# Synthesis, Molecular Structure, and Isomerisation in Solution of $(Me_3SbS)_2Me_2SnCl_2$. Concomitant Hypercoordination of Tin and Antimony

**Jens Beckmann*, Dainis Dakternieks, Andrew Duthie and Richard C. Foitzik**

Geelong / Australia, Deakin University, Centre for Chiral and Molecular Technologies

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**Abstract**. The reaction of $Me_3SbCl_2$ and $(Me_2SnS)_3$ afforded the complex $(Me_3SbS)_2Me_2SnCl_2$ in high yields, whose molecular structure features both hypercoordinated tin and antimony atoms. In solution, $(Me_3SbS)_2Me_2SnCl_2$ undergoes a reversible dissociation and ligand interchange reaction to give $Me_3SbS$, $Me_3SbCl_2$ and $(Me_2SnS)_3$.

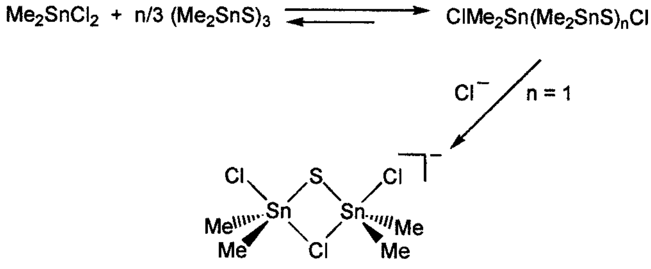
**Keywords**: Tin; Antimony; Hypercoordination; Crystal structures; NMR spectroscopy

# Synthese, Molekülstruktur und Isomerisierung von $(Me_3SbS)_2Me_2SnCl_2$ in Lösung. Gleichzeitig auftretende Hyperkoordination am Zinn und Antimon

**Inhaltsübersicht**. In der Reaktion von $Me_3SbCl_2$ mit $(Me_2SnS)_3$ entstand in hoher Ausbeute der Komplex $(Me_3SbS)_2Me_2SnCl_2$, dessen Molekülstruktur sowohl hyperkoordinierte Zinn- als auch Antimonatome aufweist. In Lösung unterliegt $(Me_3SbS)_2Me_2SnCl_2$ einer reversiblen Dissoziation- und Ligandenaustauschreaktion bei der $Me_3SbS$, $Me_3SbCl_2$ und $(Me_2SnS)_3$ entstehen.

## Introduction

Some 50 years ago *Moedritzer* and *Van Walzer* described that mixtures of dimethyltin sulfide, $(Me_2SnS)_3$, and dimethyltin dichloride, $Me_2SnCl_2$, rapidly undergo ligand interchange of chlorine and sulfur atoms and exist in equilibrium with open-chain species $ClMe_2Sn(Me_2SnS)_nCl$ (Scheme 1) [1]. In preceding work, we and others reported that upon addition of chloride anions to such mixtures with n = 1, a hypercoordinated dinuclear organotin complex $[\mu\text{-}Cl(Me_2SnCl)_2S]^-$ is formed (Scheme 1) [2]. In the context of this work we also investigated the reaction of dimethyltin sulfide, $(Me_2SnS)_3$, and trimethylantimony dichloride, $Me_3SbCl_2$, and isolated a crystalline organotin-organoantimony complex, namely $(Me_3SbS)_2Me_2SnCl_2$. Apparently, the same material was already obtained in 1967 by *Shindo* and *Okawara* from the direct reaction of $Me_3SbS$ with $Me_2SnCl_2$ [3,4]. We now describe its complete characterization by NMR spectroscopy and X-ray crystallography.



**Scheme 1**

## Discussion

The reaction of $(Me_2SnS)_3$ and $Me_3SbCl_2$ afforded the complex $(Me_3SbS)_2Me_2SnCl_2$ in high yields (Eq. (1)).

$$2\,Me_3SbCl_2 + 2/3\,(Me_2SnS)_3 \xrightarrow[-\,Me_2SnCl_2]{} (Me_3SbS)_2Me_2SnCl_2 \qquad (1)$$

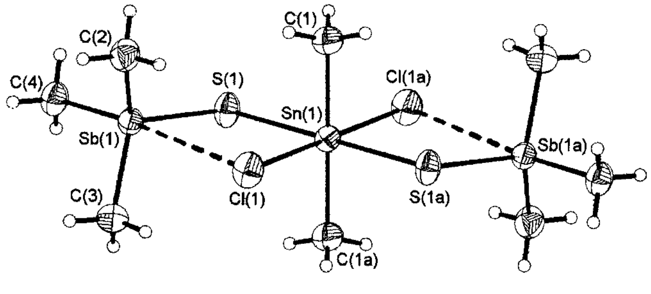


**Figure 1** General view (DIAMOND) of $(Me_3SbS)_2Me_2SnCl_2$ showing 40 % probability displacement ellipsoids and the atom numbering scheme (Symmetry operations used to generate equivalent atoms: a = −x, −y, −z).

