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# Synthesis, solution behaviour and X-ray structures of $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3$ and $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3\cdot DMSO$

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**$[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3$ (1) was prepared via (i) salt elimination reaction between RLi and $SnCl_4$ (1 : 1 molar ratio), in toluene solution, and (ii) redistribution reaction between $[2\text{-}(Me_2NCH_2)C_6H_4]_4Sn$ and $SnCl_4$ (1 : 3 molar ratio), in the absence of a solvent. Recrystallization from DMSO afforded the isolation of the DMSO adduct $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3\cdot DMSO$ (1a). The compounds were characterized by multinuclear NMR ($^1H$, $^{13}C$, $^{119}Sn$) in solution. The molecular structures of 1 and 1a were determined by single-crystal X-ray diffraction. The crystal structure of compounds 1 and 1a consists of discrete monomeric molecular units separated by normal van der Waals distances between heavy atoms. The N atom of the pendant $CH_2NMe_2$ arm is strongly coordinated to the tin atom, thus resulting in distorted trigonal bipyramidal (*C,N*)$SnCl_3$ and octahedral (*C,N*)$SnCl_3O$ cores for 1 and 1a, respectively. For both compounds hydrogen bonding generates supramolecular associations in crystal. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** hipervalent organotin (IV); solution NMR; X-ray structure; hydrogen bonding; supramolecular association

## INTRODUCTION

Several di-, tri- and tetraorganotin (IV) compounds containing at least one 2-(dimethylaminomethyl)phenyl group or related organic ligands with one or two pendant arms have been reported so far and the occurrence of the intramolecular Sn–N interaction resulting in a *C,N*-chelate pattern was investigated both in solution and solid state.[1–22] By contrast, a careful check of the literature revealed that very little is known on the monoorganotin (IV) derivatives containing a $[2\text{-}(Me_2NCH_2)C_6H_4]Sn$ moiety. Only the $[2\text{-}(Me_2NCH_2)C_6H_4]SnBr_3$ was fully characterized by NMR spectroscopy.[12] Some relevant NMR data for coordination of $NMe_2$ to Sn in the trichloride analogue were described within a study of the intramolecular Sn–N interaction using $^1H$,$^{117}Sn$ J-HMBC spectroscopy.[20] However, no detailed preparation was available in these two papers.

We report here on the synthesis, NMR characterization in solution as well as the crystal and molecular structures of $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3$ (**1**) and its DMSO adduct, $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3\cdot DMSO$ (**1a**).

## RESULTS AND DISCUSSION

### Syntheses

The monoorganotin (IV) trichloride, $[2\text{-}(Me_2NCH_2)C_6H_4]$-$SnCl_3$ (**1**), was prepared either by salt elimination reaction between RLi and $SnCl_4$ (1 : 1 molar ratio), in toluene solution, or by redistribution reaction between $[2\text{-}(Me_2NCH_2)C_6H_4]_4Sn$ and $SnCl_4$ (1 : 3 molar ratio), in the absence of a solvent (Scheme 1).

The redistribution reaction gave better results and is recommended for synthetic purposes. Recrystallization of **1** from DMSO afforded the isolation of the DMSO adduct, $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3\cdot DMSO$ (**1a**). Both compounds were obtained as air-stable, colourless, crystalline solids. They were characterized by multinuclear ($^1H$, $^{13}C$, $^{119}Sn$) NMR spectroscopy in solution and their molecular structures were established by single-crystal X-ray diffraction.

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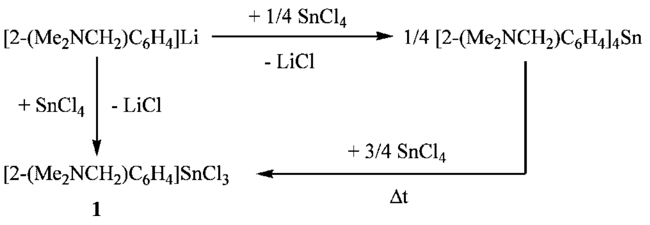
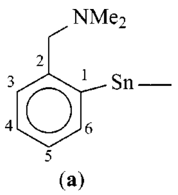


**Scheme 1.**

## NMR characterization in solution

The $^1$H and $^{13}$C resonances for **1**, at room temperature, were assigned based on H,H-COSY, H,C-HSQC and H,C-HMBC experiments, according to the numbering scheme (**a**):

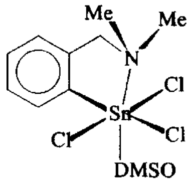


(**a**)

