Faculty of Chemistry at Dortmund University

# Spacer-bridged ditin compounds as bicentric Lewis acids and synthons for novel organotin oxo clusters

Thesis presented for obtaining the degree of Dr. rer. nat.

by

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| | |
|---|---|
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# List of abbreviations

| General abbreviations | | | |
|---|---|---|---|
| Ac | acetyl | Me | methyl |
| aq | watery | $n_i$ | portion of isomer i |
| Ar | aryl | Ph | phenyl |
| *n*-Bu | *n*-butyl | *i*-Pr | *iso*-propyl |
| *s*-Bu | *sec*-butyl | R | organic group |
| calc. | calculated | m.p. | melting point |
| DMF | dimethylformamide | *n*-Oc | *n*-octyl |
| DMSO | dimethylsulfoxide | THF | Tetrahydrofuran |
| Et | ethyl | X | halide |
| HMPA | hexamethylphosphoric triamide | Z | bridging group |

| NMR- and IR-Spectroscopy | | | |
|---|---|---|---|
| NMR | nuclear magnetic resonance spectroscopy | quart | quartet |
| $\delta$ | chemical shift | quint | quintet |
| ppm | parts per million | m | multiplet |
| $\nu\,{}^{1}/_{2}$ | linewidth | IR | Infrared spectroscopy |
| $^{n}J$ | coupling constant through *n* bonds | $\tilde{\nu}$ | wave number |
| Hz | Hertz | *i* | *ipso* |
| s | singlet | *m* | *meta* |

continued

| | | | |
|---|---|---|---|
| d | doublet | *o* | *ortho* |
| t | triplet | *p* | *para* |

| **Molecular structure determination** | | | |
|---|---|---|---|
| a, b, c | unit cell dimensions | $\rho_{meas.}$ | measured density |
| Å | Ångström | $\mu$ | Absorption coefficient |
| $\alpha$, $\beta$, $\gamma$ | angles | $F$ | Structure factor |
| ° | degree | $R$ | rest value |
| $V$ | volume of the unit cell | $wR$ | weighted rest value |
| $Z$ | number of molecules in the unit cell | $F$(000) | Number of electrons in the unit cell |
| $\rho_{calc.}$ | calculated density | $\sigma$ | standard deviation |

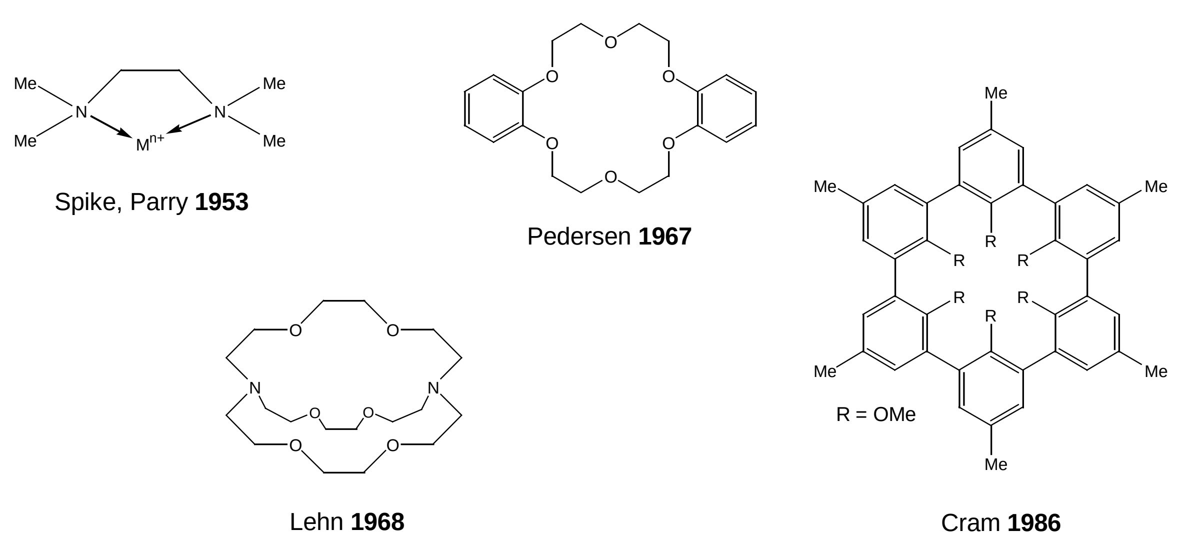
# *Chapter 1*

# 1 Recent developments in the chemistry of multicentric organotin(IV) Lewis acids

## 1.1 Complexation behaviour of neutral host molecules: introduction and attempts

### Introduction

A basis of the coordination chemistry of multidentate ligands is the observation of the complexation behaviour of ethylendiamine derivatives by Spike and Parry in 1953. A new vigour in the development of host-guest chemistry was then given by Pedersen, Lehn and Cram with the synthesis of compounds such as crown ethers, cryptands and spherands. Depending on their donor qualities and ring size these multidentate Lewis bases are able to complexe with high selectivity cations (cryptands) and neutral molecules (spherands). Pedersen, Lehn and Cram received in 1988 the Nobel Prize for their contribution in the development of coordination chemistry.



Spike, Parry **1953**

Pedersen **1967**

Lehn **1968**

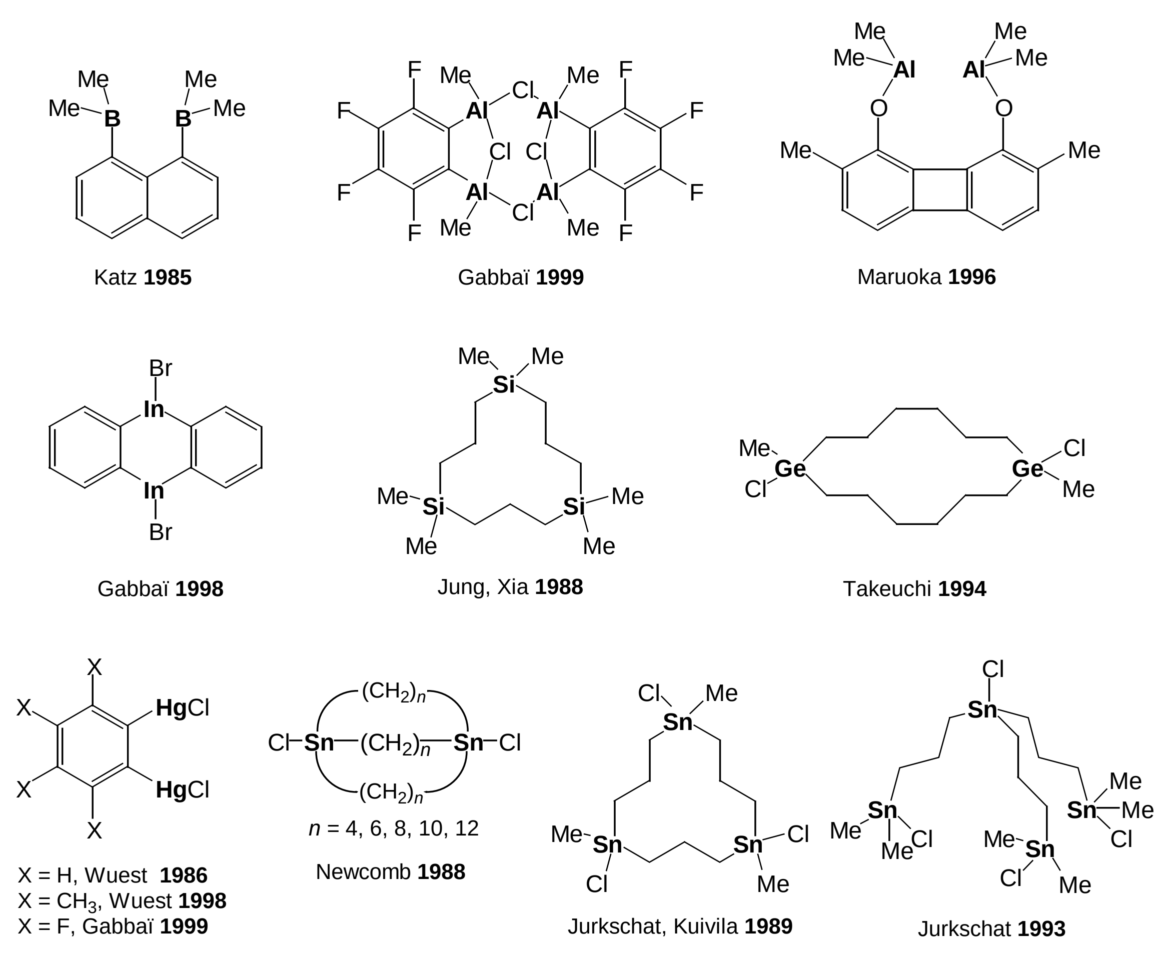
Cram **1986**

**Figure 1** Chelate, crown ether, cryptands and spherands.

One possibility for the selective complexation of anions and neutral donor molecules by tailor-made molecular hosts is given by the interaction between Lewis acids and Lewis bases. The first systematic studies on the synthesis and coordination chemistry of multicentric Lewis acids were published more than thirty years ago by Shriver and Biallas.[1,2] Their work, which explored the coordination chemistry of 1,2-ethanediylbis[difluoroborane] and related bicentric Lewis acids, provided useful informations about the ability of two adjacent sites of Lewis acidity to interact simultaneously with basic sites in other molecules. Surprisingly, their results did not immediately encourage other chemists to study multicentric Lewis acids, and only in the eighties this subject began to receive the attention it deserved.[3-19]

The synthesis of multicentric Lewis acids in which the active sites are incorporated in cyclic[9,20-26] or non-cyclic structures[8,27-41] makes it possible to reach a specific molecular recognition (Figure 2).

Elements which function as Lewis acids in these host molecules include, for instance, B,[2,42-45] Al,[6,46-49] In,[28-31,50,51] Si,[7,20,52-54] Ge,[21] Sn[8,22-27,32-41,55-58] and Hg.[9-13,28,50,59-65] High guest selectivity and high stability of the host-guest complexes are achieved when the host shows a high degree of preorganization and rigidity; in addition using bi- or multicentric Lewis acids it is possible to increase the complexation strength through chelate effects (Figure 2).