$(Me_3SbS)_2Me_2SnCl_2$ comprises a colourless crystalline material that is air-stable for several days and indefinitely stable when stored under exclusion from light and air. The stability is noteworthy as most previous publications highlight the limited stability of trialkylantimony sulfides [5].

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* Dr. Jens Beckmann
Deakin University, Centre for Chiral and Molecular Technologies
Geelong 3217/Australia
Fax: ++61-3-5227-1040
E-mail: beckmann@deakin.edu.au

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**Table 1** Selected bond lengths/Å and angles/° for $(Me_3SbS)_2$-$Me_2SnCl_2$.

| | | | |
|---|---|---|---|
| Sn(1)−C(1) | 2.126(3) | Sn(1)−Cl(1) | 2.597(1) |
| Sn(1)−S(1) | 2.746(1) | Sb(1)−C(2) | 2.103(3) |
| Sb(1)−C(3) | 2.108(3) | Sb(1)−C(4) | 2.100(3) |
| Sb(1)−S(1) | 2.305(1) | Sb(1)−Cl(1) | 3.577(1) |
| C(1)−Sn(1)−C(1a) | 180 | C(1)−Sn(1)−Cl(1) | 89.61(10) |
| C(1)−Sn(1)−Cl(1a) | 90.39(10) | C(1)−Sn(1)−S(1) | 90.42(9) |
| C(1)−Sn(1)−S(1a) | 89.58(9) | Cl(1)−Sn(1)−Cl(1a) | 180 |
| Cl(1)−Sn(1)−S(1) | 93.12(2) | Cl(1)−Sn(1)−S(1a) | 86.88(2) |
| S(1)−Sn(1)−S(1a) | 180 | C(2)−Sb(1)−C(3) | 112.57(14) |
| C(2)−Sb(1)−C(4) | 108.15(14) | C(3)−Sb(1)−C(4) | 105.08(13) |
| C(2)−Sb(1)−S(1) | 111.75(9) | C(3)−Sb(1)−S(1) | 113.06(9) |
| C(4)−Sb(1)−S(1) | 105.63(9) | Sn(1)−S(1)−Sb(1) | 106.76(3) |

Symmetry operations used to generate equivalent atoms: a = −x, −y, −z

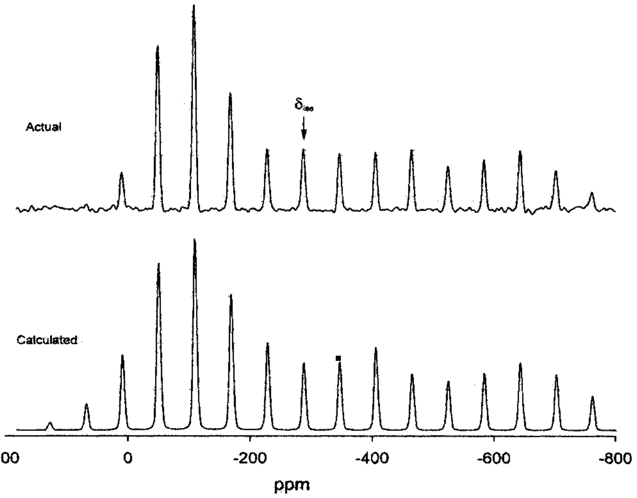

**Figure 2** Experimental and iteratively fitted $^{119}$Sn MAS NMR spectrum (149.03 MHz, $\nu_{RO}$ 8850 Hz) of $(Me_3SbS)_2Me_2SnCl_2$. The centre band at $\delta_{iso}$ −288.0 is indicated by an arrow (For the tensor analysis refer to text).