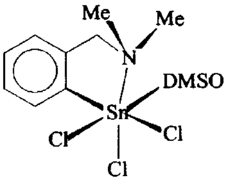
The NMR parameters for the multiplet resonance signals in the aromatic region of the $^1$H NMR spectrum of **1** were calculated on the basis of the simulated spectrum using gNMR program (Fig. 1). The $^1$H and $^{13}$C NMR data indicate that the intramolecular N → Sn interaction is present in solution, consistent with the strong Lewis acid character of the tin atom as result of the three Cl atoms bonded to it (as was also reported by Biesemans and co-workers in a study of the intramolecular Sn–N interaction using $^1$H,$^{117}$Sn J-HMBC spectroscopy).[20] The increase of the coordination number at the metal centre to 5 is further supported by the magnitude of the $^{119}$Sn chemical shift (*δ*, −213 ppm in **1**; cf. *δ*, −63 ppm for $PhSnCl_3/CH_2Cl_2$).[23]

Even at −60 °C the $^1$H NMR spectrum of **1** exhibited singlet resonances for protons of the $CH_2$ and the methyl groups bonded to nitrogen, which indicates a fast conformational change of the five-membered $SnC_3N$ non-planar chelate ring in solution, thus yielding averaged NMR signals.

The $^1$H and $^{13}$C spectra for adduct **1a** in DMSO-d$_6$ solution are very similar to those of the parent compound **1**, although broader and less well resolved. Owing to fast equilibrium it was not possible to distinguish between complexed and uncomplexed DMSO. The $^{119}$Sn spectrum of **1a** exhibits, in addition to the resonance corresponding to a major product (*δ*, −430.2 ppm), other signals of much lower intensity at *δ*, −421.7, −445.8 and −450.1 ppm (relative intensity ratio 37 : 1 : 0.6 : 2; unidentified hexacoordinated tin species). The increase in the value of the $^{119}$Sn chemical shift for **1a** (*δ*, −430.2 ppm) relative to **1** is consistent with an increase of the coordination number at tin from 5 to 6. On the basis of experimental NMR data it was not possible to distinguish between the most probable isomers **1a(I)** (O *trans* N) and **1a(II)** (O *trans* Cl, as found in solid state, see subsequent discussion).



**1a(I)**



**1a(II)**

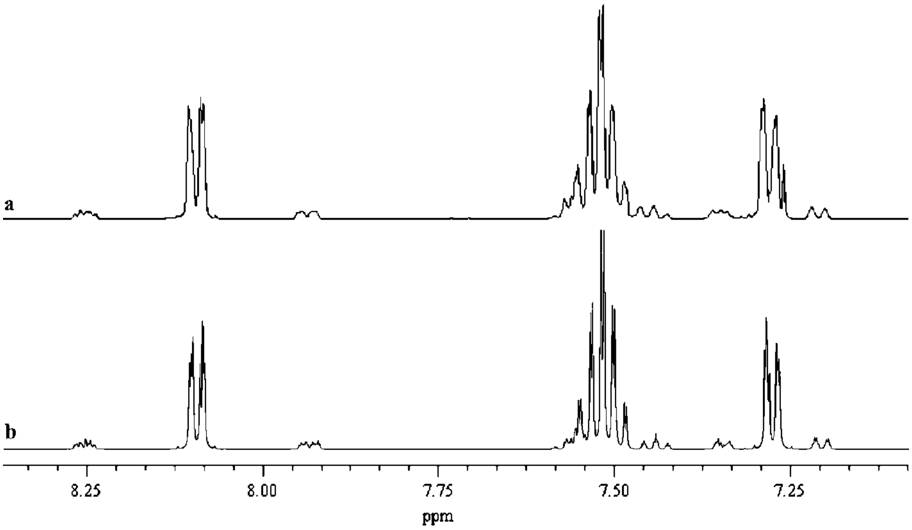


**Figure 1.** Aromatic region of the NMR spectrum of **1**: (a) experimental ($CDCl_3$, 400 MHz, 20 °C); and (b) simulated on the basis of the following parameters: 7.280 [ddd, 1H, *H*-3, $^3J_{HH}$ 6.8 (H-4), $^4J_{HH}$ 1.0 (H-5), $^5J_{HH}$ 0.9 (H-6), $^4J_{SnH}$ 57 Hz]; 7.506 [ddd, 1H, *H*-5, $^3J_{HH}$ 6.8 (H-4), $^3J_{HH}$ 6.8 (H-6), $^4J_{HH}$ 1.0 (H-3), $^4J_{SnH}$ 50 Hz]; 7.533 [ddd, 1H, *H*-4, $^3J_{HH}$ 6.8 (H-3), $^3J_{HH}$ 6.8 (H-5), $^4J_{HH}$ 1.0 (H-6), $^5J_{SnH}$ 13 Hz]; 8.093 [ddd, 1H, *H*-6, $^3J_{HH}$ 6.8 (H-5), $^4J_{HH}$ 1.0 (H-4), $^5J_{HH}$ 0.9 (H-3), $^3J_{SnH}$ 130 Hz].