Katz **1985**

Gabbaï **1999**

Maruoka **1996**

Gabbaï **1998**

Jung, Xia **1988**

Takeuchi **1994**

X = H, Wuest **1986**
X = $CH_3$, Wuest **1998**
X = F, Gabbaï **1999**

*n* = 4, 6, 8, 10, 12

Newcomb **1988**

Jurkschat, Kuivila **1989**

Jurkschat **1993**

**Figure 2** Neutral molecular hosts with Lewis acids centers

Lewis acids are broadly used in chemistry because they can bind complementary Lewis bases and thereby modify their reactivity. An important example is the activation of carbonyl compounds by the formation of complexes,[6,10,13-15,17,59,66,67] for instance in Diels Alder reactions.[68-73]

Lewis acids can also have important effects on regio- as well as stereoselectivity, and play pivotal roles as cocatalyst in olefin polymerisation reactions.[48,74-77] Moreover, strong analogies exist between the activation induced by bicentric Lewis acids and catalytic processes that play important roles in nature. In particular, double coordination of the oxygen atom of carbonyl or phosphoryl groups is similar to double coordination of phosphoryl groups by two metal cations, which is believed to be a crucial step in different enzyme-catalyzed phosphoryl transfers.[78-80] In addition to all these properties the antitumor activity of such compounds is of interest.[81] For all these reasons, Lewis acids occupy an important role in contemporary chemistry.

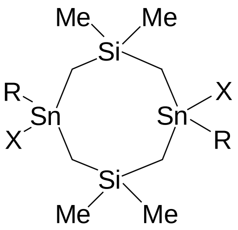
## Attempts

In the last years organometallic compounds of transition as well as of main group elements having an alkyl group bridging between two metals have been subject of increasing interest.[1,2,8,20-25,27,33-37,40,55,56,58,82-86]

The initial investigations on organotin compounds of this type were reported by Kuivila and coworkers in 1983, describing a series of bis(halomethylstannyl)methanes.[34] In recent years Jurkschat and others have continued research on bis(halostannyl)alkanes. They have shown that this kind of compounds are suitable precursors for tin-containing heterocycles[24,27,36,55,82,83,87-93] and exhibit a particular behaviour towards HMPA, DMSO and pyridine.[32,33,35,40,56,58]

In the last years different bicentric and multicentric cyclic Lewis acids were reported, where, in addition to halo-substituted tin centers, silicon atoms are found as ring-members (Figure 3).[87,88,91,92,94]

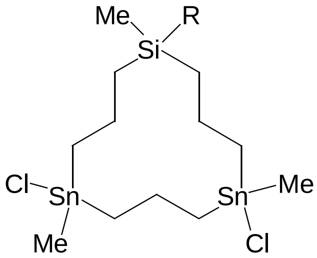
In 2000, Schulte reported the synthesis and complexation behaviour of **IV**-type compounds[87,88,91] towards anions (Figure 3). These rings containing disiloxane units (n = 3) can be attacked by both electrophiles (R = halide) and nucleophiles (R = Ph) to give ring opening polymerisation products.



**I**

R = Me; X = F, Cl
R = Cl; X = Cl

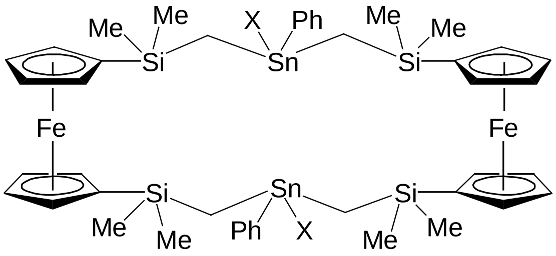
Kühn **1997**



**II**

R = F, O*i*-Pr

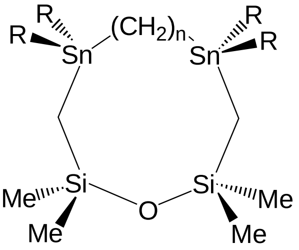
Hummeltenberg **1997**



**III**

X = F, Cl, I

Altmann **1998**



**IV**

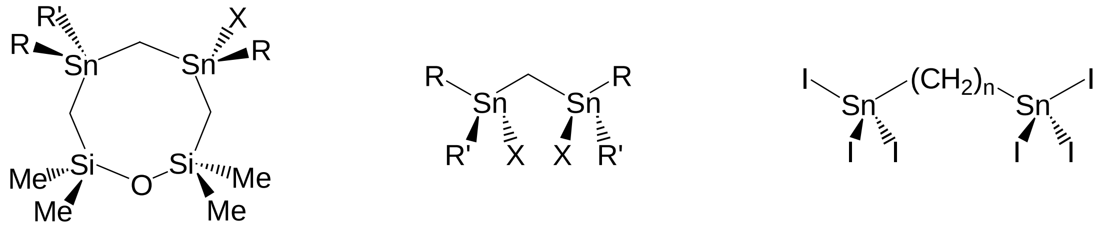
R = Ph, Cl
n = 1-3

Schulte **2000**

**Figure 3** Tin- and silicon-containing rings

In this work a series of cyclic eight-membered ditin compounds containing a siloxane unit (**A**, Figure 4) will be presented. Furthermore, their complexation behaviour towards neutral donor molecules such as DMSO, DMF and 1,3-dimethyl-imidazolidin-2-one will be investigated.

The complexation chemistry of Lewis acidic organotin(IV) halides has been intensively studied.[8,24,36,58,87,88,94-97] Reaction of alkyl-bridged di- and polystannanes with Lewis bases results in formation of the corresponding adducts.[8,22,24,32,35,36,55,95] The Lewis acidity of the tin atoms seems to increase when organo substituents are replaced by halides. For these reasons and because of the high selectivity of Lewis acidic organotin(IV) halides towards anions, bis(halostannyl)methanes (**B**, Figure 4) as well as novel bis(triiodostannyl)alkanes (**C**, Figure 4) have been synthesised. Furthermore, their complexation behaviour towards neutral donor molecules such as DMSO and DMF has been investigated.



**A**

R', X = Cl; R = Ph
R' = I; R, X = Ph
R, R' =Br, I

**B**

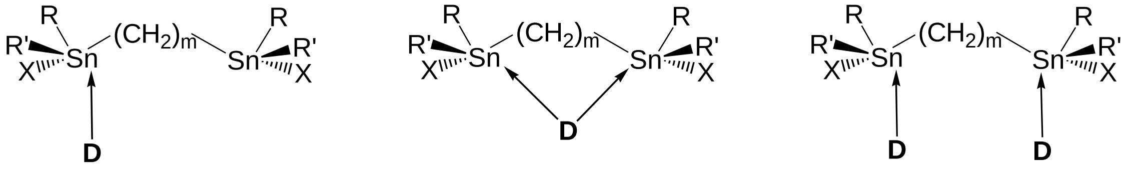
R = $CH_2SiMe_3$; R', X = I
R, R' = Ph; X = I, Br

**C**

n = 1, 3

**Figure 4** Target molecules

Previous work showed that bis(haloorganostannyl)alkanes can exhibit different coordination modes such as monocentric (**V**, Figure 5), or bicentric (**VI**, **VII** Figure 5), as well as polycentric ones. Derivative **A** and **C** for instance show **VI-** and **VII**-like structures, while a **V**-like structure is not observed.



**V** **VI** **VII**

**D** = donor molecule

R, R' = Me, Ph; X = halides
R = Me, Ph; R', X = halides
m = 1-n

**Figure 5** Possible bis(haloorganostannyl)alkanes-donor adducts.

# 1.2 Cyclic and non cyclic compounds containing the – $SiMe_2CH_2SnR_nX_{2-n}CH_2SnR_nX_{2-n}CH_2SiMe_2$ – unit (R = Ph, X = halide, n = 0-2)

## 1.2.1 Introduction

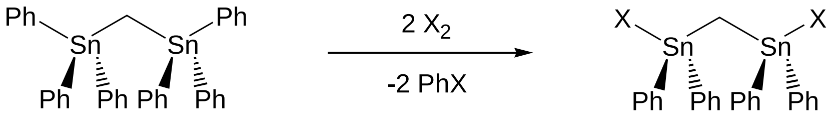
The complexation behaviour of bicentric methylene-bridged ditin compounds was intensively studied by Gielen and Jurkschat[35,56] as well as by Dakternieks and Jurkschat.[36] In 1997 Jurkschat reported the complexation behaviour of open-chain methylene-bridged tri- and tetratin compounds.[8]

The first cyclic silicon containing molecule with methylene-bridged tin atoms $Me_2Sn[CH_2Sn(Me_2)CH_2]_2SiMe_2$ was synthesized by Kühn[98] in 1997. However, in this case a replacement of the Sn-methyl groups by halogen atoms could not be achieved.

Here the synthesis of the eight-membered rings *cyclo*-$CH_2[SnR_nX_{2-n}CH_2Si(Me_2)OSi(Me_2)CH_2SnR_nX_{2-n}]$ (R = Ph, X = halide, n = 0-2) and their complexes as well as the molecular structures of the methylene-bridged ditin compounds $Ph_2Sn(X)CH_2(X)SnPh_2$ (X = I, Br) and $[Me_3SiCH_2(I_2)Sn]_2CH_2$ will be presented .

## 1.2.2 Synthesis of the cyclic and non cyclic target molecules

Treatment of bis(triphenylstannyl)methane (**1**) with two molar equivalents of iodine or bromine provided the corresponding bis(diphenylhalostannyl)methane[35,36,56] in almost quantitative yield (equation 1) as colourless oils. From these oils were isolated, respectively, bis(iododiphenylstannyl)methane (**2**) and bis(bromodiphenylstannyl)methane (**3**) as crystalline colourless solids. The molecular structures of compounds **2** and **3** will be discussed in chapter 1.2.4.

