DOI: 10.1002/ejic.200701044

Solid-State Structure and Behaviour in Solution of Hypervalent Organotin(IV) Derivatives Containing 2-(Me_2NCH_2)C_6H_4 Moieties

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Keywords: Tin / Hypervalent / Halides / X-ray diffraction / Supramolecular chemistry

Hypervalent diorganotin(IV) dihalides of the type $RBuSnX_2$ [R = 2-(Me_2NCH_2)C_6H_4; X = Cl (**1**), F (**2**)] and heterocyclic derivatives of the type $(RR^1SnS)_2$ [R^1 = Bu (**3**) and 2-(Me_2NCH_2)C_6H_4 (**4** and **4**·$2CHCl_3$)] have been prepared. Their behaviour in solution was investigated by multinuclear NMR spectroscopy. The molecular structures of these compounds were established by single-crystal X-ray diffraction. The strength of the intramolecular Sn→N coordination as a function of the substituent pattern at the tin atom is discussed. Weak intermolecular Sn···Cl interactions result in a *"zig-zag"* polymeric chain for dichloride **1**, while difluoride **2** is a polymer with a linear –Sn–F–Sn– skeleton. In both compounds, a distorted octahedral (*C,N*)$CSnX_3$ configuration is observed. The thio derivatives are monomeric and exhibit distorted trigonal bipyramidal (*C,N*)$CSnS_2$ (**3**) or distorted octahedral $(C,N)_2SnS_2$ (**4** and **4**·$2CHCl_3$) configurations.
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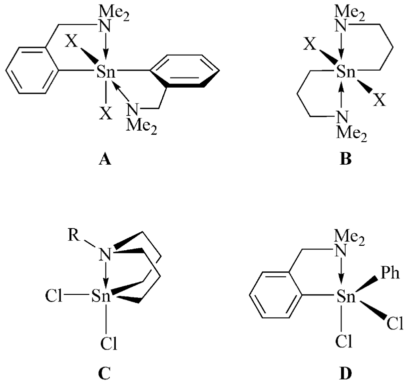
Introduction

Several symmetric diorganotin(IV) dihalides containing 2-(Me_2NCH_2)C_6H_4 groups[1–7] or related organic ligands[1,3,8–12] have been investigated so far both in solution and in the solid state. Single-crystal X-ray diffraction studies have revealed that strong intramolecular N→Sn interactions are established by both nitrogen atoms of a molecular unit. All $[2\text{-}(Me_2NCH_2)C_6H_4]_2SnX_2$ (X = F, Cl, Br, I) are monomeric, with hypervalent octahedral *cis*-X_2-*cis*-N_2-*trans*-C_2 configurations (Scheme 1, **A**).[4–7] In contrast, the related $[Me_2N(CH_2)_3]_2SnF_2$ and $[Me_2N(CH_2)_2CMe_2]_2SnCl_2$ exhibit octahedral *all-trans*-$(C,N)_2SnX_2$ configurations (Scheme 1, **B**).[10,12] The use of an organic ligand with a potential for only one intramolecular N→Sn interaction resulted in trigonal bipyramidal (*C,N,C*)SnX_2 configurations, e.g. in $RN(CH_2CH_2CH_2)_2SnCl_2$ (Scheme 1, **C**).[8,11]



Scheme 1.

Very few mixed diorganotin(IV) dihalides containing only one organic ligand that can act as a (*C,N*)-chelate moiety have been described so far: $RMeSnX_2$ (X = Cl, Br),[2] $RBuSnCl_2$,[13,14] $RPhSnX_2$ (X = F,[5] Cl[4,15]) [R = 2-(Me_2NCH_2)C_6H_4] and $[2\text{-}(Me_2NCHMe)C_6H_4]MeSnBr_2$.[2] They were mainly characterized by solution NMR spectroscopy. Attempts to convert the corresponding dichloride into the difluoride $[2\text{-}(Me_2NCHMe)C_6H_4]PhSnF_2$ by using several fluorination methods failed to produce the monomeric species. In most cases, migration of the phenyl group was noted, and ionic species were proposed to be formed on the basis of NMR spectra. Only when $[2\text{-}(Me_2NCHMe)C_6H_4]Bu_2SnF$ was used as a fluorination agent, was a sparingly soluble product obtained, for which a trimeric structure, $(RPhSnF_2)_3$, was proposed on the basis of ESI-MS spectra.[5] So far, the molecular structure for only $[2\text{-}(Me_2NCH_2)C_6H_4]PhSnCl_2$ has been established by single-crystal X-ray diffraction; it features the expected trigonal bipyramidal (*C,N*)$CSnX_2$ configuration (Scheme 1, **D**).[4,15] The molecular structures of the related compounds $[2,6\text{-}(Me_2NCH_2)_2C_6H_3](4\text{-}MeC_6H_4)SnI_2$,[9] $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]PhSnCl_2$[16] and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]BuSnCl_2$[17] feature an *all-trans*-(*N,C,N*)$CSnX_2$ configuration due to the "pincer" pattern of the aryl group bearing two pendant arms. A similar structure was proposed on the basis of detailed NMR spectroscopic studies for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]BuSnBr_2$.[18]

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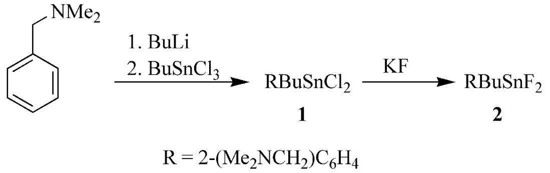
The structure of the diorganotin(IV) sulfides depends on the identity of the organic groups attached to the metal atom. The use of smaller organic groups results in polymeric ($i$$Pr_2SnS$)$_n$[19] or cyclic trimers, (R_2SnS)$_3$ (R = Me,[20] Ph[21]). With bulkier organic groups, dimers with planar Sn_2S_2 rings, e.g. ($t$$Bu_2SnS$)$_2$,[22] *trans*-[Tb(Mes)SnS]$_2$ {Tb = 2,4,6-[(Me_3Si)$_2$CH]$_3$$C_6H_2$},[23] or folded Sn_2S_2 rings, e.g. *trans*-[Tb(Mes)SnS]$_2$,[23b] were obtained. Other cyclic monoorganotin sulfides containing the bulky *o*-terphenyl ligand, –C_6H_3–2,6-Trip$_2$ (Trip = –C_6H_2–2,4,6-$i$$Pr_3$), e.g. *trans*-[Ar(HS)SnS]$_2$, were recently reported.[24] All these compounds contain tetrahedrally configured tin atoms. When organic ligands with a potential for intramolecular N→Sn coordination are attached to the tin atom, dimers with planar Sn_2S_2 rings and coordination numbers of 5 or 6 were found in the solid state, i.e. [MeN($CH_2CH_2CH_2$)$_2$SnS]$_2$ [(*C*,*N*,*C*)SnS_2 core],[25] *trans*-[{Me_2N(CH_2)$_2$$CMe_2$}PhSnS]$_2$ [(*C*,*N*)$CSnS_2$ core],[26] [{CH_2(Et)$NCH_2CH_2CH_2$}$_2$SnS]$_2$ [(*C*,*N*,*N*,*C*)SnS_2 core],[27] [{Me_2N(CH_2)$_3$}$_2$SnS]$_2$ [(*C*,*N*)$_2$-SnS_2 core].[28] For the dimer [{8-NC_9H_6(Me_3Si)CH}$_2$SnS]$_2$, the bulkiness of the organic ligand prevents the coordination of both nitrogen atoms to the metal atom, and the *trans* isomer with a trigonal bipyramidal (*C*,*N*)$CSnS_2$ core was isolated.[29] However, for [MeN($CH_2CH_2CH_2$)$_2$SnS]$_2$, a dimer–trimer equilibrium in solution was observed.[25] No organotin sulfide derivatives containing a [2-(Me_2NCH_2)-C_6H_4]Sn moiety have been described so far.

We report here the synthesis and structural characterization of the first hypervalent mixed diorganotin(IV) difluoride [2-(Me_2NCH_2)C_6H_4]$BuSnF_2$ (**2**), as well as the novel thio species *cyclo*-[{2-(Me_2NCH_2)C_6H_4}BuSnS]$_2$ (**3**) and *cyclo*-[{2-(Me_2NCH_2)C_6H_4}$_2$SnS]$_2$ (**4**). The molecular structure of [2-(Me_2NCH_2)C_6H_4]$BuSnCl_2$ is also described.