In conclusion the NMR data indicate that both compounds **1** (in $CDCl_3$) and **1a** (in DMSO-$d_6$) exhibit intramolecular N → Sn coordination in solution resulting in similar coordination cores as found in the solid state, i.e. trigonal bipyramidal (*C*, *N*)$SnCl_3$ and octahedral (*C*, *N*)$SnCl_3O$ cores for **1** and **1a**, respectively.

## Solid-state structures

Single crystals suitable for X-ray diffraction studies were obtained from $CH_2Cl_2$/n-hexane (for **1**) and dimethylsulfoxide (for **1a**) solutions. Selected interatomic distances and angles are listed in Table 1.

It was shown previously that intramolecular coordination of the nitrogen atom to a metal centre in compounds containing a $[2\text{-}(Me_2NCH_2)C_6H_4]M$ moiety induces chirality at the metal centre.[24–26] Indeed, the crystals of both compounds of **1** and **1a** contain 1 : 1 mixtures of *R* and *S* isomers [with the C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively].[27] The discrete monomeric molecular units are separated by normal van der Waals distances between heavy atoms. The molecular structures of the *R* isomer for **1** and the *S* isomer for **1a** are shown in Figs 2 and 3, respectively.

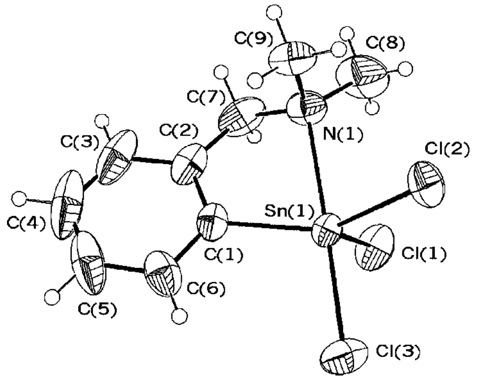


**Figure 2.** ORTEP representation at 40% probability and atom numbering scheme for *R*-**1** isomer.

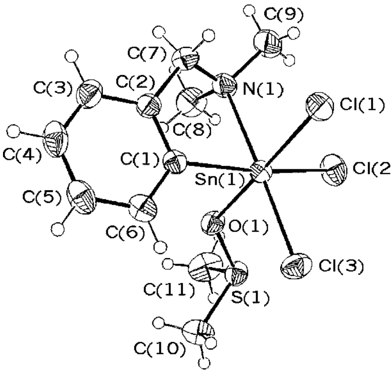


**Figure 3.** ORTEP representation at 40% probability and atom numbering scheme for *S*-**1a** isomer.

In both cases the molecular unit features a metal centre strongly coordinated by the nitrogen of the pendant arm *trans* to an Sn–chlorine bond [N(1)–Sn(1)–Cl(3) 174.56(7)° in **1**, 177.58(5)° in **1a**]. This results in different coordination environments of the metal centre, i.e. distorted trigonal bipyramidal (*C*, *N*)$SnCl_3$ core in **1** and distorted octahedral (*C*, *N*)$SnCl_3O$ core in **1a**, which contains an additional DMSO molecule coordinated to tin, *trans* to a halogen atom [Cl(1)–Sn(1)–O(1) 177.30(5)°]. The equatorial sites in **1** are occupied by the remaining two Cl atoms and the carbon atom from the organic ligand. The displacement of the Sn(1) atom from the $CCl_2$ equatorial plane in **1** on the side of the axial Cl(3) atom is 0.252 Å. The larger C(1)–Sn(1)–Cl(2) angle [134.26(8)°] in the equatorial plane of **1** is further increased to 161.47(7)° by coordination of the solvent molecule in **1a**.