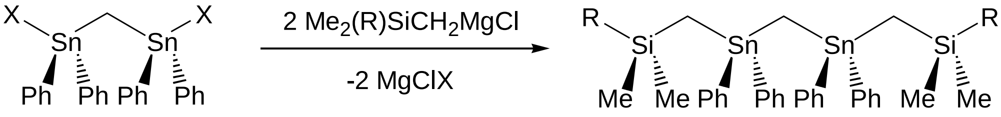


(1)

**1**

**2**, X = I
**3**, X = Br

The reaction of derivatives **2** and **3** with two molar equivalents of (dimethylsilyl)methylmagnesiumchloride,[99] (dimethylisopropoxysilyl)methylmagnesiumchloride[100] or (trimethylsilyl)methylmagnesiumchloride[99] afforded, respectively, bis{[(dimethylsilyl)methyl]diphenylstannyl}methane (**4**)[87,91], bis{[(dimethylisopropoxysilyl)methyl]diphenylstannyl}methane (**5**)[87,91] and bis{[(trimethylsilyl)methyl]diphenylstannyl}methane (**6**) (equation 2) as colourless oils in almost quantitative yield.



(2)

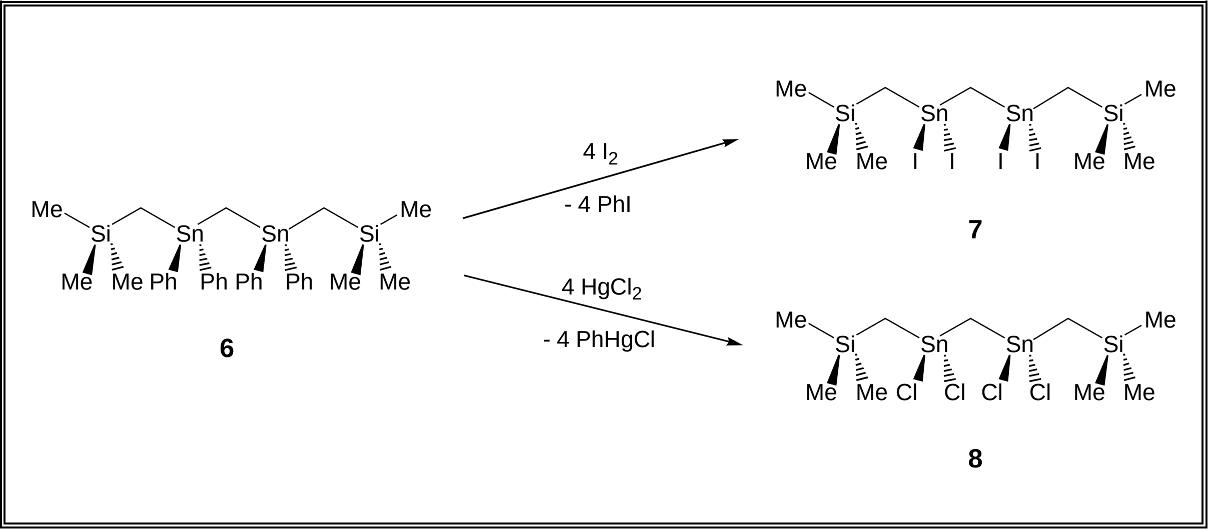
**2**, X = I
**3**, X = Br

**4**, R = H
**5**, R = O*i*-Pr
**6**, R = Me

Compound **6** was reacted with four molar equivalents of iodine or mercuric chloride to give the species **7** and **8** (Scheme 1). Compounds **7** and **8** were isolated as colourless crystals from $CH_2Cl_2$/*n*-hexane (1:1) for **7** and from *n*-hexane for **8** in 87% and 84% yield, respectively. Derivatives **7** and **8** are well soluble in chlorinated solvents, diethyl ether and acetone, but they are almost insoluble in *n*-hexane.

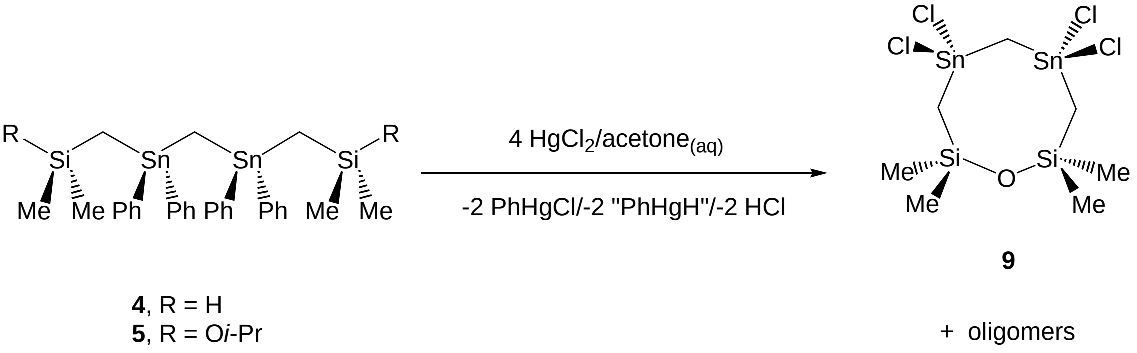
The $^{119}$Sn- and $^{29}$Si-NMR spectrum ($CH_2Cl_2$) of **7** shows a single resonance at $\delta$ -200.4 ($^{2}J(^{119}\text{Sn-}^{117/119}\text{Sn})$ = 310 Hz) and 3.8 ($^{2}J(^{29}\text{Si-}^{117/119}\text{Sn})$ = 43 Hz) ppm, respectively. The signal at $\delta$ -200.4 ppm in the $^{119}$Sn-NMR spectrum is typical for compounds with a $C_2SnI_2$ substituent pattern.[101] The molecular structure of compound **7** will be discussed in chapter 1.2.4, while suitable crystals for the structure determination of derivative **8** were not isolated.

The $^{119}$Sn- and $^{29}$Si-NMR spectra ($CDCl_3$), respectively, of **8** show a single resonance at $\delta$ 113.6 ($\nu^{1}/_{2}$ = 104 Hz) and 3.1 ($^{2}J(^{29}Si-^{117/119}Sn)$ = 47 Hz) ppm. Also in this case the signal at $\delta$ 113.6 ppm in the $^{119}$Sn-NMR spectrum is within the typical range for compounds with a $C_2SnCl_2$ substitution pattern.[101]



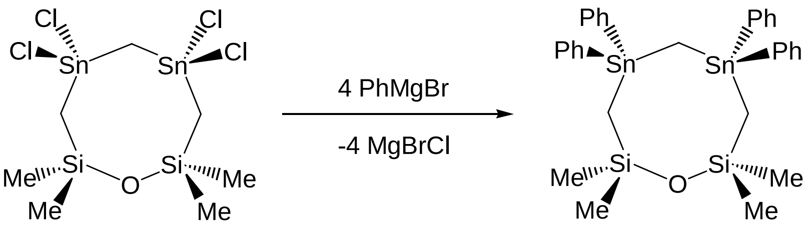
**Scheme 1** Synthesis of compounds **7** and **8**.

The treatment of compounds **4** or **5** with four molar equivalents of mercuric chloride provided the eight-membered ring species *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**) (equation 3).[87,91]



(3)

Reaction of compound **9** with four molar equivalents of phenylmagnesiumbromide produced the eight-membered ring *cyclo*-$CH_2[Sn(Ph_2)CH_2Si(Me_2)]_2O$ (**10**) (equation 4).[87,91]



**9** **10**

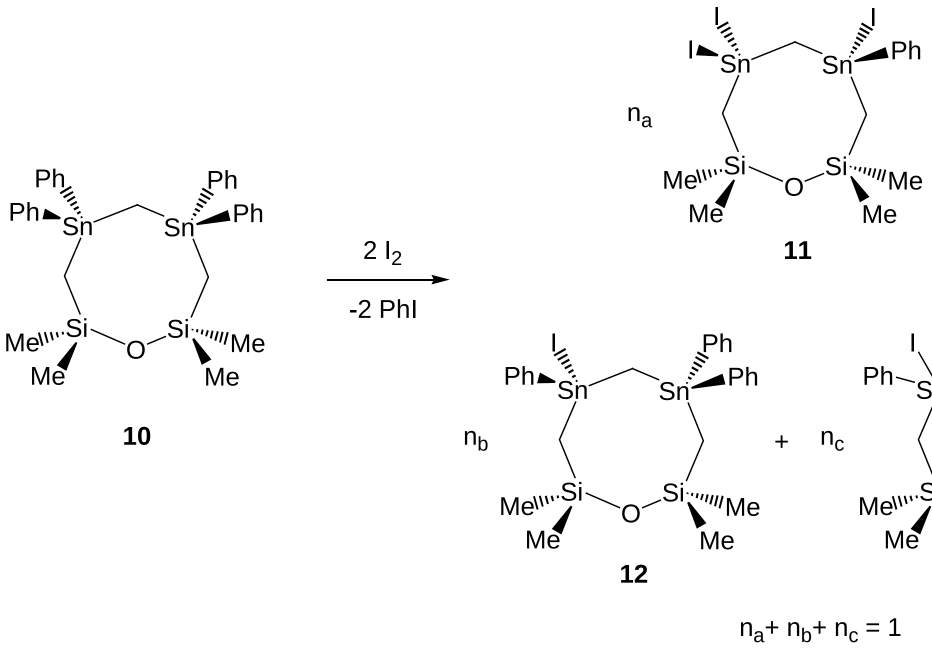
(4)

The reaction of 5,5,7,7-tetramethyl-1,1,3,3-tetraphenyl-1,3-distanna-5,7-disila-6-oxa-cyclooctane (**10**) with two molar equivalents of iodine (equation 5) afforded a viscous crude product, the $^{119}$Sn-NMR spectrum (*n*-hexane) of which showed two major signals at $\delta$ -45.8 (38%, $^{1}J(^{119}Sn–^{13}C)$ = 49 Hz, $^{1}J(^{119}Sn–^{13}C)$ = 263 Hz, $^{2}J(^{119}Sn–^{117/119}Sn)$ = 139 Hz) and –208.0 (43%, $^{1}J(^{119}Sn–^{13}C)$ = 55 Hz, $^{2}J(^{119}Sn–^{117/119}Sn)$ = 134 Hz) ppm as well as three minor resonances at $\delta$ -28.6, -38.5 and -70.3 ppm (total integral approximately 18% of the major signals). The signals at $\delta$ -45.5 and –208.0 ppm belong to the eight-membered ring species *cyclo*-[Sn(I$_2$)CH$_2$Sn(I)Ph{CH$_2$Si(Me$_2$)}$_2$O] (**11**). The other signals are assigned to the eight-membered ring species *cyclo*-[Sn(Ph$_2$)CH$_2$Sn(I)Ph{CH$_2$Si(Me$_2$)}$_2$O] (**12**) and to the *cis*- *trans*-isomers of *cyclo*-CH$_2$[Sn(I)PhCH$_2$Si(Me$_2$)]$_2$O] (**13**).

