.09 (100) $[M - NCS]^+$. FT-IR (υ, cm^{-1}): 752m, 838s, 997m, 1210m, 1283m, 1345w, 1437s, 1507s, 2051vs.

*$[2\text{-}(Me_2NCH_2)C_6H_4]_2Sn(S_2CNEt_2)(NCS)$ (**15**)*: from Et_2NCS_2Na x $3H_2O$ (0.189 g, 0.84 mmol) and $[2\text{-}(Me_2NCH_2)C_6H_4]_2Sn(NCS)_2$ (0.423 g, 0.84 mmol), as a colorless sticky product. Yield: 0.343 g, 68.8%. Anal. Found: C, 48.52; H, 5.81; N, 9.47; S, 16.58%. Calc. for $C_{24}H_{34}N_4S_3Sn$ (Mw = 593.45): C, 48.57; H, 5.78; N, 9.44; S, 16.21%; ^1H NMR ($CDCl_3$, 600 MHz, 20 °C): $\delta = 1.32$ (t, 6H, $S_2CN(CH_2CH_3)_2$, $^3J_{HH}$ 7.2 Hz), 2.29 (s, br., 12H, $CH_2N(CH_3)_2$), 3.77 (s, br., 2H $CH_2N(CH_3)_2$ + 4H $S_2CN(CH_2CH_3)_2$), 3.98 (s, br., 2H, $CH_2N(CH_3)_2$), 7.29–7.43 (m, 2H, C_6H_4, H_3, $^4J_{SnH} = 46.1$ Hz), 7.48–7.61 (m, 4H, C_6H_4, $H_{4,5}$), 7.97–8.28 (m, 2H, C_6H_4, H_6, $^3J_{SnH} = 105.8$ Hz), ^{13}C NMR ($CDCl_3$, 150.90 MHz, 20 °C): $\delta = 12.16$ (s, $S_2CN(CH_2CH_3)_2$), 46.94 (s, br., $CH_2N(CH_3)_2$), 50.69 (s, $S_2CN(CH_2CH_3)_2$), 64.05 (s, $CH_2N(CH_3)_2$, $^3J_{SnC} = 47.8$ Hz), 128.57 (s, C_6H_4, C_4, $^3J_{SnC} = 96.1$ Hz), 129.45 (s, C_6H_4, C_3, $^3J_{SnC} = 101.4$ Hz), 131.56 (s, C_6H_4, C_5), 134.41 (s, C_6H_4, C_6), 139.07 (s, C_6H_4, C_1), 140.39 (s, C_6H_4, C_2), 140.42 (s, SCN), 193.95 (s, $S_2CN(CH_2CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.21 MHz, 20 °C): $\delta = -359.6$(s). MS (ESI+, MeOH), *m/z* (%): 536.12 (100) $[M - NCS]^+$. FT-IR (υ, cm^{-1}): 754 m, 838s, 995m, 1207m, 1282m, 1343w, 1439s, 1507s, 2047vs.

4.5. X-ray structure determination

Single crystals of **7**, **8**, **12** and **14** suitable for X-ray diffraction studies were obtained from a CH_2Cl_2/n-hexane mixture (1/5, v/v) at room temperature.

The details of the crystal structure determination and refinement are given in ESI, Table S1. The crystals were attached with paraton/N oil to cryoloops and the data were collected on a Bruker SMART APEX CCDC diffractometer using Mo Ka radiation (λ = 0.71073 Å) at 297 K. The structures were solved by direct methods and refined by full-matrix least-square procedures on F^2 with SHELX-2013 [39]. All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atoms positions. The intermolecular interactions were evidenced using the Platon program [40]. The drawings were created with the Diamond program [41].

Acknowledgements

The financial support from National University Research Council of Romania (Research Project PNII-ID-PCE-2011-3-0659) is greatly acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.10.030.

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