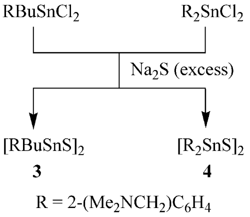
Results and Discussion

The asymmetrically substituted diorganotin(IV) dihalides, $RBuSnX_2$ [X = Cl (**1**), F (**2**)], were prepared in good yields according to Scheme 2. The reaction of the lithium salt of the organic ligand with $BuSnCl_3$ afforded [2-(Me_2NCH_2)C_6H_4]$BuSnCl_2$ (**1**), which in turn was used to obtain the corresponding [2-(Me_2NCH_2)C_6H_4]$BuSnF_2$ (**2**) by a halide exchange reaction with excess KF in a methanol/CH_2Cl_2/water mixture.



Scheme 2.

Reaction in H_2O/CH_2Cl_2 of diorganotin dichlorides **1** and [2-(Me_2NCH_2)C_6H_4]$_2$$SnCl_2$ with excess sodium sulfide, Na_2S, provided the corresponding diorganotin sulfides, *cyclo*-[{2-(Me_2NCH_2)C_6H_4}BuSnS]$_2$ (**3**) and *cyclo*-[{2-(Me_2NCH_2)C_6H_4}$_2$SnS]$_2$ (**4**), respectively (Scheme 3).



Scheme 3.

All compounds are colourless, air-stable solids. Diorganotin dichloride **1** and its thio derivatives **3** and **4** are soluble in common organic solvents. Diorganotin difluoride **2** exhibits a very low solubility in $CHCl_3$, CH_2Cl_2, benzene, toluene or dmso.

Solid-State Structures of the Diorganotin Dihalides

Single crystals suitable for X-ray diffraction studies were obtained from $CHCl_3$/*n*-hexane for **1**, toluene for **3** and CH_2Cl_2/*n*-hexane for **4**. Recrystallization of **4** from $CHCl_3$ afforded **4**·2$CHCl_3$. Crystals of difluoride **2** were obtained from a CH_2Cl_2/*n*-hexane (approximately 1:4) mixture by very slow evaporation of the solvents over two weeks.

The molecular structures of compounds **1**–**4** feature some common patterns: (i) in all cases, the nitrogen atom of the pendant Me_2NCH_2 arm is strongly coordinated to the metal centre in a *trans* configuration with respect to a halogen or a sulfur atom; this results in an increase in the coordination number at tin; (ii) the five-membered SnC_3N ring is not planar but folded along the Sn(1)···$C_{methylene}$ axis; the nitrogen atom lies above the best plane defined by the Sn(1), C(1), C(2) and $C_{methylene}$ atoms. This induces planar chirality [the aromatic ring and the nitrogen atom being the chiral plane and the pilot atom, respectively; isomers are given as S_N and R_N in the subsequent discussion][30] as described for related organotin[7,31–34] and other main-group-metal compounds,[35–39] and indeed all compounds reported here crystallize as racemates.

As a result of the strong intramolecular N→Sn interaction [Sn(1)–N(1) = 2.458(5) Å] in a *trans* configuration with respect to a chlorine atom [N(1)–Sn(1)–Cl(1) = 171.61(15)°], the molecule of diorganotin dichloride **1** contains a distorted trigonal bipyramidal (*C*,*N*)$CSnCl_2$ core (hypervalent 10-Sn-5 species),[40,41] and therefore a second type of chirality is induced (given as C_{Sn} and A_{Sn} in the subsequent discussion).[42] In the crystal of **1** a 1:1 mixture of the R_NC_{Sn} and S_NA_{Sn} isomers is present. The ORTEP diagram of isomer (S_NA_{Sn})-[2-(Me_2NCH_2)C_6H_4]$BuSnCl_2$ is shown in Figure 1, and selected interatomic distances and angles are listed in Table 1.

The difference in the chlorine atoms is reflected in the lengths of their bonds to the tin atom: the shorter bond [Sn(1)–Cl(2) = 2.3779(16) Å] is placed in the equatorial position, while the longer one [Sn(1)–Cl(1) = 2.4484(15) Å] occupies the axial position in a *trans* configuration with respect to the strong tin–nitrogen interaction. A similar behaviour was observed in the related compound [2-

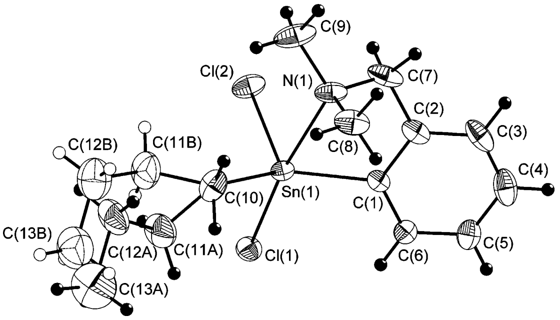


Figure 1. ORTEP representation at the 20% probability level and atom-numbering scheme for the isomer (S_NA_{Sn})-**1**.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**.

1		**2**	
Sn(1)–N(1)	2.458(5)	Sn(1)–N(1)	2.494(4)
Sn(1)–C(1)	2.123(5)	Sn(1)–C(1)	2.113(4)
Sn(1)–C(10)	2.125(6)	Sn(1)–C(10)	2.113(6)
Sn(1)–Cl(1)	2.4484(15)	Sn(1)–F(1)	1.985(2)
Sn(1)–Cl(2)	2.3779(16)	Sn(1)–F(2)	2.1372(3)
Sn(1)–Cl(1b)	3.6401(17)	Sn(1)–F(3)	2.1572(3)
N(1)–Sn(1)–Cl(1)	171.61(15)	N(1)–Sn(1)–F(1)	170.57(11)
C(1)–Sn(1)–C(10)	143.0(2)	C(1)–Sn(1)–C(10)	163.4(2)
Cl(2)–Sn(1)–Cl(1b)	177.35(5)	F(2)–Sn(1)–F(3)	178.53(1)
Cl(2)–Sn(1)–C(1)	106.46(15)	F(2)–Sn(1)–C(1)	89.85(10)
Cl(2)–Sn(1)–C(10)	107.1(2)	F(2)–Sn(1)–C(10)	93.0(2)
Cl(2)–Sn(1)–N(1)	86.59(13)	F(2)–Sn(1)–N(1)	85.70(8)
Cl(2)–Sn(1)–Cl(1)	93.42(6)	F(2)–Sn(1)–F(1)	88.63(8)
Cl(1b)–Sn(1)–C(1)	75.40(14)	F(3)–Sn(1)–C(1)	88.70(10)
Cl(1b)–Sn(1)–C(10)	70.56(23)	F(3)–Sn(1)–C(10)	88.4(2)
Cl(1b)–Sn(1)–N(1)	92.09(12)	F(3)–Sn(1)–N(1)	93.74(8)
Cl(1b)–Sn(1)–Cl(1)	88.22(45)	F(3)–Sn(1)–F(1)	91.74(8)
C(1)–Sn(1)–Cl(1)	95.91(15)	C(1)–Sn(1)–F(1)	96.54(14)
Cl(1)–Sn(1)–C(10)	97.1(3)	F(1)–Sn(1)–C(10)	99.9(2)
C(10)–Sn(1)–N(1)	90.9(3)	C(10)–Sn(1)–N(1)	87.9(2)
N(1)–Sn(1)–C(1)	76.1(2)	N(1)–Sn(1)–C(1)	75.94(14)
Sn(1)–Cl(1)–Sn(1a)	157.82(6)	Sn(1a)–F(2)–Sn(1)	180.0
		Sn(1)–F(3)–Sn(1b)	180.0

$(Me_2NCH_2)C_6H_4]PhSnCl_2$ [Sn(1)–Cl(1)$_{ax}$ = 2.4481(11) Å; Sn(1)–Cl(2)$_{eq}$ = 2.3547(11) Å].[15]

In the crystal of compound **1**, alternating S_NA_{Sn} and R_NC_{Sn} isomers are associated into a "*zig-zag*" polymeric chain built through weak intermolecular Sn···Cl interactions [Sn(1)···Cl(1b) = 3.640(2) Å; cf. Σr_{cov}(Sn,Cl) = 2.39 Å, Σr_{vdW}(Sn,Cl) ≈ 4.01 Å],[43] which involve the chlorine atom at the axial position in the molecular unit (Figure 3a). The vector of the Sn···Cl interaction bisects the C(1)–Sn(1)–C(10) [143.0(2)°] equatorial angle of the parent trigonal bipyramidal core of the molecular unit, in a *trans* configuration with respect to the Cl(2) atom [Cl(2)–Sn(1)···Cl(1b) = 177.35(5)°], which is not involved in intermolecular interactions. The butyl groups and the dimethylaminomethyl groups are placed on opposite sides of the polymeric chain plane defined by tin atoms and bridging chlorine atoms.

By contrast, diorganotin difluoride **2** exhibits a completely different solid-state structure. It features six-coordinate tin atoms in a chain polymeric structure, the latter being realized by almost symmetric Sn–F–Sn bridges (Table 1). The repeating fragment is shown in Figure 2 [fluorine atoms F(2) and F(3) each have half occupancy], and selected interatomic distances and angles are listed in Table 1.