Compound **11** was isolated from CH$_2$Cl$_2$/*n*-hexane (1:1) in 58% yield. The eight-membered ring **11** is a colourless crystalline solid which is soluble in dichloromethane, diethyl ether, acetone, but less soluble in *n*-hexane. Compounds **12** and **13** could not be isolated from the reaction mixture.

The $^{119}$Sn-NMR spectrum of the eight-membered ring **11** (CDCl$_3$) shows two signal of same intensity and coupling at $\delta$ -40.0 and –196.5 ppm ($^{2}J(^{119}Sn-^{117/119}Sn)$ = 115 Hz). In the $^{29}$Si-NMR spectrum (CDCl$_3$) two signals are present at $\delta$ 11.9 ($^{2}J(^{29}Si-^{117/119}Sn)$ = 54 Hz) and 12.8 ($^{2}J(^{29}Si-^{117/119}Sn)$ = 48 Hz) ppm.

The molecular structure of **11** will be presented in chapter 1.2.5 together with the other ring species **14**, **15**, **16** and their complexes **17**, **18**, **19** and **20**.

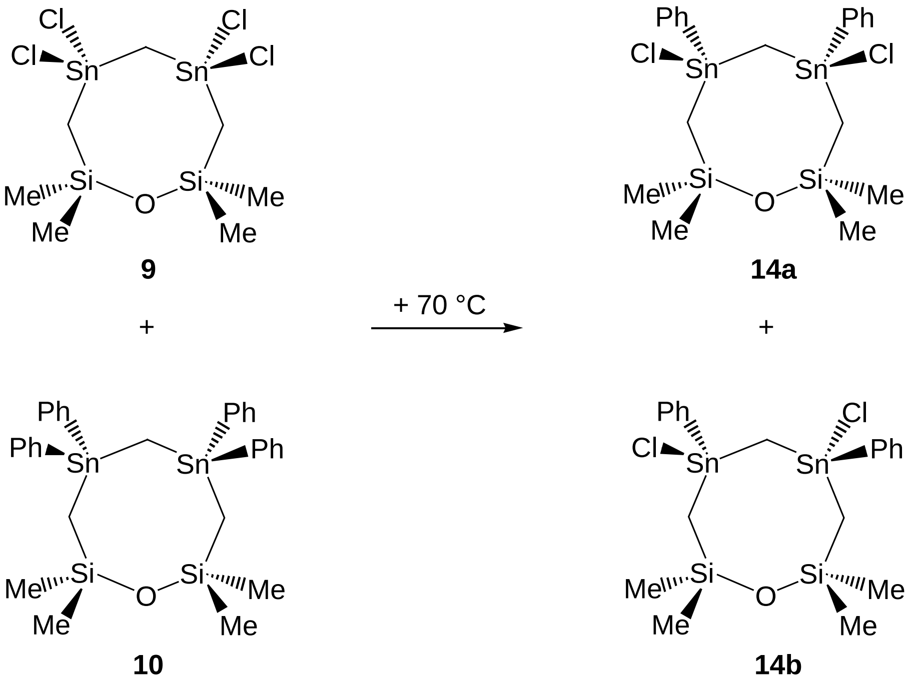


(5)

Treatment of *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O]$ (**9**) with one molar equivalent of *cyclo*-$CH_2\{Sn(Ph_2)CH_2Si(Me_2)]_2O]$ (**10**) at 70 °C provided the species **14** with monohalide substitution at each tin atom (equation 6). Compound **14** was isolated as a colourless crystalline solid from $CH_2Cl_2$/*n*-hexane (1:1) in 52% yield. Compound **14** is well soluble in chlorinated solvents and diethyl ether.

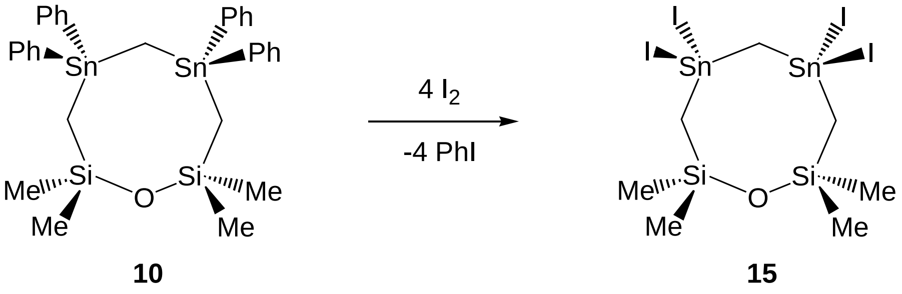
In $CDCl_3$, the tin atoms of **14** are equivalent on the $^{119}$Sn-NMR time scale, and a single resonance is observed at $\delta$ 89.4 ppm ($\nu\ ^1/_2$ = 145 Hz). The $^{119}$Sn-NMR spectrum in $CD_2Cl_2$ at -50 °C shows two signals at $\delta$ 87.6 (78%, $^2J(^{119}Sn-^{117}Sn)$ = 113 Hz) and 88.4 (22%, $\nu\,^1/_2$ = 30 Hz) ppm but the spectrum remains virtually the same at -80 °C with only a single resonance at $\delta$ 85.5 ppm ($\nu\,^1/_2$ = 47 Hz). The $^{29}$Si-NMR spectrum ($CDCl_3$) shows two signals at $\delta$ 12.2 (52%, $^2J(^{29}Si-^{117/119}Sn)$ = 57 Hz) and 13.2 (48%, $^2J(^{29}Si-^{117/119}Sn)$= 51 Hz) ppm. The NMR spectra indicate the existence in solution of the *cis*- *trans*-isomers **14a** and **14b**. At room temperature, the *cis-trans* isomerisation is fast on the $^{119}$Sn-NMR time scale but slow on the $^{29}$Si-NMR time scale. Similar findings have been reported by Altmann in 2000 for fc($SiMe_2CH_2SnClPhCH_2SiMe_2)_2$fc (fc = 1,1'-disubstituted ferrocene unit).[94,128]

The molecular structure of **14** will be discussed in chapter 1.2.5.



(6)

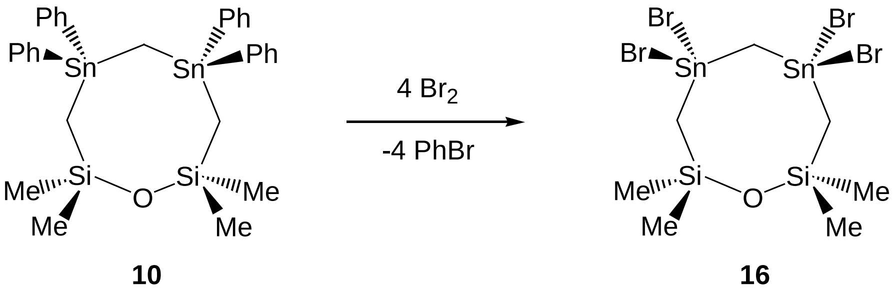
Reaction of the tetraphenyl-substituted eight-membered ring **10** with four molar equivalents of iodine afforded the tetraiodo-derivative **15** (equation 7). Compound **15** was recrystallised from $CH_2Cl_2$/*n*-hexane (1:1) to give colourless crystals in 54% yield. Compound **15** is well soluble in dichloromethane, acetone and diethyl ether.



(7)

The $^{119}$Sn- and $^{29}$Si-NMR spectra of the eight-membered ring **15** ($CDCl_3$) show single resonances at $\delta$ -222.0 ($^{119}$Sn) ($^{1}J(^{119}Sn-^{13}C)$ = 277 Hz) and 12.9 ($^{29}$Si) ($^{2}J(^{29}Si-^{117/119}Sn)$ = 56 Hz) ppm. The signal at $\delta$ -222.0 ppm in the $^{119}$Sn-NMR spectrum is typical for compounds with a $C_2SnI_2$ substitution pattern as already observed for derivative **7**.[101] The molecular structure of **15** will be discussed in chapter 1.2.5.

In order to conclude the serie of ring compounds with dihalide substitution at the tin atoms *cyclo*-$CH_2[Sn(Ph_2)CH_2Si(Me_2)]_2O]$ (**10**) was treated with four molar equivalents of bromine providing the tetrabromo-substituted derivative **16** (equation 8).



(8)

Derivative **16** was isolated from $CH_2Cl_2$/*n*-hexane (1:1) as a colourless crystalline solid in 51% yield. It is soluble in dichloromethane and diethyl ether but less soluble in *n*-hexane.

The $^{119}$Sn- and $^{29}$Si-NMR spectra in $CDCl_3$ of the eight-membered ring **16** show single resonances at $\delta$ 29.4 ($^2J(^{117}Sn-^{119}Sn)$ = 305 Hz) and 14.2 ($^2J(^{29}Si-^{117/119}Sn)$ = 57 Hz) ppm, respectively.

Again the signal at $\delta$ 29.4 ppm in the $^{119}$Sn-NMR spectrum is within the typical range for compounds with a $C_2SnBr_2$ substitution pattern.[101] The molecular structure of **16** will be discussed in chapter 1.2.5.

### 1.2.3 Complexation behaviour of 1,1,3,3-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane towards DMSO, DMF and 1,3-dimethyl-imidazolidin-2-one

The complexation behaviour of *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**) towards chloride and fluoride ions was already investigated by Schulte and others.[87] Schulte reported in 2001 the quantitative formation of 1:1 complexes with chloride as well as with fluoride ions.