**Table 1.** Important interatomic distance (Å) and angles (deg) in $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3$ (**1**) and $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3 \cdot$ DMSO (**1a**)

| | 1 | 1a |
|---|---|---|
| Sn(1)–C(1) | 2.104(3) | 2.127(2) |
| Sn(1)–Cl(1) | 2.3283(8) | 2.4406(6) |
| Sn(1)–Cl(2) | 2.3445(8) | 2.3781(7) |
| Sn(1)–Cl(3) | 2.3845(9) | 2.4124(6) |
| Sn(1)–N(1) | 2.391(3) | 2.393(2) |
| Sn(1)–O(1) | | 2.223(2) |
| Cl(3)–Sn(1)–N(1) | 174.56(7) | 177.58(5) |
| Cl(1)–Sn(1)–O(1) | | 177.30(5) |
| C(1)–Sn(1)–Cl(2) | 134.26(8) | 161.47(7) |
| Cl(1)–Sn(1)–C(1) | 114.75(8) | 97.03(6) |
| Cl(1)–Sn(1)–Cl(2) | 107.10(4) | 93.10(3) |
| O(1)–Sn(1)–C(1) | | 84.08(7) |
| O(1)–Sn(1)–Cl(2) | | 85.19(5) |
| Cl(3)–Sn(1)–C(1) | 100.83(9) | 101.62(7) |
| Cl(3)–Sn(1)–Cl(1) | 96.27(4) | 94.53(3) |
| Cl(3)–Sn(1)–Cl(2) | 91.90(3) | 92.97(3) |
| Cl(3)–Sn(1)–O(1) | | 87.65(5) |
| N(1)–Sn(1)–C(1) | 77.03(11) | 77.46(8) |
| N(1)–Sn(1)–Cl(1) | 89.16(7) | 87.81(6) |
| N(1)–Sn(1)–Cl(2) | 86.21(7) | 87.50(6) |
| N(1)–Sn(1)–O(1) | | 90.03(7) |

The resulting five-membered $SnC_3N$ rings are folded along the $Sn(1)\cdots C_{methylene}$ axis [$SnC_3$/SnCN dihedral angle: 43.6° in **1**, and 37.3° in **1a**, respectively], with the nitrogen atom 0.293 Å (**1**) and 0.260 Å (**1a**) out from the best plane of the rest of the atoms. The deviations of the bond angles at the metal atom from the ideal values, are mainly due to the constraints imposed by the small bite of the *C*,*N*-bidentate ligand (Table 1).

The Sn(1)–N(1) distances in **1** [2.391(3) Å] and **1a** [2.393(2) Å] are shorter than in the related pentacoordinate $[2\text{-}(Me_2NCH_2)C_6H_4]R_2SnCl$ [R = Me, 2.488(7) Å;[15] R = Ph, 2.519(2) Å[18]] or [2-($Me_2NCH_2$)$C_6H_4$]Ph$SnCl_2$ [2.47(1) Å][15] and hexacoordinate [2-($Me_2NCH_2$)$C_6H_4$]$_2$$SnCl_2$ [2.646(3) Å; Varga *et al.*, in preparation], reflecting the stronger Lewis acid character of the Sn centre (owing to the presence of the three electronegative Cl atoms).

The Sn(1)–Cl(3) bond distance [2.3845(9) Å] in **1** and Sn(1)–Cl(3) [2.4124(6) Å] and Sn(1)–Cl(1) [2.4406(6) Å] bond distances in **1a** are significantly larger than in the tetrahedral $Ph_3SnCl$ [2.354(9) and 2.356(8) Å, for the two independent molecules present in the unit cell],[28] consistent with nature of the corresponding *trans* atom.

A closer check of the crystal structure of **1** and **1a** revealed several hydrogen bonding interactions resulting in different supramolecular architectures. Within a molecule of **1** there are three intramolecular short Cl···H contacts which involve all three Cl atoms: Cl(1)···H(8a) 2.76, Cl(2)···H(9b) 2.83, and Cl(3)···H(6) 3.00 Å [Fig. 4(a)] [cf. sum of the respective van der Waals radii is $\Sigma_{vdW}$(Cl,H) ca. 3.01 Å].[29] In the crystal