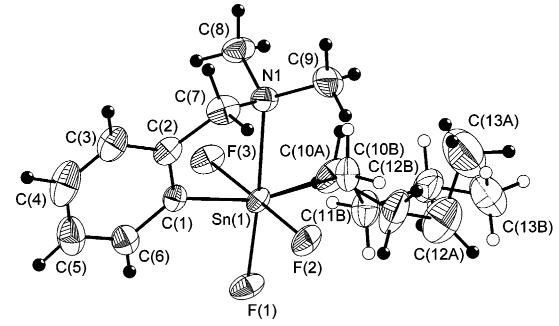


Figure 2. ORTEP representation at the 30% probability level and atom-numbering scheme for the *S*-**2** repeating fragment.

The tin atom shows a distorted octahedral configuration; C(1) and C(10), and F(1) and N(1) are mutually *trans*. The Sn(1)–N(1) distance of 2.494(4) Å is longer than the corresponding distance in $[Me_2N(CH_2)_3]_2SnF_2{\cdot}2H_2O$ (2.366 Å).[12] The chain polymer is built from R_N and S_N isomers alternating with respect to the nonplanar SnC_3N ring. The resulting octahedral environment around the metal centre thus features *trans* orientation of the fluorine atoms involved in Sn–F–Sn bridges (hypervalent 12-Sn-6 species),[40,41] while in the related dichloride **1**, the bridging halogen atoms occupy *cis* positions in the octahedral (*C*,*N*)-$CSnCl_3$ core. Notably, there are fluorine–hydrogen contacts [F(1)···H(9Ba) = 2.53 Å] established between pairs of R_N and S_N isomers [cf. Σr_{vdW}(F,H) ≈ 2.55 Å[43]].

In contrast to the "*zig-zag*" polymeric chain in **1** [Cl(1)–Sn(1)···Cl(1b) = 88.22(45)°, Sn(1)–Cl(1)···Sn(1a) = 157.82(6)°], the polymeric chain in the crystal of diorganotin difluoride **2** is almost linear [F(2)–Sn(1)–F(3) = 178.53(1)°, Sn(1a)–F(2)–Sn(1) = 180.0°, Sn(1)–F(3)–Sn(1b) = 180.0°] (Figure 3b).

The different behaviour of the fluorine atoms in **2** is reflected in their Sn–F bond lengths. Thus, the bond between tin and the terminal fluorine atom is the shortest one, and its magnitude [Sn(1)–F(1) = 1.985(2) Å] is similar to that observed for the related monomeric compounds $[2\text{-}(Me_2NCH_2)C_6H_4]_2SnF_2$ [1.9726(14), 1.9774(13) Å] and $[2\text{-}(Me_2NCH_2)C_6H_4]_2SnF_2{\cdot}CH_2Cl_2$ [1.988(3) Å], which also contain terminal fluorine atoms in octahedral *cis*-F_2-*cis*-N_2-*trans*-C_2 cores.[7] The other two tin–fluorine bond lengths [Sn(1)–F(2) 2.1372(3), Sn(1)–F(3) = 2.1572(3) Å] are considerably longer and even exceed the Sn–F bond lengths in $[Me_2N(CH_2)_3]_2SnF_2{\cdot}2H_2O$ [2.084(6) Å].[12]

Behaviour of the Diorganotin Dihalides in Solution

The ^{1}H and ^{13}C NMR resonances for compounds **1–4** were assigned on the basis of 2D experiments, according to the atom numbering shown in Scheme 4.

The ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopic data obtained by us for diorganotin dichloride **1** are consistent with

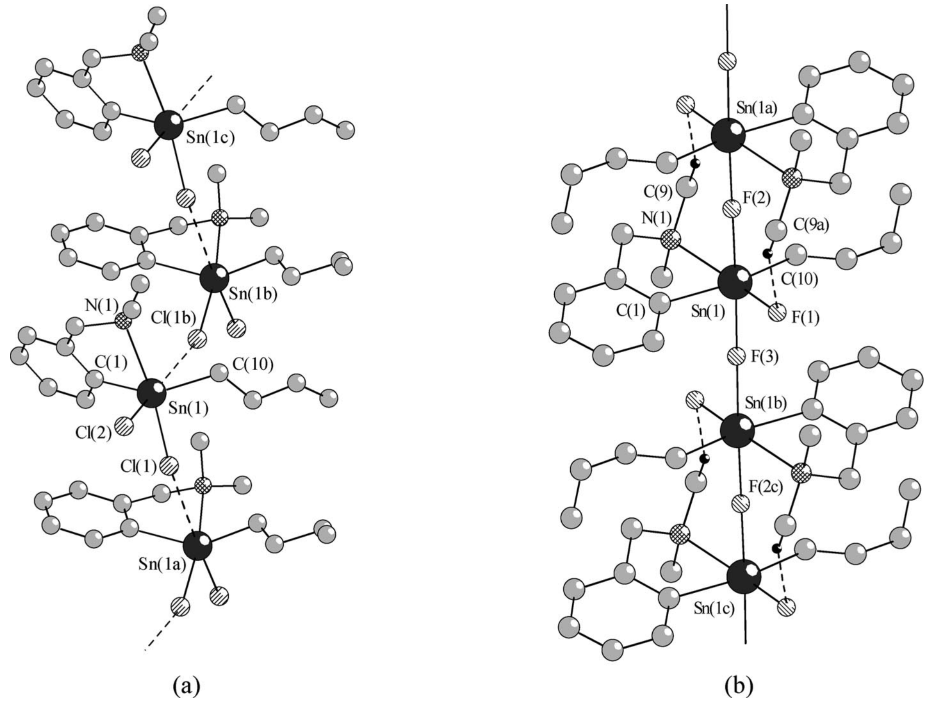
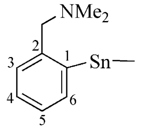


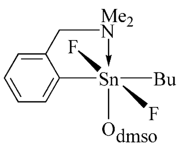
Figure 3. View of the chain polymers in the crystal of dichloride **1** [symmetry-equivalent atoms (0.5 – *x*, –0.5 + *y*, *z*), (0.5 – *x*, 0.5 + *y*, *z*) and (*x*, 1 + *y*, *z*) are given by a, b and c, respectively] (a), and difluoride **2** [symmetry-equivalent atoms (–*x*, 2 – *y*, –*z*), (–*x*, 1 – *y*, –*z*) and (*x*, –1 + *y*, *z*) are given by a, b and c, respectively; only H9B atoms involved in intermolecular interactions in **2** are shown] (b).



Scheme 4.

a trigonal bipyramidal structure in solution, as was previously suggested on the basis of NMR spectroscopic studies (^1H, ^{13}C, ^{15}N, ^{119}Sn NMR, including ^1H,^{117}Sn J-HMBC studies) for the same compound isolated as a high-boiling liquid.[13,14]

The use of two organic ligands with a potential for intramolecular coordination is known to result in monomeric, octahedral R_2SnF_2 species,[5,7,12,44] with increased solubility in organic solvents. Diorganotin(IV) difluorides [$Me_2N(CH_2)_3]_2SnF_2\cdot 2H_2O$ and {2,6-[$(EtO)_2P(O)]_2$-4-*t*Bu-C_6H_2}-$PhSnF_2$ are straightforward examples for such behaviour.[12,45] In the case of compound **2**, the presence of only one dimethylaminomethyl group with a potential for intramolecular coordination is not enough to provide a monomeric species; an octahedral coordination of the tin atom is achieved by intermolecular F→Sn coordination to give a polymer. Its very low solubility prevents detailed NMR spectroscopic studies in solution. Thus, the ^1H NMR spectrum in $CDCl_3$ solution gave only broad unresolved resonances. The ^{19}F NMR spectrum in $CDCl_3$ showed two broad resonances of equal integral ratio flanked by unresolved $^{117/119}Sn$ satellites of ca. 2.500 Hz of similar magnitude as those observed for the monomeric, octahedral species [2-(Me_2NCH_2)$C_6H_4]_2SnF_2$ ($^1J_{F,Sn}$ = 2663 Hz)[7] and [$Me_2N(CH_2)_3]_2SnF_2\cdot 2H_2O$ ($^1J_{F,Sn} \approx$ 2700–2800 Hz).[12] In [D_6]dmso solution, the ^1H NMR spectrum is similar to that recorded in $CDCl_3$ solution, whereas only one broad ^{19}F resonance (δ = –161.5 ppm, $^1J_{F,Sn}$ = 2796 Hz) was observed in the ^{19}F NMR spectrum. This suggests that coordination of dmso to the tin atom gives rise to the formation of a dmso complex as shown in Scheme 5. The formation of a similar species was also suggested for dichloride **1** in dmso solution.[13]



Scheme 5.