In order to investigate the complexation behaviour of these compounds towards neutral donor molecules some experiments were carried out. *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**) was reacted with two molar equivalents of DMSO providing the 1:2 complex **17** (equation 9).

**9**

**17**

(9)

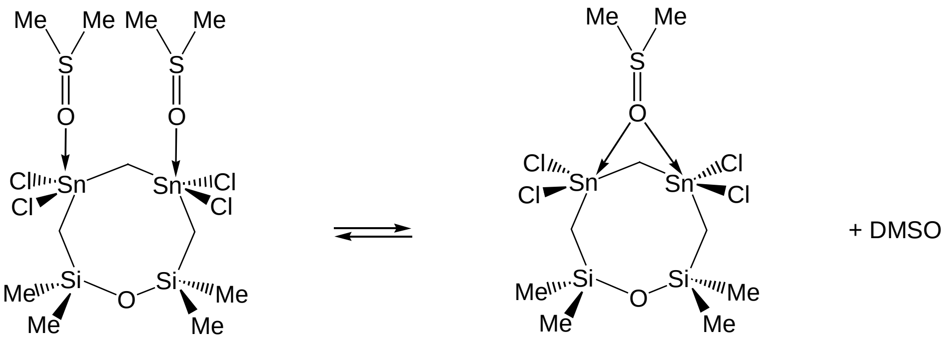
Compound **17** was isolated as colourless crystals in 75% yield. It is well soluble in dichloromethane and diethyl ether but less soluble in *n*-hexane.

The $^{119}$Sn- and $^{29}$Si-NMR spectra of **17** ($CDCl_3$) show signals at $\delta$ 16.6 ($\nu^{1}/_{2}$ = 81 Hz) and 11.4 ($^{2}J(^{29}\text{Si-}^{117/119}\text{Sn})$ = 53 Hz) ppm, respectively.

The molecular structure of **17** will be discussed in chapter 1.2.5.

When derivative **17** is dissolved in $CH_2Cl_2$/*n*-hexane 1:1, another complex with only one molecule of DMSO is obtained. The formation of the 1:1 complex **18** can be explained with the presence of an equilibrium between **17** and **18** in solution (equation 10).

Adduct **18** is a colourless crystalline solid whose molecular structure will be discussed in chapter 1.2.5. Other investigations on compound **18** could not be carried out.

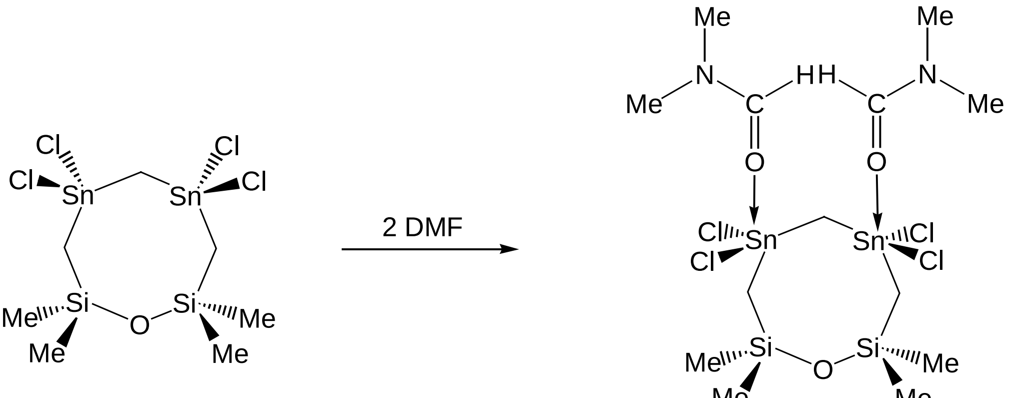


(10)

**17** **18**

Reaction of compound **9** with two molar equivalents of DMF provided the 1:2 complex **19** (equation 11). Adduct **19** was isolated from $CH_2Cl_2$ as colourless crystalline solid in 56% yield. Compound **19** is well soluble in dichloromethane and diethyl ether but it is almost insoluble in *n*-hexane. The $^{119}$Sn- and $^{29}$Si-NMR spectra of **19** ($CH_2Cl_2$) show resonances at $\delta$ -30.5 ($^2J(^{119}\text{Sn}-^{117/119}\text{Sn})$ = 864 Hz) and 11.2 ($^2J(^{29}\text{Si}-^{117/119}\text{Sn})$ = 56 Hz) ppm, respectively.

The molecular structure of **19** will be discussed in chapter 1.2.5.



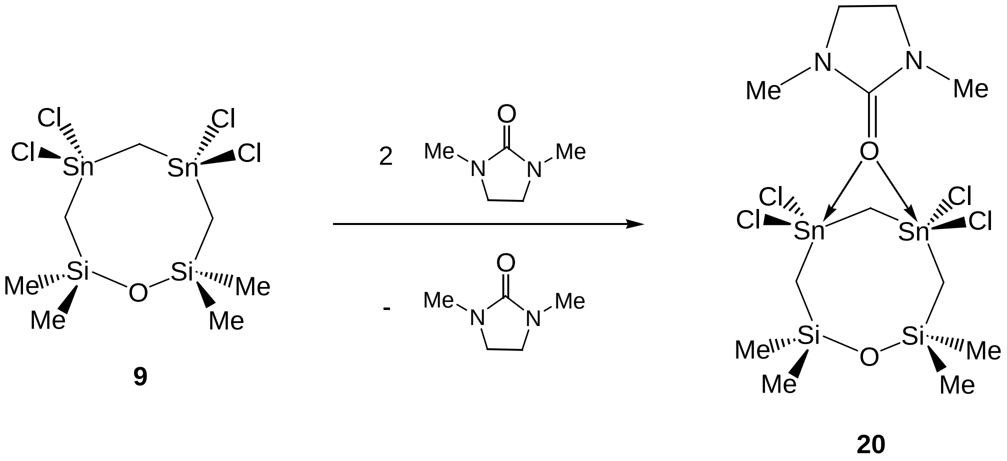
(11)

**9** **19**

The reaction of compound **9** with two molar equivalents of 1,3-dimethyl-imidazolidin-2-one afforded exclusively the 1:1 complex **20** (equation 12). Complex **20** was isolated from $CH_2Cl_2$ as colourless crystals in 58% yield. It is well soluble in dichloromethane and diethyl ether but almost insoluble in *n*-hexane.

The $^{119}$Sn- and $^{29}$Si-NMR spectra of **17** in $CDCl_3$ show signals at $\delta$ 20.3 ($\nu^{1}/_{2}$ = 52 Hz) and 12.0 ($^{2}J(^{29}\mathrm{Si}–^{117/119}\mathrm{Sn})$ = 56 Hz) ppm, respectively. These data show the equivalence of the silicon and the tin atoms on the NMR timescales and suggest the structure in solution to be similar to that found in the solid state.

The molecular structure of **20** will be discussed in chapter 1.2.5.



(12)

## 1.2.4 Molecular structures of bis(iododiphenylstannyl)methane (2), bis(bromodiphenylstannyl)methane (3) and bis{diiodo[(trimethylsylil)-methyl]stannyl}methane (7)

Suitable crystals for the molecular structure determination of compounds **2**, **3** were obtained by slow evaporation of the solvent in a $CH_2Cl_2$ solution and of derivative **7** by slow evaporation of dichloromethane in a 1:1 $CH_2Cl_2$/*n*-hexane solution at room temperature. Compound **2** crystallises in the space monoclinic group $P2_1/c$ with four molecules in the unit cell. Derivative **3** crystallises in the orthorhombic space group *Pbca* with eight molecules in the unit cell. Compound **7** crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell.

The molecular structures of **2**, **3** and **7** are illustrated in Figures 6, 7 and 10. Figures 8 and 9 show the one-dimensional polymeric chain and the structure on the Sn(1), Br(1) and Br(1A) plane of compound **3**. Selected bond lengths and angles for **2**, **3** and **7** are listed in Tables 1, 2 and 3, respectively.

In compound **2** the intermolecular Sn···I distances are longer than the sum of the van der Waals radii of tin (2.20 Å)[104] and iodine (2.10 Å)[104].

Sn(1) is tetracoordinated with a nearly ideal tetrahedral coordination geometry while Sn(2) is [4+1] coordinated, with a monocapped tetrahedral coordination geometry (Figure 6).

The Sn-C bond distances range from 2.126(3) to 2.136(3) Å, while the Sn(1)-I(1) and Sn(2)-I(2) bonds has distances of 2.7146(3) and 2.7365(3) Å. In addition, at Sn(2) one intramolecular Sn(2)···I(1) interaction of 4.1109(3) Å is present. The latter Sn···I distance is shorter than the sum of the van der Waals radii of tin and iodine.[104] The Sn(1)-I(1) bond is shorter than the Sn(2)-I(2) bond and the two Sn(1)-C(1) and Sn(2)-C(1) bonds are slightly asymmetric. At Sn(2) the I(1)-Sn(2)-I(2) angle amounting to 167.162(9)° differ from the ideal value of 180°. The Sn(1)-C(1)-Sn(2) bond angle amounts to 119.34(13)° with a significant deviation from the ideal value of 109°.