The molecular structure of $(Me_3SbS)_2Me_2SnCl_2$ is shown in Figure 1; selected bond lengths and angles are given in Table 1. The Sn atom lies across a crystallographic centre of inversion and features a slightly distorted octahedral coordination defined by a $C_2Cl_2S_2$ donor set. The Sn−C, Sn−Cl and Sn−S bond lengths at 2.126(3), 2.597(1) and 2.746(1) Å, respectively, compare best with those of $Me_2SnCl_2 \cdot 2dmtu$ (2.122(5), 2.616(1) and 2.729(1) Å; dmtu = 1,3-dimethylthiourea [6]) and $Me_2SnCl_2 \cdot 2pyth$ (2.099(9), 2.623(2) and 2.729(2) Å, pyth = 2(1H)-pyridinethione [7]).The $^{119}$Sn MAS NMR spectrum of $(Me_3SbS)_2Me_2SnCl_2$ is consistent with a hexacoordinated Sn atom and shows a signal at $\delta_{iso}$ −288.0 with an accompanying set of spinning sidebands indicative of a large shielding anisotropy (SA), which were used to perform a tensor analysis according to the method of *Herzfeld* and *Berger* [8]. The tensor components of the shielding anisotropy $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$ were determined as −54, 83 and 835 ppm; the spectrum is shown in Figure 2. Thus, the anisotropy $\zeta$ and symmetry $\eta$ amount to 547 ppm and 0.25, respectively. The $^{13}$C MAS NMR spectrum reveals three of the four expected signals at δ 43.0, 13.8 and 11.3. The resonance at δ 43.0 displays unresolved tin satellites and thus allows an unambiguous assignment to the $Me_2Sn$ group. The large ($^1J(^{13}C\text{-}^{119/117}Sn)$ coupling of 1004 Hz is fully consistent with the C(1)−Sn(1)−C(1a) angle of 180° and the underlying relationship proposed by *Lockhart* et al. [9−11]. The signals at δ 13.8 and 11.3 were assigned to the $Me_3Sb$ group. Based on the higher intensity of the latter signal the expected third signal of the $Me_3Sb$ group is likely to be superimposed. The arrangement of the Sb atoms lies midway between a tetrahedron and a trigonal bipyramid (geometrical goodness [12] $\Delta\Sigma(\theta)$ 18.5°) and is defined by a $C_3S$ donor set and an additional intramolecular Cl contact (4+1 coordination). Somewhat contradicting Bent's rule, two carbon atoms and one sulfur atom occupy the equatorial positions whereas the remaining carbon atom and the chlorine atom are situated in the axial positions. The individual Sb−C bond lengths differ only slightly from the average value of 2.104(3) Å. The Sb−S bond length amounts to as 2.305(1) Å and is slightly longer than in $Ph_3SbS$ (Sb−S: 2.245(6) Å), the only triorganoantimony sulfide yet investigated by X-ray diffraction [13]. The Sb···Cl distance of 3.577(1) Å is shorter than the sum of van-der-Waals radii (Sb: 2.20 Å Cl: 1.81 Å) by 0.43 Å.

As already concluded by *Shindo* and *Okawara* on the basis of molecular weight determinations and $^1$H NMR spectroscopy, $(Me_3SbS)_2Me_2SnCl_2$, undergoes a reversible dissociation / ligand interchange of chlorine and sulfur atoms in $CHCl_3$ to give a mixture of $Me_3SbCl_2$, $Me_3SbS$, and $(Me_2SnS)_3$ (Eq. (2)) [3,4]. In agreement with this interpretation, the $^{119}$Sn NMR spectrum ($CDCl_3$) of $(Me_3SbS)_2Me_2SnCl_2$ shows a signal at δ 133.3 with a ($^2J(^{119}Sn\text{-}S\text{-}^{117}Sn)$ coupling of 191 Hz that was assigned to $(Me_3SnS)_3$ [14]. The $^{13}$C NMR spectrum ($CDCl_3$) shows three signals at δ 22.7, 7.0, and 4.6 ($^1J(^{13}C\text{-}^{119}Sn)$ 406 Hz), which were unambiguously assigned to $Me_3SbCl_2$, $Me_3SbS$, and $(Me_2SnS)_3$, respectively.

$$\underset{\text{solid-state}}{(Me_3SbS)_2Me_2SnCl_2} \rightleftharpoons \underset{\text{solution }(CDCl_3)}{1/3\ (Me_2SnS)_3 + Me_3SbS + Me_3SbCl_2} \qquad (2)$$

Apparently, the observation of a rapid and reversible dissociation / ligand interchange reaction suggests that all concerned Sn−Cl, Sn−S, Sb−Cl, and Sb−S bonds are kinetically labile on the laboratory time scale and that low activation barriers exist for all reaction steps involved. In contrast, the thermodynamic driving force for this process appears to be less straightforward. While the presumed initial dissociation of $(Me_3SbS)_2Me_2SnCl_2$ into $Me_2SnCl_2$ and two molecules of $Me_3SbS$ might be attributed to an entropy gain in solution, the reasons for the subsequent ligand interchange reaction between $Me_2SnCl_2$ and one molecule of $Me_3SbS$ giving one third $(Me_2SnS)_3$ and $Me_3SbCl_2$ might be tentatively explained by the $Me_2Sn$ moiety having a slightly higher affinity to sulfur than the $Me_3Sb$ moieties. The preference of $(Me_3SbS)_2Me_2SnCl_2$ in the solid-state might be attributed to the maximum energy gain associated with the hypercoodination of the Sn and Sb atoms.