Solid-State Structures of Compounds 3 and 4

Selected interatomic distances and bond angles of diorganotin sulfides **3** and **4** are listed in Tables 2 and 3. In both cases, the crystals consist of discrete dinuclear units of the *trans*-R_NC_{Sn}/S_NA_{Sn} (for **3**, Figure 4a) and $R_{N1}S_{N2}/S_{N1a}R_{N2a}$ (for **4**, Figure 4b) isomers (due to the crystallographically imposed inversion symmetry), with no intermolecular distances shorter than the sum of the van der Waals radii between the heavy atoms or a heavy atom and hydrogen atoms.

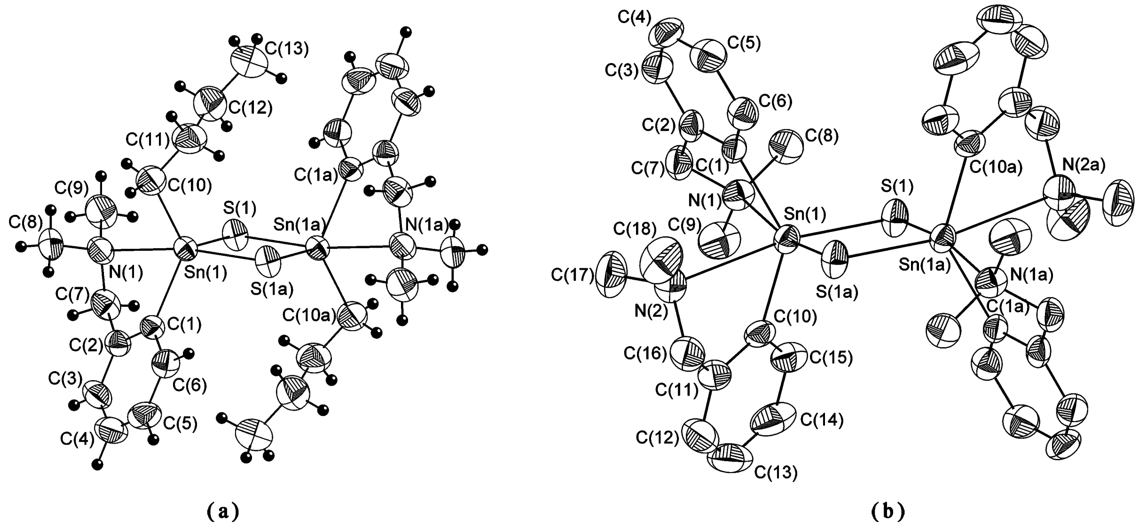


Figure 4. ORTEP representation at the 30% probability level and atom-numbering scheme for *trans*-R_NC_{Sn}/S_NA_{Sn}-**3** [symmetry-equivalent atoms (1 – *x*, 2 – *y*, 1 – *z*) are given by a] (a), and $R_{N1}S_{N2}/S_{N1a}S_{N2a}$-**4** [symmetry-equivalent atoms (1.67 – *x*, 1.33 – *y*, 1.33 – *z*) are given by a, and hydrogen atoms have been omitted for clarity] (b).

Table 2. Selected bond lengths [Å] and angles [°] for compound **3**.

Sn(1)–N(1)	2.607(4)	N(1)–Sn(1)–S(1a)	171.53(9)
Sn(1)–C(1)	2.152(4)	C(1)–Sn(1)–C(10)	123.27(17)
Sn(1)–C(10)	2.151(5)	C(10)–Sn(1)–S(1)	118.29(15)
Sn(1)–S(1)	2.4091(12)	C(1)–Sn(1)–S(1)	112.51(11)
Sn(1)–S(1a)	2.5157(12)	S(1a)–Sn(1)–C(1)	99.76(11)
		S(1a)–Sn(1)–C(10)	100.88(15)
		S(1a)–Sn(1)–S(1)	93.26(4)
		N(1)–Sn(1)–C(1)	72.41(15)
		N(1)–Sn(1)–C(10)	86.39(17)
		N(1)–Sn(1)–S(1)	86.99(10)
		Sn(1)–S(1)–Sn(1a)	86.74(4)

Table 3. Selected bond lengths [Å] and angles [°] for compounds **4** and **4**·2CHCl$_3$.

4		**4**·2CH$_2$Cl$_2$	
Sn(1)–N(1)	2.816(4)	Sn(1)–N(1)	3.034(4)
Sn(1)–N(2)	2.855(6)	Sn(1)–N(2)	2.771(5)
Sn(1)–C(1)	2.152(5)	Sn(1)–C(1)	2.146(3)
Sn(1)–C(10)	2.134(5)	Sn(1)–C(10)	2.148(3)
Sn(1)–S(1)	2.4485(16)	Sn(1)–S(1)	2.4447(10)
Sn(1)–S(1a)	2.4661(16)	Sn(1)–S(1a)	2.4800(10)
N(1)–Sn(1)–S(1a)	170.74(11)	N(1)–Sn(1)–S(1)	169.06(7)
N(2)–Sn(1)–S(1)	170.18(11)	N(2)–Sn(1)–S(1a)	169.91(9)
C(1)–Sn(1)–C(10)	133.4(2)	C(1)–Sn(1)–C(10)	131.60(13)
S(1)–Sn(1)–C(1)	110.29(14)	S(1a)–Sn(1)–C(1)	106.86(9)
S(1)–Sn(1)–N(1)	84.97(11)	S(1a)–Sn(1)–N(1)	81.56(8)
S(1)–Sn(1)–C(10)	105.07(16)	S(1a)–Sn(1)–C(10)	103.40(10)
S(1)–Sn(1)–S(1a)	91.59(5)	S(1a)–Sn(1)–S(1)	91.25(3)
N(2)–Sn(1)–C(1)	78.96(17)	N(2)–Sn(1)–C(1)	82.98(13)
N(2)–Sn(1)–N(1)	101.76(14)	N(2)–Sn(1)–N(1)	104.75(11)
N(2)–Sn(1)–C(10)	68.93(19)	N(2)–Sn(1)–C(10)	70.49(13)
N(2)–Sn(1)–S(1a)	82.79(11)	N(2)–Sn(1)–S(1)	83.57(8)
C(1)–Sn(1)–N(1)	69.78(18)	C(1)–Sn(1)–N(1)	68.07(12)
N(1)–Sn(1)–C(10)	84.37(19)	N(1)–Sn(1)–C(10)	80.26(12)
C(10)–Sn(1)–S(1a)	104.83(15)	C(10)–Sn(1)–S(1)	109.57(9)
S(1a)–Sn(1)–C(1)	103.60(15)	S(1)–Sn(1)–C(1)	106.62(10)
Sn(1)–S(1)–Sn(1a)	88.41(5)	Sn(1)–S(1)–Sn(1a)	88.75(3)

The molecular structures of compounds **3** and **4** resemble those of the related diorganotin sulfides [{Me$_2$N(CH$_2$)$_2$-CMe$_2$}PhSnS]$_2$[26] and [{Me$_2$N(CH$_2$)$_3$}$_2$SnS]$_2$.[28] Compound **3** crystallizes as the *trans*-isomer, and in both molecules of **3** and **4** the central four-membered Sn$_2$S$_2$ ring is planar. The S–Sn–S bridge is significantly asymmetric in **3** [Sn(1)–S(1) = 2.409(1) Å, Sn(1)–S(1a) = 2.516(1) Å], while the Sn$_2$S$_2$ ring is almost a square for **4** [Sn(1)–S(1) = 2.449(2) Å, Sn(1)–S(1a) = 2.466(2) Å]. The distortion from the ideal square is also reflected in the endocyclic angles at the tin and sulfur atoms [**3**: S(1)–Sn(1)–S(1a) = 93.26(4)°, Sn(1)–S(1)–Sn(1a) = 86.74(4)°; **4**: S(1)–Sn(1)–S(1a) = 91.59(5)°, Sn(1)–S(1)–Sn(1a) = 88.41(5)°], the deviation being more pronounced for **3**.

As result of the decreased Lewis acidity of the tin atom in compound **3**, the Sn(1)–N(1) distance of 2.607(4) Å is longer than the corresponding distance of 2.458(5) Å determined for the related diorganotin dichloride **1**. This medium-strength Sn–N interaction is placed in a *trans* configuration with respect to the longer Sn(1)–S(1a) bond length [2.5157(12) Å; N(1)–Sn(1)–S(1a) = 171.53(9)°].