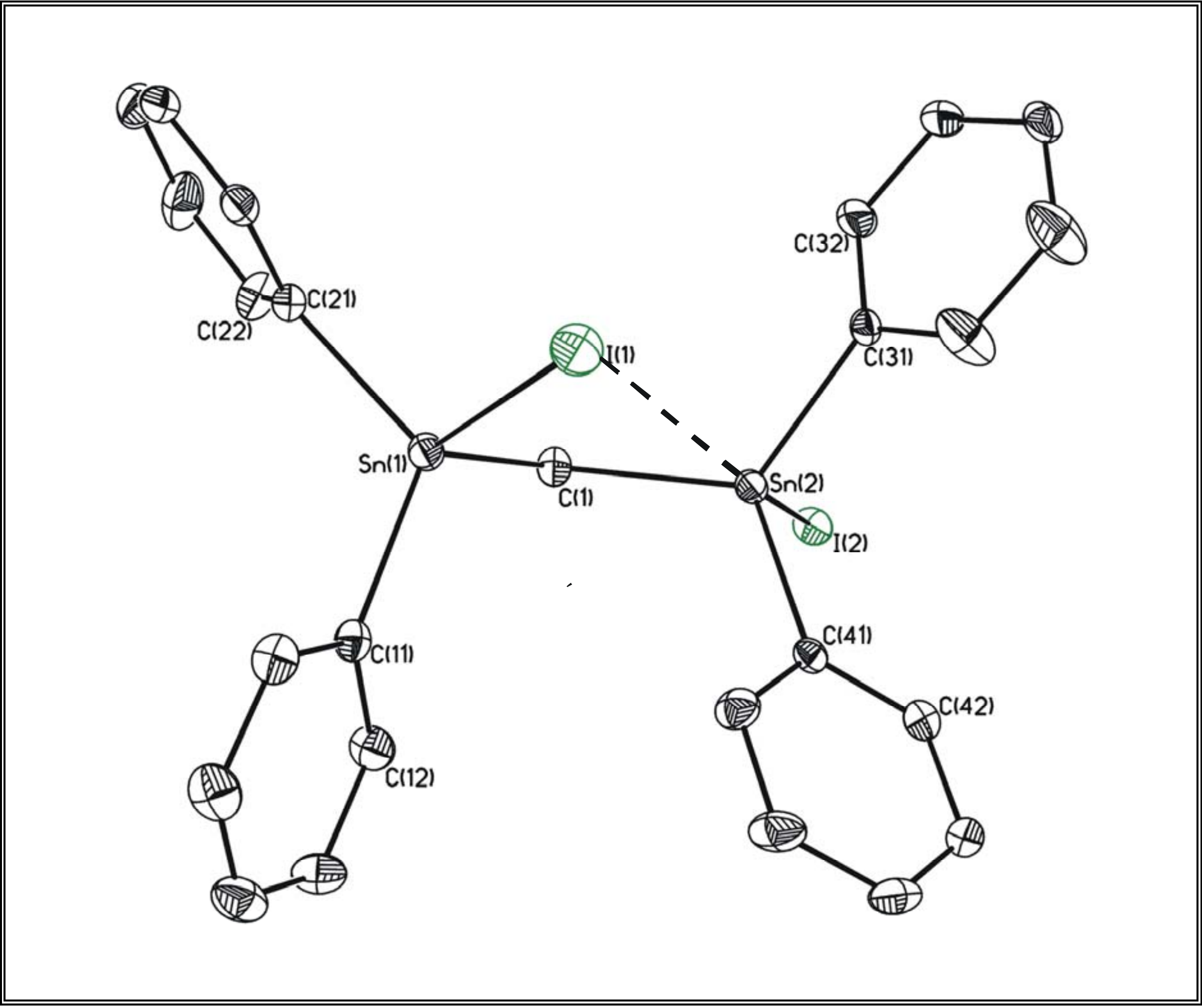


**Figure 6** Molecular structure (SHELXL-97) of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme.

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

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.131(3) | Sn(2)-C(31) | 2.126(3) |
| Sn(1)-C(11) | 2.130(3) | Sn(2)-C(41) | 2.135(3) |
| Sn(1)-C(21) | 2.135(3) | Sn(2)-I(1) | 4.1109(3) |
| Sn(1)-I(1) | 2.7146(3) | Sn(2)-I(2) | 2.7365(3) |
| Sn(2)-C(1) | 2.136(3) | | |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(11) | 113.32(11) | C(1)-Sn(2)-I(2) | 101.48(8) |
| C(1)-Sn(1)-C(21) | 108.82(11) | C(31)-Sn(2)-C(41) | 110.72(11) |
| C(1)-Sn(1)-I(1) | 106.14(8) | C(31)-Sn(2)-I(1) | 75.74(7) |

**Table 1** continued.

| | | | |
|---|---|---|---|
| C(11)-Sn(1)-C(21) | 118.69(11) | C(31)-Sn(2)-I(2) | 103.42(7) |
| C(11)-Sn(1)-I(1) | 104.28(8) | C(41)-Sn(2)-I(1) | 86.45(7) |
| C(21)-Sn(1)-I(1) | 104.35(9) | C(41)-Sn(2)-I(2) | 105.57(7) |
| C(1)-Sn(2)-C(31) | 119.83(11) | I(1)-Sn(2)-I(2) | 167.162(9) |
| C(1)-Sn(2)-C(41) | 113.73(11) | Sn(1)-C(1)-Sn(2) | 119.34(13) |
| C(1)-Sn(2)-I(1) | 68.86(8) | Sn(1)-I(1)-Sn(2) | 61.351(6) |

Contrary to derivative **2**, bis(bromodiphenylstannyl)methane (**3**) shows intermolecular coordination with neighbour molecules realizing in this way a one-dimensional polymeric chain (Figure 8). The two tin centers Sn(1) and Sn(2) are [4+1] coordinated and caracterised by a monocapped distorted tetrahedral coordination geometry (Figure 7). This configuration is realised by intramolecular Sn(2)···Br(1) and intermolecular Sn(1)···Br(1A) contacts of 3.4232(13) and 3.2496(12) Å, respectively. Notably, the intermolecular Sn(1)···Br(1A) distance is shorter than the intramolecular Sn(2)···Br(1) distance. The intra- and intermolecular Sn···Br contacts are shorter than the sum of the van der Waals radii of tin and bromine (2.00 Å).[104] The Sn-C bond lengths are as expected and fall in the range between 2.107(8) and 2.123(10) Å. The two Sn(1)-C(1) and Sn(2)-C(1) bonds are slightly asymmetric and in general the bonds relative to Sn(1) are shorter than those to Sn(2). The Sn(1)-Br(1) and Sn(2)-Br(2) distances amount to 2.5578(12) and 2.5844(13) Å, respectively.

The Br(1)-Sn(1)-Br(1A) and Br(1)-Sn(2)-Br(2) angles, which amount to 173.62(4)° and 175.64(4)°, respectively, differ slightly from the ideal value of 180°.

The Sn(1)-C(1)-Sn(2) bond angle amounts to 116.9(4)° with a significant deviation from the ideal value of 109°.

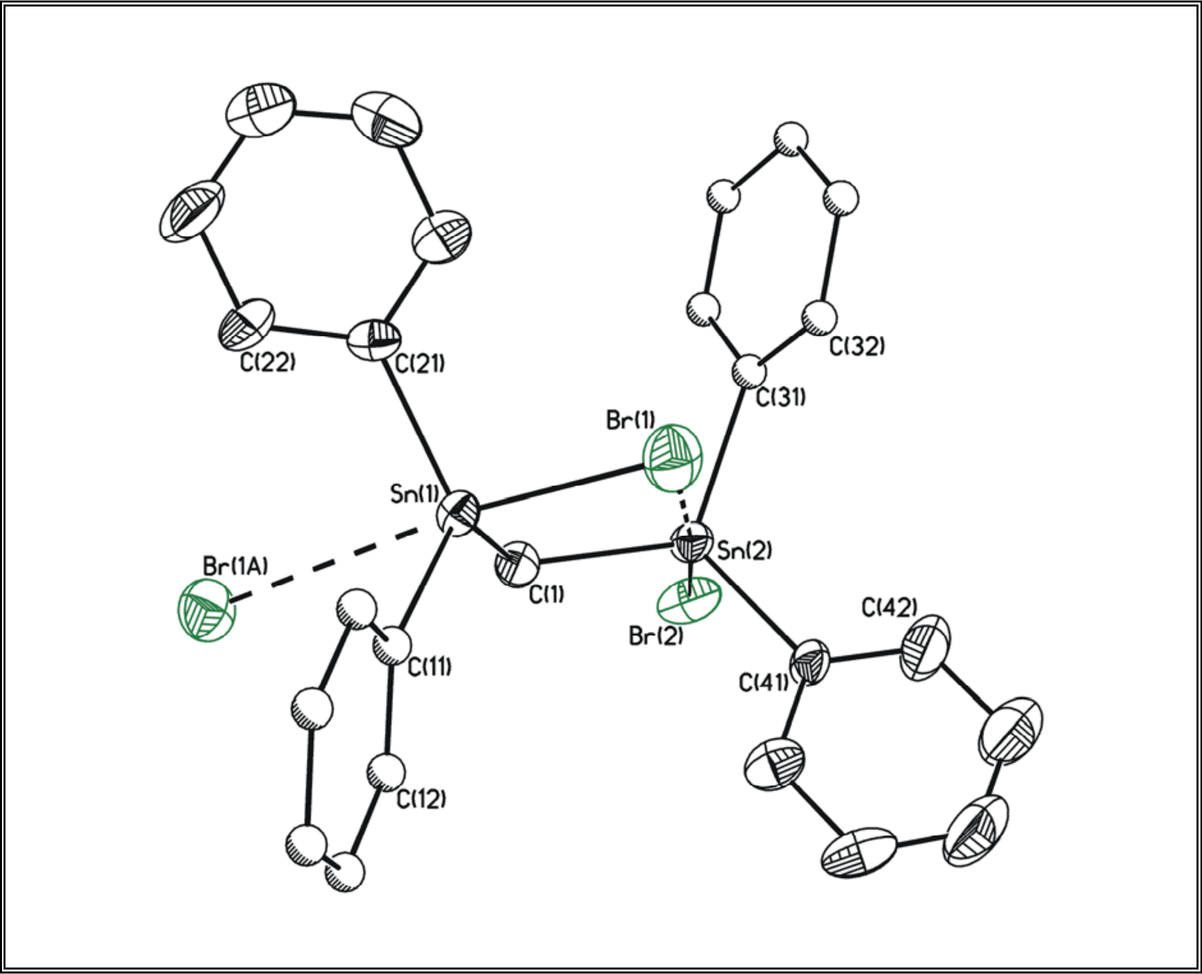


**Figure 7** Molecular structure (SHELXL-97) of **3** showing 30% probability displacement ellipsoids and the atom numbering scheme. Two phenyl groups are disordered over two positions and were isotropically refined as regular hexagons.