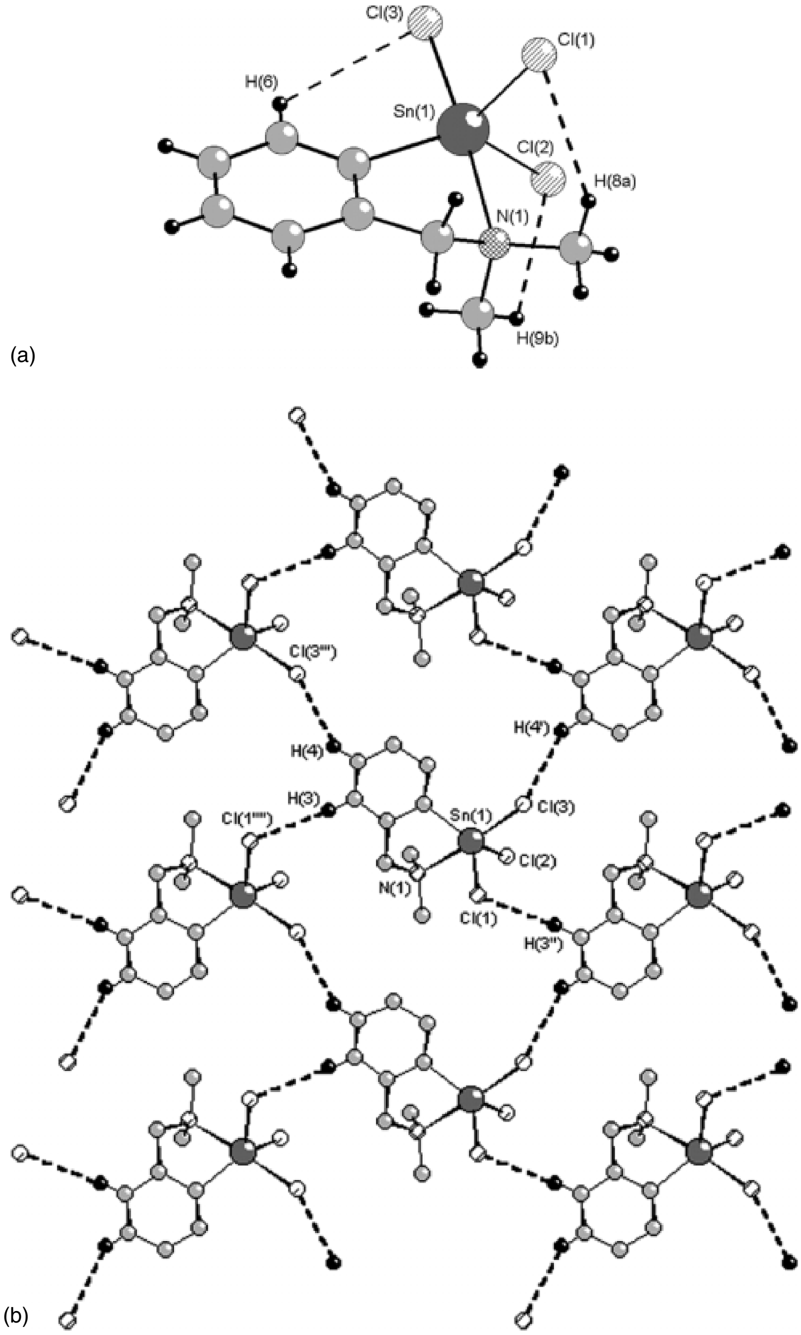


**Figure 4.** Hydrogen bonding in the crystal of **1**: (a) intramolecular hydrogen bonding; and (b) view along a axis of layer network based on intermolecular hydrogen bonding (only hydrogens involved in intermolecular interactions are shown).

of **1** alternating rows formed by *R*-isomers and *S*-isomers, respectively, can be distinguished, the molecules of one row not being connected by intermolecular interactions. Each molecule of one row involves two of its halogen atoms [Cl(1)···H(3″) 2.95, Cl(3)···H(4′) 2.92 Å] and two of the aromatic protons [H(3)···Cl(1″″) 2.95, H(4)···Cl(3‴) 2.92 Å] in intermolecular hydrogen bonding with two molecules of each neighboring rows. The result is a two dimensional network of honeycomb aspect [Fig. 4(b)].

The Cl(2) atoms, which are not involved in intermolecular hydrogen bonds, are placed on the same side of the layered structure. A compact packing is achieved in the crystal of **1** (Fig. 5) with pairs of layers facing the chlorine-rich sides.

In the molecule of **1a** only two of the Cl atoms are involved in short intramolecular Cl···H contacts with hydrogen atoms of one of the methyl groups attached to nitrogen, i.e. Cl(1)···H(9b) 2.88, Cl(2)···H(9a) 2.88 Å [the distance between Cl(3)and the aromatic H(6) atom is 3.08 Å, at the limit of a van der Waals contact] [Fig. 6(a)]. Polymeric chains are formed by *R* and *S* isomers, respectively, through intermolecular contacts between the Cl(2) atom and one hydrogen of the DMSO molecule coordinated to the metal centre [Cl(2)···H(10b″) 2.91 Å] [Fig. 6(b)]. In the crystal these polymeric chains are arranged in a parallel fashion along with axis *b* and no further interchains contacts are established.