As in compound **1**, the tin atom in compound **3** shows a distorted trigonal bipyramidal configuration (hypervalent 10-Sn-5 species),[40,41] the distortion being less pronounced for **3**; C(1), C(10) and S(1) occupy the equatorial and N(1) and S(1a) occupy the axial positions. The C(1)–Sn(1)–C(10) angle of 123.27(17)° is smaller than the corresponding angle in diorganotin dichloride **1** [143.0(2)°]. The tin atom is displaced by 0.315 Å from the equatorial C$_2$S plane defined by C(1), C(10) and S(1) in direction of S(1a).

In compound **4**, the tin atom shows a strongly distorted octahedral configuration (hypervalent 12-Sn-6 species)[40,41] with a C(1)–Sn(1)–C(10) angle of 133.4(2)°; the nitrogen atoms have a *cis* configuration. The distortion from the ideal octahedral geometry is mainly the result of the restrictions imposed by the five-membered SnC$_3$N rings. The Sn(1)–N(1) and Sn(1)–N(2) distances of 2.816(4) and 2.855(6) Å, respectively, are almost equal to and even longer than those in **3**. However, they are still shorter than

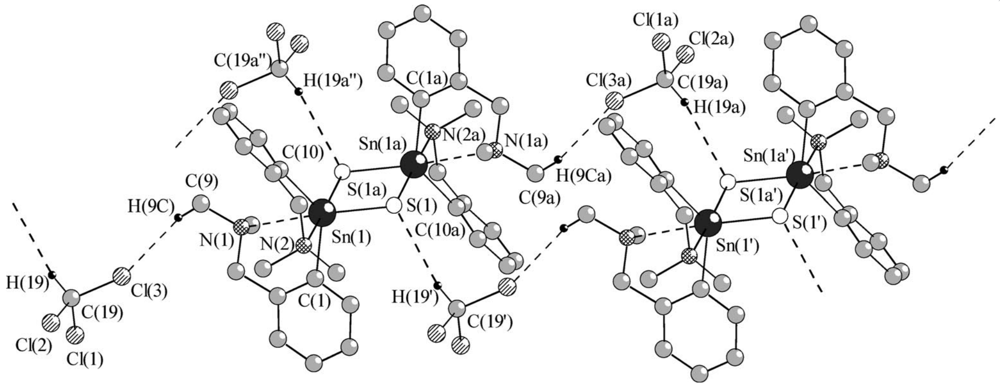


Figure 5. View of the chain polymer based on Cl···H and S···H contacts in the crystal of **4**·2$CHCl_3$ (only hydrogen atoms involved in intermolecular interactions are shown). Symmetry-equivalent atoms (1 – *x*, 1 – *y*, –*z*), (*x*, –1 + *y*, –1 + *z*), (1 – *x*, –*y*, –1 – *z*) and (1 – *x*, 2 – *y*, 1 – *z*) are given by a, ′, a′ and a′′, respectively.

the sum of the van der Waals radii of the corresponding atoms [Σr_{vdW}(Sn,N) ≈ 3.74 Å[43]].

Compound **4** was recrystallized from chloroform to give its solvate **4**·2$CHCl_3$. In contrast to compound **4** alone, the intramolecular Sn(1)–N(1) and Sn(1)–N(2) distances in **4**·2$CHCl_3$ are rather different [3.034(4) and 2.771(5) Å, respectively]. This might be the result of weak Cl(3)···H(9C) (2.98 Å) and S(1)···H(19′) (2.88 Å) hydrogen bridges that give a chain composed of **4** and bridging $CHCl_3$ molecules (Figure 5).

Behaviour of the Diorganotin Sulfides in Solution

The ^{1}H NMR spectrum of *cyclo*-[{2-(Me_2NCH_2)C_6H_4}-BuSnS]$_2$ (**3**) ($CDCl_3$, room temp.) contains two sets of resonances both in the alkyl and aryl region, in a ca. 1.5:1 integral ratio. The ^{13}C NMR spectrum is also consistent with the presence of two species. This behaviour might be due to the presence in solution of both *cis* and *trans* isomers of **3**. The ^{1}H and ^{13}C NMR chemical shifts were assigned for isomer **3a** (major product) and **3b** (minor product) on the basis of the integral ratio and by using 2D correlation spectra. We suggest that the major component is the less sterically hindered *trans* isomer, which was also found in the solid state. A similar behaviour was previously reported for the related diorganotin sulfide [$Me_2N(CH_2)_3PhSnS$]$_2$[28] and the organoantimony(III) derivative, *cyclo*-[{2-(Me_2NCH_2)-C_6H_4}SbS]$_2$.[36]

The magnitude of the ^{119}Sn chemical shifts (δ = –48.3 and –50.5 ppm for isomers **3a** and **3b**, respectively) is consistent with a five-coordinate metal atom in solution. The singlet pattern of the resonances for the NMe_2 and CH_2 protons observed for compounds **1** and **3** in $CDCl_3$ is consistent with stereochemical lability of the metal atom in these compounds at room temperature.[2]

The ^{1}H NMR spectrum of **4** in $CDCl_3$ at room temperature shows broad and sharp singlet resonances for the CH_2 and NMe_2 protons, respectively, in addition to the expected resonances in the aromatic region. This is in contrast to the parent [2-(Me_2NCH_2)C_6H_4]$_2SnCl_2$,[7] for which an AB system was observed for the CH_2 protons, and suggests that exchange of the chlorine atoms by sulfur atoms results in a considerable decrease in the configurational stability of the tin atom in **4**. A similar behaviour was observed for the diorganotin difluoride [2-(Me_2NCH_2)C_6H_4]$_2SnF_2$.[7]

Conclusions

The first mixed diorganotin(IV) difluoride, [2-(Me_2NCH_2)C_6H_4]$BuSnF_2$, was prepared, and its molecular structure was established by X-ray diffraction. The crystal contains a chain polymer in which six-coordinate tin atoms are linked through almost symmetric, linear Sn–F–Sn bridges (hypervalent 12-Sn-6 species). By contrast, in the crystal of the related dichloride, [2-(Me_2NCH_2)C_6H_4]$BuSnCl_2$, a "*zig-zag*" polymeric chain is formed by alternating S_NA_{Sn} and R_NC_{Sn} isomers linked through angular, asymmetric Sn···Cl–Sn bridges. Both of the novel diorganotin sulfides *cyclo*-[{2-(Me_2NCH_2)C_6H_4}RSnS]$_2$ [R = Bu, 2-(Me_2-NCH_2)C_6H_4] feature a central, planar, four-membered Sn_2S_2 ring. The crystal contains only the *trans* isomer for R = Bu [trigonal bipyramidal (*C,N*)$CSnS_2$ configuration; hypervalent 10-Sn-5 species]. For R = 2-(Me_2NCH_2)C_6H_4 an octahedral *cis*-S_2-*cis*-N_2-*trans*-C_2 configuration is observed (hypervalent 12-Sn-6 species). The NMR spectroscopic data for the diorganotin dihalides and the diaryltin(IV) sulfide are consistent with similar structures in $CDCl_3$ solutions. For the diorganotin(IV) sulfide containing different substituents, NMR spectroscopic data suggest the presence of *cis* and *trans* isomers in solution.

Experimental Section

General Remarks: Room-temperature ^{1}H and ^{13}C NMR spectra (including 2D experiments) were recorded in dried $CDCl_3$ or [D_6]dmso with a Bruker AVANCE DRX 400 instrument. The ^{19}F NMR spectrum was recorded with a Bruker AVANCE DRX 400 instrument, while ^{119}Sn NMR spectra were obtained by using Bruker DPX 400 instruments. The chemical shifts are reported in ppm relative to the residual peak of the solvent {ref. $CHCl_3$: δ(^{1}H) = 7.26, δ(^{13}C) = 77.0 ppm; ref. [D_6]dmso: δ(^{1}H) = 2.50, δ(^{13}C) = 39.43 ppm} for ^{1}H and ^{13}C NMR spectra, and relative to $CFCl_3$

for ^{19}F NMR and neat $SnMe_4$ for ^{119}Sn NMR spectra. Elemental analyses were performed by Facultatea de Farmacie, Universitatea de Medicina si Farmacie "Iuliu Hatieganu", Cluj-Napoca (Romania). All manipulations were carried out under an inert atmosphere of argon (Linde, 99.999%) by using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. Starting materials such as $BuSnCl_3$, KF, $Na_2S\cdot xH_2O$, *N*,*N*-dimethylbenzylamine and *n*-butyllithium were commercially available. The compounds $[2\text{-}(Me_2NCH_2)C_6H_4]Li$[46] and $[2\text{-}(Me_2NCH_2)C_6H_4]_2SnCl_2$[7] were prepared according to published methods.