Compound **3** has a polymeric structure in which the molecules are connected by intermolecular Sn···Br contacts (Figure 8). A similar structure with a zig-zag pattern has been reported for the corresponding $[Ph_2Sn(Cl)]_2CH_2$, in which only one of the two chloride interacts with three tin centers by two intramolecular and one intermolecular bonds.[40]

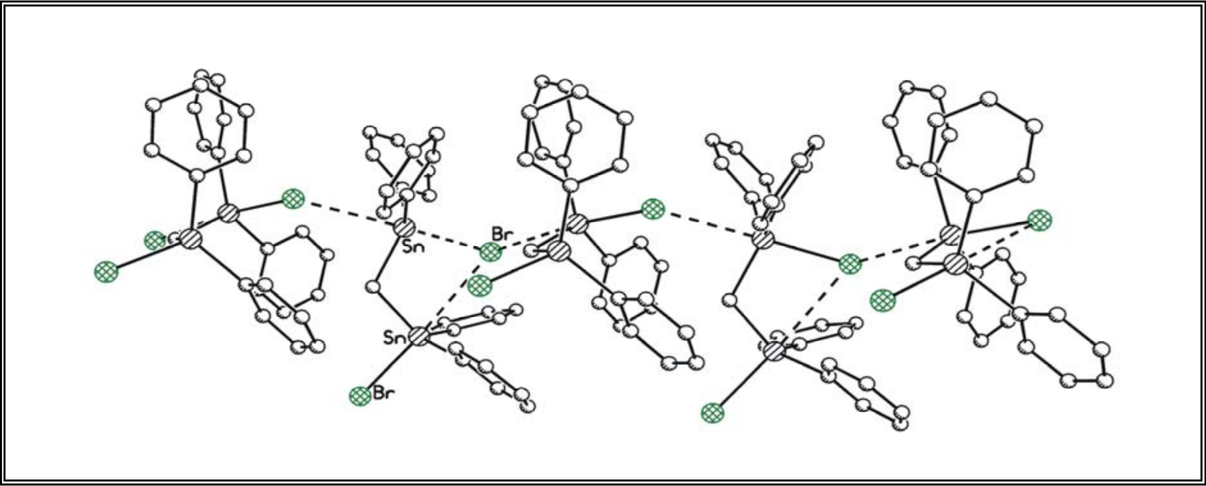


**Figure 8** One-dimensional polymeric chain structure of compound **3**.

In the one-dimensional chain structure of **3**, the intermolecularly coordinated bromine atom is alternatively also intramolecularly coordinated. Furthermore in this polymeric chain all Sn(1), Br(1) and Br(1A) atoms are on the same plane realising the structure shown in Figure 9.

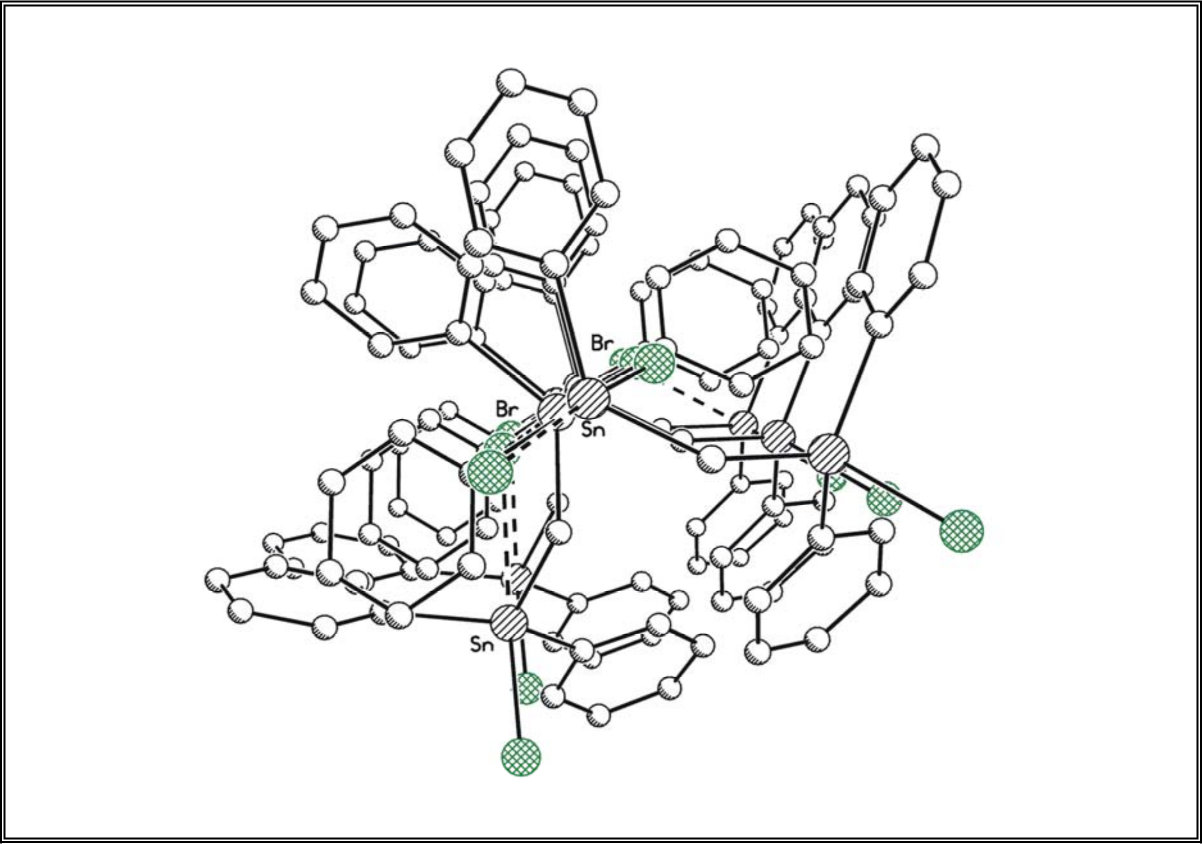


**Figure 9** Structure of **3** on the Sn(1), Br(1) and Br(1A) plane.

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

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.108(8) | Sn(2)-C(1) | 2.121(8) |
| Sn(1)-C(11) | 2.109(11) | Sn(2)-C(31) | 2.123(10) |
| Sn(1)-C(21) | 2.107(8) | Sn(2)-C(41) | 2.115(89) |
| Sn(1)-Br(1) | 2.5578(12) | Sn(2)-Br(1) | 3.4232(13) |
| Sn(1)-Br(1A) | 3.2496(12) | Sn(2)-Br(2) | 2.5844(13) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(11) | 122.9(5) | C(1)-Sn(2)-C(41) | 115.5(3) |
| C(1)-Sn(1)-C(21) | 117.7(3) | C(1)-Sn(2)-Br(1) | 74.0(2) |
| C(1)-Sn(1)-Br(1) | 96.5(2) | C(1)-Sn(2)-Br(2) | 101.7(2) |
| C(1)-Sn(1)-Br(1A) | 82.9(2) | C(31)-Sn(2)-C(41) | 114.7(5) |
| C(11)-Sn(1)-C(21) | 112.8(5) | C(31)-Sn(2)-Br(1) | 78.0(4) |
| C(11)-Sn(1)-Br(1) | 100.5(5) | C(31)-Sn(2)-Br(2) | 104.7(4) |
| C(11)-Sn(1)-Br(1A) | 74.7(5) | C(41)-Sn(2)-Br(1) | 79.6(2) |
| C(21)-Sn(1)-Br(1) | 99.0(3) | C(41)-Sn(2)-Br(2) | 102.1(2) |
| C(21)-Sn(1)-Br(1A) | 86.9(2) | Br(1)-Sn(2)-Br(2) | 175.64(4) |
| Br(1)-Sn(1)-Br(1A) | 173.62(4) | Sn(1)-C(1)-Sn(2) | 116.9(4) |
| C(1)-Sn(2)-C(31) | 115.4(4) | Sn(1)-Br(1)-Sn(2) | 72.46(3) |

The molecular structure of the tetraiodo-substituted compound **7**, as well as the diiodo-substituted derivative **2**, does not show intermolecular coordination with neighbour molecules as it could be expected (Figure 10). Both tin atoms Sn(1) and Sn(2) have a monocapped tetrahedral coordination geometry with a [4+1] coordination.

The deviation from an ideal tetrahedral or trigonal bipyramidal coordination geometry can be estimated by Dräger's method.[105-107] In this method only the six angles of a tetrahedral configuration are considered. In the transition to trigonal bipyramid three of these angles are converted to equatorial angles and the sum of them increase from 328.5° to 360°. The other three angles become axial angles and the sum of these angles decrease from 328.5° to 270°. The difference of both sums

($\Delta(\sum\vartheta) = \Delta\vartheta_{eq} - \Delta\vartheta_{ax}$) amounts to 0° for an ideal tetrahedron and 90° for an ideal trigonal bipyramid.

In case of compound **7**, the sums are $\Delta(\sum\vartheta)$ = 17.7° for Sn(1) and $\Delta(\sum\vartheta)$ = 17.3° for Sn(2).

The Sn-C bond lengths range from 2.124(5) to 2.135(5) Å, while the Sn-I bond distances are as expected and within the range 2.6988(5)-2.7067(5) Å. The intramolecular Sn(1)···I(4) and Sn(2)···I(2) interactions have distances of 4.1470(5) and 4.1052(5) Å, respectively. The latter distances are shorter than the sum of the van der Waals radii of tin and iodine.[104] Furthermore the two Sn(1)-C(1) and Sn(2)-C(1) bonds are almost symmetric.

The I(1)-Sn(1)-I(4) and I(2)-Sn(2)-I(3) angles amount to 169.850(16) and 173.746(16)°. For the shorter Sn(2)···I(2) contact there is a smaller deviation from the ideal value of 180°.

The Sn(1)-C(1)-Sn(2) angle amounts to 114.6(2)° with a deviation from the ideal value of 109°.