## Experimental

$(Me_2SnS)_3$ was prepared according to a literature procedure [15]. $Me_3SbCl_2$ was purchased from Aldrich. NMR spectra were obtained using a Jeol Eclipse Plus 400 spectrometer (at 399.78 Mz ($^1$H), 100.54 ($^{13}$C) and 149.05 ($^{119}$Sn)) and were referenced against $SiMe_4$ and $SnMe_4$. The solid-state NMR spectra were measured using the same instrument equipped with a 4 mm MAS probe and adamantane (δ 38.6 / 29.5) and *c*-$Hex_4Sn$ (δ −97.35) as secondary references. The $^{119}$Sn MAS NMR spectra were obtained using cross polarization (contact time 5 ms, recycle delay 40s). The isotropic chemical shifts $\delta_{iso}$ were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies. The tensor analyses were performed using the method of Herzfeld and Berger[8] implemented in DmFit 2002 [16]. The definitions used: $\delta_{iso}$ (ppm) $= -\sigma_{iso} = -(\sigma_{11}+\sigma_{22}+\sigma_{33}) / 3$; $\zeta$ (ppm) $= \sigma_{33}-\sigma_{iso}$ and $\eta = |\sigma_{22}-\sigma_{11}|/|\sigma_{33}-\sigma_{iso}|$ where $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$ (ppm) are the principal tensor components of the shielding anisotropy (SA), defined as follows $|\sigma_{33}-\sigma_{iso}|>|\sigma_{11}-\sigma_{iso}|>|\sigma_{22}-\sigma_{iso}|$.

**Synthesis of $(Me_3SbS)_2Me_2SnCl_2$.** A mixture of $Me_3SbCl_2$ (713 mg, 3.00 mmol) and $(Me_2SnS)_3$ (543 mg, 1.00 mmol) in methanol (30 mL) was heated for 15 min at 50 °C to give a clear solution. Cooling at −10 °C afforded large crystals of $(Me_3SbS)_2Me_2SnCl_2$ (840 mg, 1.36 mmol, 91 %; mp. 139.8-140.0 °C, Lit. 147.0-147.5 °C [3]).

Anal. Calcd. for $C_8H_{24}Cl_2S_2Sb_2Sn$ (617.57): C, 15.56; H, 3.92. Found C, 15.45; H, 3.99 %.

**$^1$H NMR** ($CDCl_3$) δ: 2.36 (3H; $Me_3SbCl_2$), 1.55 (3H; $Me_3SbS$), 0.87 (2H, $^2J(^1H\text{-}C\text{-}^{119}Sn)$ 62 Hz; $(Me_2SnS)_3$) (Identical to the reported $^1$H NMR spectrum within 0.01 ppm [3])

## Crystallography

Single crystals of $(Me_3SbS)_2Me_2SnCl_2$ suitable for X-ray crystallography were obtained by slow evaporation of a methanol solution. Data and structure solution at T = 293(2) K: $C_8H_{24}Cl_2S_2Sb_2Sn$, $M_r$ = 617.57, monoclinic, *P*1 $2_1$/n, crystal dimensions: 0.20 × 0.30 × 0.40 mm$^3$, $a = 9.2887(5)$, $b = 10.0768(6)$, $c = 10.2982(6)$ Å, $\beta = 98.7850(10)°$, $V = 952.61(9)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 2.153$ Mg m$^{-3}$, $F(000) = 580$, $\mu = 4.593$ mm$^{-1}$. Intensity data were collected on Bruker SMART Apex CCD diffractometer fitted with Mo-Kα radiation (graphite crystal monochromator, λ = 0.71073 Å) to a maximum of $\theta_{max} = 27.49°$ via ω scans (completeness 99.5 % to $\theta_{max}$). Data were reduced and corrected for absorption using the programs SAINT and SADABS [17]. The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002 [18]. Full-matrix least-squares refinement on $F^2$, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. The weighting scheme employed was of the type $w = [\sigma^2(F_0{}^2) + (0.0319\,P)^2 + 0.3605\,P]^{-1}$ where $P = (F_0{}^2 + 2\,F_c{}^2) / 3$. $R_1 = 0.0207$ for 2048 $[I>2\sigma(I)]$ reflections and $wR_2 = 0.0567$ for 2173 independent reflections; GooF = 1.090. The max. and min. residual electron densities were 0.447 / −0.611 e Å$^{-3}$. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 208109. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-(0)12 23-33 60 33 or e-mail: deposit@ccdc.cam.ac.uk).

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