## CONCLUSIONS

[2-(Dimethylaminomethyl)phenyl]tin (IV) trichloride (**1**) and its 1 : 1 DMSO adduct (**1a**) were prepared and characterized both in solution and solid state. Multinuclear NMR studies support the intramolecular coordination of the amino pendant arm and thus increase in the coordination number of the metal centre to 5 and 6 in **1** and **1a**, respectively. In solid state both compounds crystallize as 1 : 1 mixtures of *R* and *S* isomers; in the crystal a network of intermolecular hydrogen bonding generates different supramolecular architectures, i.e. a layer structure in **1** and polymeric chains in **1a**.

## EXPERIMENTAL

Tin tetrachloride, *N*,*N*-dimethylbenzylamine and butyllithium were commercially available (Merck Eurolab GmbH). Literature methods were used to prepare $[2\text{-}(Me_2NCH_2)C_6H_4]Li$,[30] and $[2\text{-}(Me_2NCH_2)C_6H_4]_4Sn$.[15] All manipulations were carried out under vacuum or argon atmosphere by Schlenk techniques. Solvents were dried and freshly distilled prior to use. Room-temperature $^1H$ and $^{13}C$ NMR spectra for **1** (in dried $CDCl_3$) and **1a** (in DMSO-$d_6$), including two-dimensional experiments for **1**, were recorded on a Bruker Avance DRX 400 instrument operating at 400.16 and 100.62 MHz, respectively. The chemical shifts are reported in ppm relative to the residual peak of solvent (ref. $CHCl_3$: $^1H$ 7.26, $^{13}C$ 77.0 ppm; DMSO-$d_6$: $^1H$ 2.50, $^{13}C$ 39.43 ppm). Abbreviations used in multiplicities are: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet. The $^{119}Sn$ NMR spectra (at 111.81 MHz; chemical shifts reported in ppm relative to neat $SnMe_4$), as well as low temperature $^1H$ NMR for **1**, were recorded on a Varian Unity 300 instrument.

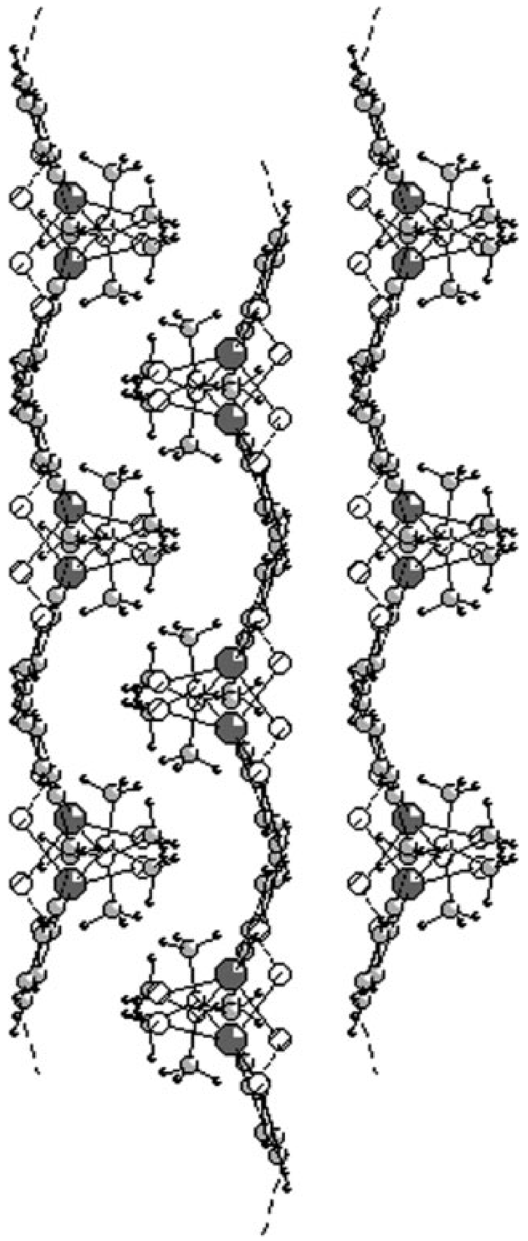


**Figure 5.** Packing of the hydrogen bonding-based layers in the crystal of **1** (view along *c*-axis).

### Preparation of $[2\text{-}(Me_2NCH_2)C_6H_4]SnCl_3$ (1)

### *Method A*

A suspension of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ (0.786 g, 5.57 mmol) in 50 ml anhydrous toluene was added dropwise under