Synthesis of $[2\text{-}(Me_2NCH_2)C_6H_4]BuSnCl_2$ (1): A suspension of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ (5.43 g, 38.46 mmol) in anhydrous *n*-hexane (100 mL) was added dropwise, at room temperature, under argon, to a stirred solution of $BuSnCl_3$ (6 mL, 38.46 mmol) in an anhydrous *n*-hexane/diethyl ether (200 mL, 2:1 v/v) mixture. The reaction mixture was stirred for one day at room temperature. The solvent was removed under vacuum, and the solid residue was extracted with portions of hot petroleum ether (100 mL) until no solid deposited when the solution extract was cooled. The title compound was obtained as a white solid (11.3 g, 86%), m.p. 71–73 °C (b.p. 170–172 °C/9 Pa).[13] ^{1}H NMR ($CDCl_3$, 400 MHz, +20 °C): δ = 0.95 (t, ^3J = 7.3 Hz, 3 H, $\mathrm{Sn{-}CH_2CH_2CH_2C}H_3$), 1.46 (tq, ^3J = 7.4 Hz, 2 H, $\mathrm{Sn{-}CH_2CH_2C}H_2\mathrm{CH_3}$), 1.78 (t, ^3J = 7.5 Hz, 2 H, $\mathrm{Sn{-}C}H_2\mathrm{CH_2CH_2CH_3}$), 1.92 (m, 2 H, $\mathrm{Sn{-}CH_2C}H_2\mathrm{CH_2CH_3}$), 2.42 (s, 6 H, $\mathrm{N{-}C}H_3$), 3.73 (s, 2 H, $\mathrm{{-}C}H_2\mathrm{{-}N}$), 7.19 (m, $^4J_{Sn,H}$ = 33.0 Hz, 1 H, 3-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.41 (m, 2 H, 4,5-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 8.18 (m, $^3J_{Sn,H}$ = 85.6 Hz, 1 H, 6-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, +20 °C): δ = 13.6 (s, C_δ), 26.2 (s, $^2J_{Sn,C}$ = 111.6/115.7 Hz, C_γ), 26.5 (s, $^1J_{Sn,C}$ = 651.7/681.7 Hz, C_α), 27.3 (s, $^3J_{Sn,C}$ = 42.4 Hz, C_β), 45.0 (s, $\mathrm{N{-}}C\mathrm{H_3}$), 63.4 (s, $^2J_{Sn,C}$ = 34.3 Hz, $\mathrm{{-}}C\mathrm{H_2{-}N}$), 127.4 (s, $^3J_{Sn,C}$ = 72.9 Hz, C-3), 128.6 (s, $^3J_{Sn,C}$ = 85.8/87.6 Hz, C-5), 130.9 (s, $^4J_{Sn,C}$ = 15.0 Hz, C-4), 137.2 (s, $^2J_{Sn,C}$ = 64.3 Hz, C-6), 139.1 (s, $^1J_{Sn,C}$ = 828.0/866.6 Hz, C-1), 141.2 (s, $^2J_{Sn,C}$ = 47.3 Hz, C-2) ppm. ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, +20 °C): δ = –103.0 (s) ppm. $C_{13}H_{21}Cl_2NSn$ (380.91): calcd. C 40.99, H 5.56, N 3.68; found C 40.55, H 5.43, N 3.27.

Synthesis of $[2\text{-}(Me_2NCH_2)C_6H_4]BuSnF_2$ (2): A suspension of **1** (0.4 g, 1.18 mmol) in MeOH (5 mL) was treated with methylene dichloride until the solid compound was dissolved completely. An aqueous solution of KF (0.34 g, 5.88 mmol, 500% excess) was added, and the reaction mixture was stirred for 3 h at room temperature. The organic layer was separated, the water layer was washed with methylene dichloride (2 × 5 mL), and the combined organic phases were dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and the title compound was obtained as a white solid (0.38 g, 93%), m.p. 230 °C (dec.). ^{1}H NMR ($CDCl_3$, 400 MHz, +20 °C): δ = 0.82 (s, br, 3 H, $\mathrm{Sn{-}CH_2CH_2CH_2C}H_3$), 1.53 (m, 6 H, $\mathrm{Sn{-}C}H_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 2.38 (s, 6 H, $\mathrm{N{-}C}H_3$), 3.64 (s, br, 2 H, $\mathrm{{-}C}H_2\mathrm{{-}N}$), 7.07 (s, br, 1 H, 3-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.26 (s, br, 2 H, 4,5-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.86 (s, br, 1 H, 6-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, +20 °C): δ = –161.2 (s, br, $^1J_{F,Sn}$ = 2480 Hz, 2 F), –159.4 (s, br, $^1J_{F,Sn}$ = 2465 Hz, 1 F) ppm. ^{1}H NMR ([D$_6$]dmso, 400 MHz, +20 °C): δ = 0.88 (s, br, 3 H, $\mathrm{Sn{-}CH_2CH_2CH_2C}H_3$), 1.32 (s, br, 4 H, $\mathrm{Sn{-}CH_2C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 1.63 (s, br, 2 H, $\mathrm{Sn{-}C}H_2\mathrm{CH_2CH_2CH_3}$), 2.29 (s, 6 H, $\mathrm{N{-}C}H_3$), 3.58 (s, br, 2 H, $\mathrm{{-}C}H_2\mathrm{{-}N}$), 7.16 (s, br, 1 H, 3-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.30 (s, br, 2 H, 4,5-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.73 (s, br, 1 H, 6-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$) ppm. ^{19}F NMR ([D$_6$]dmso, 376.5 MHz, +20 °C): δ = –161.5 (s, br, $^1J_{F,Sn}$ = 2796 Hz) ppm. $C_{13}H_{21}F_2NSn$ (348.00): calcd. C 44.87, H 6.08, N 4.02; found C 44.58, H 5.63, N 4.27.

Synthesis of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}BuSnS]_2$ (3): A solution of **1** (1.0 g, 2.63 mmol) in CH_2Cl_2 (30 mL) was treated with an aqueous solution of Na_2S (1.0 g, 13.1 mmol, 500% excess), and the mixture was stirred for 3 h at room temperature. The organic layer was separated, the water solution was washed with methylene dichloride (2 × 5 mL), and the combined organic phases were dried with anhydrous Na_2SO_4. After removal of the solvent under vacuum, the title compound was isolated as a white crystalline solid, which was recrystallized from toluene (0.84 g, 93%), m.p. 118–120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, +20 °C) isomer **3a** (major product): δ = 0.70 (t, ^3J = 7.4 Hz, 3 H, $\mathrm{Sn{-}CH_2CH_2CH_2C}H_3$), 1.28 (m, 4 H, $\mathrm{Sn{-}CH_2CH_2C}H_2\mathrm{CH_3}$ + $\mathrm{Sn{-}C}H_2\mathrm{CH_2CH_2CH_3}$), 1.63 (m, 2 H, $\mathrm{Sn{-}CH_2C}H_2\mathrm{CH_2CH_3}$), 2.33 (s, 6 H, $\mathrm{N{-}C}H_3$; overlapping with the corresponding resonance for isomer **3b**), 3.65 (s, 2 H, $\mathrm{{-}C}H_2\mathrm{{-}N}$), 7.11 (d, ^3J = 7.3 Hz, 1 H, 3-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.31 (dd, ^3J = 7.3 Hz, 1 H, 4-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.38 (dd, ^3J = 7.3 Hz, 1 H, 5-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 8.27 (d, ^3J = 7.1, $^3J_{Sn,H}$ = 72.1 Hz, 1 H, 6-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$) ppm; isomer **3b** (minor product), δ = 0.93 (t, ^3J = 7.3 Hz, 3 H, $\mathrm{Sn{-}CH_2CH_2CH_2C}H_3$), 1.43 (m, 4 H, $\mathrm{Sn{-}CH_2CH_2C}H_2\mathrm{CH_3}$ + $\mathrm{Sn{-}C}H_2\mathrm{CH_2CH_2CH_3}$), 1.86 (m, 2 H, $\mathrm{Sn{-}CH_2C}H_2\mathrm{CH_2CH_3}$), 2.33 (s, 6 H, $\mathrm{N{-}C}H_3$; overlapping with the corresponding resonance for isomer **3a**), 3.61 (s, 2 H, $\mathrm{{-}C}H_2\mathrm{{-}N}$), 7.04 (m, 1 H, 3-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.21 (m, 2 H, 4,5-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 8.06 (m, $^3J_{Sn,H}$ = 75.0 Hz, 1 H, 6-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$) ppm. ^{13}C NMR ($CDCl_3$,100.6 MHz, +20 °C) isomer **3a** (major product): δ = 13.61 (s, C_δ), 23.23 (s, $^1J_{Sn,C}$ = 522.0/542.4 Hz, C_α), 26.33 (s, $^2J_{Sn,C}$ = 93.6 Hz, C_γ), 27.9 (s, $^3J_{Sn,C}$ = 29.8 Hz, C_β), 45.63 (s, $\mathrm{N{-}}C\mathrm{H_3}$), 64.3 (s, $^2J_{Sn,C}$ = 28.3 Hz, $\mathrm{{-}}C\mathrm{H_2{-}N}$; overlapping with the corresponding resonance for isomer **3b**), 126.64 (s, $^3J_{Sn,C}$ = 56.3 Hz, C-3), 127.54 (s, $^3J_{Sn,C}$ = 69.7 Hz, C-5), 128.87 (s, $^4J_{Sn,C}$ = 13.4 Hz, C-4), 137.2 (s, $^2J_{Sn,C}$ = 55.6 Hz, C-6), 142.5 (s, $^2J_{Sn,C}$ = 39.1 Hz, C-2), 144.2 (s, C-1) ppm; isomer **3b** (minor product), δ = 13.74 (s, C_δ), 23.16 (s, C_α), 26.65 (s, $^2J_{Sn,C}$ = 93.0 Hz, C_γ), 28.5 (s, $^3J_{Sn,C}$ = 28.6 Hz, C_β), 45.68 (s, $\mathrm{N{-}}C\mathrm{H_3}$), 64.3 (s, $\mathrm{{-}}C\mathrm{H_2{-}N}$, overlapping by the corresponding resonance for isomer **3a**), 125.54 (s, $^3J_{Sn,C}$ = 56.5 Hz, C-3), 127.40 (s, $^3J_{Sn,C}$ = 69.5 Hz, C-5), 128.76 (s, $^4J_{Sn,C}$ = 13.2 Hz, C-4), 137.0 (s, $^2J_{Sn,C}$ = 56.0 Hz, C-6), 142.3 (s, $^2J_{Sn,C}$ = 38.8 Hz, C-2), 143.9 (s, C-1) ppm. ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, +20 °C) isomer **3a** (major product): δ = –48.3 (s, $^2J_{Sn,C}$ = 56.2 Hz) ppm; isomer **3b** (minor product), δ = –50.5 (s, $^2J_{Sn,C}$ = 59.5 Hz) ppm. $C_{26}H_{42}N_2S_2Sn_2$ (684.12): calcd. C 45.65, H 6.19, N 4.09; found C 45.55, H 6.43, N 4.3.