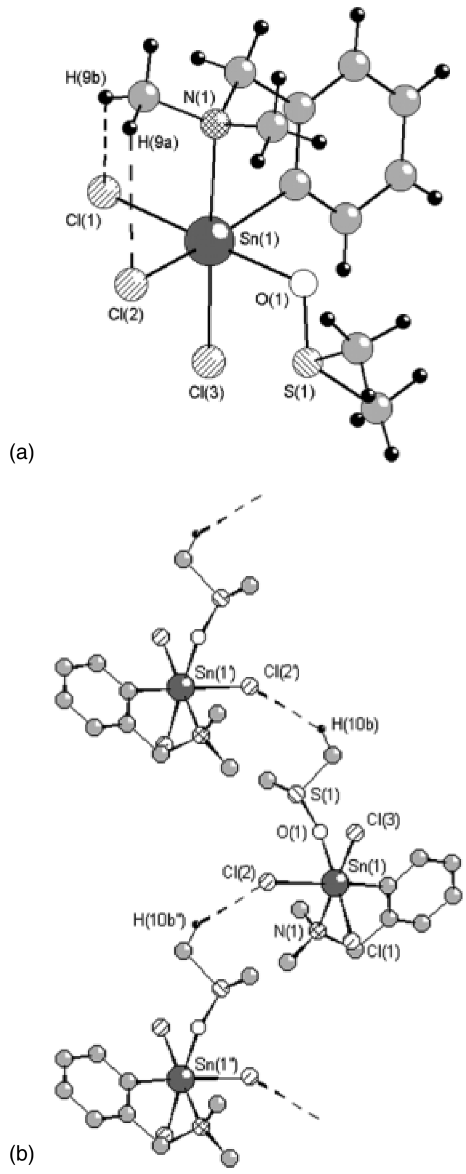


**Figure 6.** Hydrogen bonding in the crystal of **1a**: (a) intramolecular hydrogen bonding; and (b) view along *c* axis of polymer chain formed by *S* isomers via intermolecular hydrogen bonding (only hydrogens involved in intermolecular interactions are shown).

stirring to a cooled (−78 °C) solution of $SnCl_4$ (1.45 g, 5.57 mmol) in 100 ml toluene. The reaction mixture was stirred for 1 h at −78 °C, and then stirred overnight to reach the room temperature. Then it was filtered under inert (Ar) atmosphere and the solvent was removed *in vacuo*. The light-brown solid residue was recrystallized from $CH_2Cl_2/n$-hexane to give 0.5 g (25%) of the title compound as colorless crystals.

### *Method B*

$SnCl_4$ (0.596 g, 2.29 mmol) was added to [2-($Me_2NCH_2$)$C_6H_4$]$_4$Sn (0.5 g, 0.76 mmol) under inert atmosphere and the mixture was slowly heated until a homogenous melt was obtained. The heating was maintained for 15 min and then the mixture was allowed to reach room temperature. The solid residue was dissolved in $CH_2Cl_2$ and $n$-hexane (approximately 1 : 4, v : v) was slowly added to avoid mixing of the solvents. After standing for 2 days, 0.8 g (73%) of **1** were obtained as colourless crystals, m.p. 122–124 °C. Analyses: found, C 29.88, H 3.15, N 3.79; calcd, for $C_9H_{12}Cl_3NSn$ (359.25) C 30.09, H 3.37, N 3.90%. $^1$H-NMR: $\delta$, 2.58 [s, 6H, NC$H_3$, $^3J_{SnH}$ 11.7 Hz], 3.82 [s, 2H, C$H_2$, $^3J_{SnH}$ 8.1 Hz], 7.28 (m, 1H, *H*-3), 7.52 (m, 2H, *H*-4,5), 8.09 (m, 1H, *H*-6). $^{13}$C-NMR: $\delta$, 45.25 (NCH$_3$, $^2J_{SnC}$ n.d.), 61.54 (CH$_2$, $^2J_{SnC}$ 75.6 Hz), 128.14 (*C*-3, $^3J_{SnC}$ 105.5/109.3 Hz), 129.65 (*C*-5, $^3J_{SnC}$ 122.9/128.0 Hz), 132.51 (*C*-4, $^4J_{SnC}$ 23.0 Hz), 136.20 (*C*-1), 136.33 (*C*-6, $^2J_{SnC}$ 84.8 Hz), 139.01 (*C*-2, $^2J_{SnC}$ 87.8/91.0 Hz). $^{119}$Sn-NMR: $\delta$, −213.

## Preparation of [2-($Me_2NCH_2$)$C_6H_4$]$SnCl_3$·DMSO (1a)

Aliquots of 0.25 g (0.69 mmol) of [2-($Me_2NCH_2$)$C_6H_4$]$SnCl_3$ were suspended in 1 ml of DMSO and the mixture was heated until the solid dissolved. After standing for one day, 0.25 g (82.1%) colourless crystals of [2-($Me_2NCH_2$)$C_6H_4$]$SnCl_3$·DMSO (**1a**) were isolated, m.p. 191–193 °C. $^1$H-NMR: $\delta$, 2.56 [s, 6H, NC$H_3$], 3.86 [s, 2H, C$H_2$], 7.20 (m, 1H, *H*-3, $^4J_{SnH}$ 42 Hz), 7.35 (m, 2H, *H*-4,5), 7.67 (m, 1H, *H*-6, $^3J_{SnH}$ 98 Hz). $^{13}$C-NMR: $\delta$, 45.86 (NCH$_3$, $^2J_{SnC}$ n.d.), 61.12 (CH$_2$, $^2J_{SnC}$ 84.2 Hz), 127.06 (*C*-3, $^3J_{SnC}$ 116.2 Hz), 128.21 (*C*-5, $^3J_{SnC}$ 129 Hz), 129.45 (*C*-4), 131.51 (*C*-6, $^2J_{SnC}$ 82.7 Hz), 136.33 (*C*-2, $^2J_{SnC}$ 107.5 Hz), 147.11 (*C*-1, $^2J_{SnC}$ 1485.7/1551.9 Hz). $^{119}$Sn-NMR: $\delta$, −430.2.

## Crystallography

Colourless, block crystals of [2-($Me_2NCH_2$)$C_6H_4$]$SnCl_3$ (**1**) and [2-($Me_2NCH_2$)$C_6H_4$]$SnCl_3$·DMSO (**1a**) were mounted on a cryoloop. Data collection and processing for both compounds was carried out using a Bruker AXS SMART APEX system, with graphite-monochromated MoKa radiation at 291 K. The structures were solved by direct methods SHELXS-97[31] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL-97.[32] The details of the crystal structure determination and refinement for both compounds are given in Table 2.

The structures were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from international tables for X-ray crystallography.[33] The drawings were created with the ORTEP[34] and DIAMOND[35] programs.

Crystallographic data for the structural analysis of compounds **1** and **1a** have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos 243261, 243262). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ,

**Table 2.** Crystal data and structure refinement for [2-($Me_2NCH_2$)$C_6H_4$]$SnCl_3$ (**1**) and [2-($Me_2NCH_2$)$C_6H_4$]$SnCl_3$·DMSO (**1a**)

| Compound | 1 | 1a |
|---|---|---|
| Empirical formula | $C_9H_{12}Cl_3NSn$ | $C_{11}H_{18}Cl_3NOSSn$ |
| Formula weight | 359.24 | 437.36 |
| Temperature (K) | 273(2) | 297(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| Unit cell dimensions | | |
| $a$ (Å) | 9.5462(9) | 9.3985(8) |
| $b$ (Å) | 8.7665(8) | 12.8838(11) |
| $c$ (Å) | 15.5185(14) | 13.8196(12) |
| $\beta$ (°) | 93.419(2) | 97.9230(10) |
| Volume (Å$^3$) | 1296.4(2) | 1657.4(2) |
| $Z$ | 4 | 4 |
| $D_c$(g/cm$^3$) | 1.841 | 1.753 |
| Absorption coefficient (mm$^{-1}$) | 2.553 | 2.140 |
| *F(000)* | 696 | 864 |
| Crystal size, mm | 0.42 × 0.32 × 0.30 | 0.54 × 0.43 × 0.16 |
| $\theta$ range for data collections (°) | 2.14 to 26.37 | 2.17 to 26.37 |
| Reflections collected | 7376 | 13036 |
| Independent reflections | 2635 [R(int) = 0.0178] | 3387 [R(int) = 0.0261] |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 2635/0/142 | 3387/0/167 |
| Goodness-of-fit on $F^2$ | 1.078 | 1.102 |
| Final $R$ indicies [$I > 2\sigma(I)$] | $R_1 = 0.0250, wR_2 = 0.0554$ | $R_1 = 0.0241, wR_2 = 0.0566$ |
| $R$ indicies (all data) | $R_1 = 0.0275, wR_2 = 0.0566$ | $R_1 = 0.0266, wR_2 = 0.0577$ |
| Largest difference peak and hole, Å$^{-3}$ | 0.445 and −0.436 | 0.293 and −0.592 |

UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; or www: www.ccdc.cam.ac.uk).

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