Synthesis of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2SnS]_2$ (4): A solution of $[2\text{-}(Me_2NCH_2)C_6H_4]_2SnCl_2$ (1.0 g, 2.18 mmol) in CH_2Cl_2 (30 mL) was treated with an aqueous solution of Na_2S (0.85 g, 10.9 mmol, 500% excess), and the mixture was stirred for 3 h at room temperature. The organic layer was separated, the water solution was washed with methylene dichloride (2 × 5 mL), and the combined organic phases were dried with anhydrous Na_2SO_4. After removal of the solvent under vacuum, the title compound was isolated as a white crystalline solid (0.25 g, 90%), m.p. 264–266 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, +20 °C): δ = 1.90 (s, 12 H, $\mathrm{N{-}C}H_3$), 3.41 (s, br, 4 H, $\mathrm{{-}C}H_2\mathrm{{-}N}$), 7.02 (d, ^3J = 7.3, $^4J_{Sn,H}$ = 31.0 Hz, 2 H, 3-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 7.21 (m, 4 H, 4,5-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$), 8.33 (s, br, $^3J_{Sn,H}$ = 84.7 Hz, 2 H, 6-H, $\mathrm{{-}C_6}H_4\mathrm{{-}}$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, +20 °C): δ = 46.1 (s, $\mathrm{N{-}}C\mathrm{H_3}$), 65.3 (s, $^3J_{Sn,C}$ = 20.1 Hz, $\mathrm{{-}}C\mathrm{H_2{-}N}$), 126.98 (s, $^3J_{Sn,C}$ = 68.0 Hz, C-3), 127.10 (s, $^3J_{Sn,C}$ = 76.9 Hz, C-5), 128.1 (s, $^4J_{Sn,C}$ = 14.0 Hz, C-4), 136.6 (s, $^2J_{Sn,C}$ = 67.6 Hz, C-6), 142.6 (s, $^2J_{Sn,C}$ = 46.3 Hz, C-2), 145.1 (s, C-1) ppm. ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, +20 °C): δ = –137.2 (s, br) ppm. $C_{36}H_{48}N_4S_2Sn_2$ (838.34): calcd. C 51.58, H 5.77, N 6.68; found C 51.33, H 5.43, N 6.38.

X-ray Crystallographic Study: The details of crystal structure determination and refinement for compounds **1**–**4** and **4**·2$CHCl_3$ are given in Table 4. Data were collected with a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-K_α radiation

Table 4. Crystallographic data for compounds **1**–**4** and **4**·2CHCl$_3$.

	1	**2**	**3**	**4**	**4**·2CHCl$_3$
Empirical formula	$C_{13}H_{21}Cl_2NSn$	$C_{13}H_{21}F_2NSn$	$C_{26}H_{42}N_2S_2Sn_2$	$C_{36}H_{48}N_4S_2Sn_2$	$C_{38}H_{50}Cl_6N_4S_2Sn_2$
M	380.90	348.00	684.12	838.34	1077.08
Crystal system	orthorhombic	triclinic	triclinic	rhombohedral	triclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
a [Å]	12.6403(14)	8.4248(8)	8.7891(11)	32.479(11)	9.7904(12)
b [Å]	8.0073(9)	8.5881(8)	9.2281(12)	32.479(11)	10.3420(13)
c [Å]	32.611(4)	10.2403(10)	9.6193(12)	9.599(5)	12.4377(15)
α [°]	90	73.3360(10)	90.801(2)	90	109.624(2)
β [°]	90	89.376(2)	109.171(2)	90	96.921(2)
γ [°]	90	87.778(2)	94.283(2)	120	104.355(2)
V [Å^3]	3300.7(6)	709.27(12)	734.25(16)	8769(6)	1120.1(2)
Z	8	2	1	9	1
$D_{calcd.}$ [g/cm^3]	1.533	1.630	1.547	1.429	1.597
F(000)	1520	348	344	3816	540
Crystal size [mm]	0.58 × 0.19 × 0.16	0.05 × 0.05 × 0.36	0.23 × 0.14 × 0.14	0.17 × 0.21 × 0.25	0.27 × 0.15 × 0.07
μ(Mo-K_α) [mm^{-1}]	1.854	1.803	1.859	1.417	1.598
θ range [°]	2.04–26.37	2.1–26.4	2.21–26.37	2.24–26.42	1.78–26.37
Completeness to 2θ	1.000	0.994	0.993	0.992	0.995
No. of reflections collected	24649	7640	7886	22222	12130
No. of independent reflections	3364 (R_{int} = 0.039)	2895 (R_{int} = 0.024)	2981 (R_{int} = 0.0370)	3981 (R_{int} = 0.0947)	4559 (R_{int} = 0.0438)
No. of parameters	186	198	148	203	239
Absorption correction	multi-scan[49]	multi-scan[49]	multi-scan[49]	multi-scan[49]	multi-scan[49]
μ(Mo-K_α) [mm^{-1}]	1.854	1.803	1.859	1.417	1.598
R_1 [$I > 2\sigma(I)$]	0.0557	0.0315	0.0395	0.0549	0.0400
wR_2	0.1212	0.0935	0.0939	0.1170	0.0875
GOF on F^2	1.244	1.084	1.098	1.044	1.090
Largest diff. electron density [e/Å^3]	0.828/–1.268	0.72/–0.64	1.124/–0.756	0.879/–1.171	0.628/–0.705
CCDC number	230623	230624	644927	644926	644928

(λ = 0.71073 Å). For this purpose, the crystals were attached with epoxy glue on cryoloops, and the data were collected at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. The butyl chains of compound **1** and **2** are disordered over two positions; for **1** three atoms (the carbon bonded to tin is not disordered) have been refined with a site occupancy of 54:46, while for **2** all of the carbons are disordered with an occupancy of 59:41. In both cases, the C–C bonds were restrained to 1.54 Å. The software package SHELX-97 was used for structure solving and refinement.[47] The drawings were created with the program DIAMOND.[48]

CCDC-230623 (**1**), -230624 (**2**), -644927 (**3**), -644926 (**4**) and -644928 (**4**·2CHCl$_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support from the Ministry of Education and Research of Romania (Excellency Research Program, Research Projects No. 63 – Contract No. 1435/2006 and No. CEx-05-D11-16/2005) is greatly appreciated. We also thank the NATIONAL CENTER FOR X-RAY DIFFRACTION (“Babes-Bolyai” University, Cluj-Napoca, Romania) for support in the solid-state structure determinations.

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[1] J. T. B. H. Jastrzebski, G. van Koten, *Adv. Organomet. Chem.* **1993**, *35*, 241–294.

[2] G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, *J. Organomet. Chem.* **1979**, *177*, 283–292.

[3] J. T. B. H. Jastrzebski, D. M. Grove, J. Boersma, G. van Koten, J. M. Ernsting, *Magn. Reson. Chem.* **1991**, *29*, S25–S30.

[4] P. Novák, Z. Padělková, L. Kolářová, I. Cisařová, A. Růžička, J. Holeček, *Appl. Organomet. Chem.* **2005**, *19*, 1101–1108.

[5] P. Novák, J. Brus, I. Cisařová, A. Růžička, J. Holeček, *J. Fluorine Chem.* **2005**, *126*, 1531–1538.

[6] Z. Padělková, I. Cisařová, A. Růžička, *Acta Crystallogr., Sect. E* **2005**, *61*, m2691–m2693.

[7] R. A. Varga, A. Rotar, M. Schürmann, K. Jurkschat, C. Silvestru, *Eur. J. Inorg. Chem.* **2006**, 1475–1486.

[8] K. Jurkschat, J. Schilling, C. Mügge, A. Tzschach, J. Meunier-Piret, M. van Meerssche, M. Gielen, R. Willem, *Organometallics* **1988**, *7*, 38–46.

[9] J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, M. de Wit, Y. Wang, D. Heijdenrijk, C. H. Stam, *J. Organomet. Chem.* **1991**, *407*, 301–311.

[10] D. Schollmeyer, H. Hartung, C. Klaus, K. Jurkschat, *Main Group Met. Chem.* **1991**, *14*, 27–32.

[11] M. Beuter, U. Kolb, A. Zickgraf, E. Bräu, M. Bletz, M. Dräger, *Polyhedron* **1997**, *16*, 4005–4015.

[12] N. Pieper, C. Klaus-Mrestani, M. Schürmann, K. Jurkschat, M. Biesemans, I. Verbruggen, J. C. Martins, R. Willem, *Organometallics* **1997**, *16*, 1043–1052.

[13] A. Růžička, V. Pejchal, J. Holeček, A. Lyčka, K. Jacob, *Collect. Czech. Chem. Commun.* **1998**, *63*, 977–989.

[14] M. Biesemans, J. C. Martins, R. Willem, A. Lyčka, A. Růžička, J. Holeček, *Magn. Reson. Chem.* **2002**, *40*, 65–69.

[15] R. Rippstein, G. Kickelbick, U. Schubert, *Monatsh. Chem.* **1999**, *130*, 385–399.

[16] A. Růžička, R. Jambor, J. Brus, I. Cisařová, J. Holeček, *Inorg. Chim. Acta* **2001**, *323*, 163–170.

[17] S. H. L. Thoonen, H. van Hoek, E. de Wolf, M. Lutz, A. L. Spek, B.-J. Deelman, G. van Koten, *J. Organomet. Chem.* **2006**, *691*, 1544–1553.

[18] A. Růžička, R. Jambor, I. Cisařová, J. Holeček, *Chem. Eur. J.* **2003**, *9*, 2411–2418.

[19] H. Puff, A. Bongartz, R. Sievers, R. Zimmer, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 939.
[20] a) B. Menzebach, P. Bleckmann, *J. Organomet. Chem.* **1975**, *91*, 291–294; b) H.-J. Jacobsen, B. Krebs, *J. Organomet. Chem.* **1977**, *136*, 333–338; c) E. R. T. Tiekink, *Main Group Met. Chem.* **1993**, *16*, 65–69; d) Y. Farina, I. Baba, A. H. Othman, I. A. Razak, H.-K. Fun, S. W. Ng, *Acta Crystallogr., Sect. E* **2001**, *57*, m37–m40.
[21] a) N. R. Kunchur, S. Borhani, *J. Appl. Crystallogr.* **1976**, *9*, 508; b) A. J. Edwards, B. F. Hoskins, *Acta Crystallogr., Sect. C* **1990**, *46*, 1397–1399; c) B. M. Schmidt, M. Drager, *J. Organomet. Chem.* **1990**, *399*, 63–76; d) H. Lange, U. Herzog, U. Bohme, G. Rheinwald, *J. Organomet. Chem.* **2002**, *660*, 43–49.
[22] a) H. Puff, R. Gattermayer, R. Hundt, R. Zimmer, *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 547; b) H. Puff, G. Bertram, B. Ebeling, M. Franken, R. Gattermayer, R. Hundt, W. Schuh, R. Zimmer, *J. Organomet. Chem.* **1989**, *379*, 235–245.
[23] a) N. Tokitoh, Y. Matsuhashi, M. Goto, R. Okazaki, *Chem. Lett.* **1992**, 1595–1598; b) Y. Matsuhashi, N. Tokitoh, R. Okazaki, M. Goto, *Organometallics* **1993**, *12*, 2573–2583.
[24] M. Saito, H. Hashimoto, T. Tajima, M. Ikeda, *J. Organomet. Chem.* **2007**, *692*, 2729–2735.
[25] B. M. Schmidt, M. Dräger, K. Jurkschat, *J. Organomet. Chem.* **1991**, *410*, 43–52.
[26] D. Dakternieks, R. Tozer, K. Jurkschat, E. R. T. Tiekink, *Z. Kristallogr.* **1996**, *211*, 857–858.
[27] D. Schollmeyer, J. Kalbitz, H. Hartung, A. Tzschach, K. Jurkschat, *Bull. Soc. Chim. Belg.* **1988**, *97*, 1075–1080.
[28] K. Jurkschat, S. van Dreumel, G. Dyson, T. J. Bastow, M. E. Smith, M. Dräger, *Polyhedron* **1992**, *11*, 2747–2755.
[29] W.-P. Leung, W.-H. Kwok, L. T. C. Law, Z.-Y. Zhou, T. C. W. Mak, *Chem. Commun.* **1996**, 505–506.
[30] *IUPAC Nomenclature of Organic Chemistry*, Pergamon Press, Oxford, **1979**.
[31] R. A. Varga, C. Silvestru, C. Deleanu, *Appl. Organomet. Chem.* **2005**, *19*, 153–160.
[32] R. A. Varga, C. Silvestru, *Acta Crystallogr., Sect. E* **2006**, *62*, m1964–m1965.
[33] R. A. Varga, C. Silvestru, *Acta Crystallogr., Sect. C* **2007**, *63*, m48–m50.
[34] A. Rotar, R. A. Varga, C. Silvestru, *Acta Crystallogr., Sect. C* **2007**, *63*, m355–m356.
[35] L. M. Opriş, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.* **2003**, 4367–4374.
[36] L. M. Opriş, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.* **2004**, 3575–3585.
[37] M. Kulcsar, A. Silvestru, C. Silvestru, J. E. Drake, C. L. B. Macdonald, M. B. Hursthouse, M. E. Light, *J. Organomet. Chem.* **2005**, *690*, 3217–3228.
[38] M. Kulcsar, A. Beleaga, C. Silvestru, A. Nicolescu, C. Deleanu, C. Todasca, A. Silvestru, *Dalton Trans.* **2007**, 2187–2196.
[39] A. P. Soran, C. Silvestru, H. J. Breunig, G. Balázs, J. C. Green, *Organometallics* **2007**, *26*, 1196–2103.
[40] K. Akiba (Ed.), *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, **1999**.
[41] The *N–X–L* nomenclature system has been described previously: *N* valence shell electrons about a central atom X with *L* ligands: C. W. Perkins, J. C. Martin, A. J. Arduengo III, W. Lau, A. Alegria, K. Kochi, *J. Am. Chem. Soc.* **1980**, *102*, 7753–7759.
[42] N. G. Connelly, T. Damhus, R. M. Hartshorn, A. T. Hutton (Eds.), *Nomenclature of Inorganic Chemistry – IUPAC Recommendations 2005*, RSC Publishing, Cambridge, **2005**.
[43] J. Emsley, *Die Elemente*, Walter de Gruyter: Berlin, **1994**.
[44] W.-P. Leung, W.-H. Kwok, Z.-Y. Zhou, T. C. W. Mak, *Organometallics* **2003**, *22*, 1751–1755.
[45] M. Mehring, I. Vrasidas, D. Horn, M. Schürmann, K. Jurkschat, *Organometallics* **2001**, *20*, 4647–4653.
[46] A. Meller, H. Hoppe, W. Maringgele, A. Haase, M. Noltemeyer, *Organometallics* **1998**, *17*, 123–124.
[47] G. M. Sheldrik, *SHELX-97*, University of Göttingen, Germany, **1997**.
[48] *DIAMOND – Visual Crystal Structure Information System*, CRYSTAL IMPACT, Postfach 1251, 53002 Bonn, Germany, **2001**.
[49] G. M. Sheldrick, *SADABS, Program for Area Detector Absorption Correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, **1996**.

Received: September 26, 2007