Furthermore, the Sn-C-Sn angles of compounds **2**, **3** and **7** are comparable with the corresponding angles in related methylene-bridged ditin compounds $(Ph_2SnCl)_2CH_2$ (113.4(10)°),[40] $(PhSnBr_2)_2CH_2$ (115.1(5)°)[102] and $(Ph_3Sn)_2CH_2$ (122.8(1) / 122.4(1)°).[103]

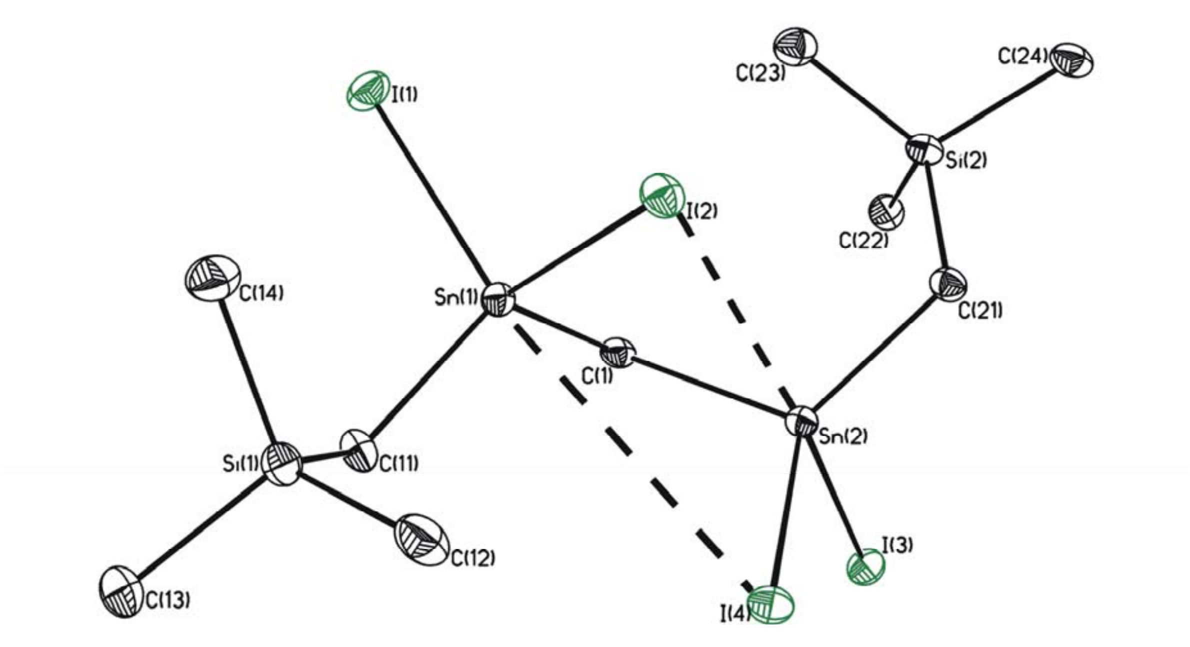


**Figure 10** Molecular structure (SHELXL-97) of **7** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 3** Selected bond lengths [Å] and bond angles [°] of **7**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.135(5) | Sn(2)-C(21) | 2.124(5) |
| Sn(1)-C(11) | 2.126(5) | Sn(2)-I(2) | 4.1052(5) |
| Sn(1)-I(1) | 2.6988(5) | Sn(2)-I(3) | 2.7067(5) |
| Sn(1)-I(2) | 2.7015(5) | Sn(2)-I(4) | 2.7048(5) |
| Sn(1)-I(4) | 4.1470(5) | Si(1)-C(11) | 1.883(5) |
| Sn(2)-C(1) | 2.134(5) | Si(2)-C(21) | 1.884(5) |
| **Bond angles [°]** | | | |
| C(1)-Sn(1)-C(11) | 114.68(19) | I(3)-Sn(2)-I(4) | 100.322(16) |
| C(1)-Sn(1)-I(1) | 106.48(13) | Sn(1)-C(1)-Sn(2) | 114.6(2) |
| C(1)-Sn(1)-I(2) | 107.93(14) | Sn(1)-I(2)-Sn(2) | 59.519(11) |
| C(1)-Sn(1)-I(4) | 66.80(13) | Sn(1)-I(4)-Sn(2) | 58.823(12) |
| C(11)-Sn(1)-I(1) | 109.92(16) | Sn(1)-C(11)-Si(1) | 119.5(3) |
| C(11)-Sn(1)-I(2) | 114.20(14) | Sn(2)-C(21)-Si(2) | 113.3(3) |

**Table 3** continued.

| | | | |
|---|---|---|---|
| C(11)-Sn(1)-I(4) | 80.14(16) | C(11)-Si(1)-C(12) | 111.2(3) |
| I(1)-Sn(1)-I(2) | 102.712(16) | C(11)-Si(1)-C(13) | 107.2(2) |
| I(1)-Sn(1)-I(4) | 169.850(16) | C(11)-Si(1)-C(14) | 108.9(3) |
| I(2)-Sn(1)-I(4) | 73.363(13) | C(12)-Si(1)-C(13) | 109.1(3) |
| C(1)-Sn(2)-C(21) | 116.7(2) | C(12)-Si(1)-C(14) | 111.5(3) |
| C(1)-Sn(2)-I(2) | 69.98(13) | C(13)-Si(1)-C(14) | 108.9(3) |
| C(1)-Sn(2)-I(3) | 109.40(13) | C(21)-Si(2)-C(22) | 108.4(2) |
| C(1)-Sn(2)-I(4) | 104.61(13) | C(21)-Si(2)-C(23) | 110.8(2) |
| C(21)-Sn(2)-I(2) | 75.96(14) | C(21)-Si(2)-C(24) | 109.2(3) |
| C(21)-Sn(2)-I(3) | 109.37(14) | C(22)-Si(2)-C(23) | 109.0(3) |
| C(21)-Sn(2)-I(4) | 115.09(14) | C(22)-Si(2)-C(24) | 109.2(3) |
| I(2)-Sn(2)-I(3) | 173.746(16) | C(23)-Si(2)-C(24) | 110.2(3) |
| I(2)-Sn(2)-I(4) | 74.090(12) | | |

### 1.2.5 Molecular structures of the eight-membered ring compounds 11, 14, 15, 16 and their complexes 17, 18, 19, 20

Suitable crystals for the molecular structure determination of compounds **11**, **14**, **15**, **16**, **17**, **18**, **19** and **20** were obtained by slow evaporation of their $CH_2Cl_2$/*n*-hexane solutions (1:1) at room temperature. Derivative **11** crystallises in the triclinic space group *P*-1 with two molecules in the unit cell. Compound **14** crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Compound **15** crystallises in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell. Compound **16** crystallises in the triclinic space group *P*-1 with eight molecules in the unit cell. Compound **17** crystallises in the triclinic space group *P*-1 with two molecules in the unit cell. Compound **18** crystallises in the triclinic space group *P*-1 with two molecules in the unit cell. Compound **19** crystallises in the triclinic space group *P*-1 with two molecules in the unit cell. Derivative **20** crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell.

The molecular structures of **11**, **14**, **15**, **16**, **17**, **18**, **19** and **20** are illustrated in Figures 10, 11, 12, 13, 14, 15, 16 and 17. Selected bond lengths and angles as well as torsion angles for **11**, **14**, **15**, **16**, **17**, **18**, **19** and **20** are listed in Tables 4, 5, 6, 7, 8, 9, 10 and 11, respectively.

The eight-membered triiodo-substituted ring **11** crystallises in a polymeric structure with intermolecular Sn(2)···I(3A) contacts (Figure 11). The coordination geometry at Sn(1) and Sn(2) can be best described for both tin atoms as a bicapped distorted tetrahedron. The configuration is realised by three intramolecular Sn(1)···O(1), Sn(1)···I(2), Sn(2)···O(1) interactions of 3.627(3), 3.9875(6), 3.039(3), respectively, and one intermolecular Sn(2)···I(3A) interaction of 4.3096(6) Å. The intramolecular Sn···O distances are at the borderline or shorter than the sum of the van der Waals radii of tin (2.20 Å)[104] and oxygen (1.50 Å).[104] Intramolecular Sn···O distances of 2.884(3)-3.067(2) Å and 2.38(4) Å have been reported for compounds in which the tin and the oxygen atoms are part of four-[108-109] and five-membered[110,111] rings, respectively. Also the Sn(1)···I(2) and Sn(2)···I(3A) distances are shorter than or at the borderline of the sum of the van der Waals radii of tin and iodine (2.10 Å).[104] The Sn-C bond distances are as expected and range from 2.123(5) to 2.148(5) Å. The Sn(1)-I(1), Sn(2)-I(2) Sn(2)-I(3) bonds have lengths of 2.7271(6), 2.6935(5) and 2.7311(5) Å, respectively. Furthermore the two Sn(1)-C(1) and Sn(2)-C(1) distances are slightly asymmetric.

The I(1)-Sn(1)-I(2), C(11)-Sn(1)-O(1), I(2)-Sn(2)-I(3A) and I(3)-Sn(2)-O(1) angles amount to 169.334(16)°, 132.85(15)°, 165.200(16)° and 168.97(7)°, respectively. The deviation of these angles from the ideal value of 180° can be explained as a result of ring constraints. The weak intramolecular Sn···O interactions are associated with the Si(1)-O(1)-Si(2) angle of 143.2(2)°, which is smaller than that of compound **9**[87,91] and which is at the lower end of a range of corresponding angles in eight-membered *cyclo*-stannasiloxanes that have no such contacts.[102]

The silicon atoms have an almost ideal tetrahedral coordination geometry. The Si(1)-O(1) and Si(2)-O(1) bond lengths with 1.639(4) and 1.641(4) Å are within the range of standard Si-O bond lengths reported in the literature,[112-114] indicating that the intramolecular Sn···O contacts mentioned above are mainly of electrostatic nature.[87]

The molecular structure of **11** shows that Sn(1) and Sn(2) are not equivalent and moreover, the Sn(1) is chiral.

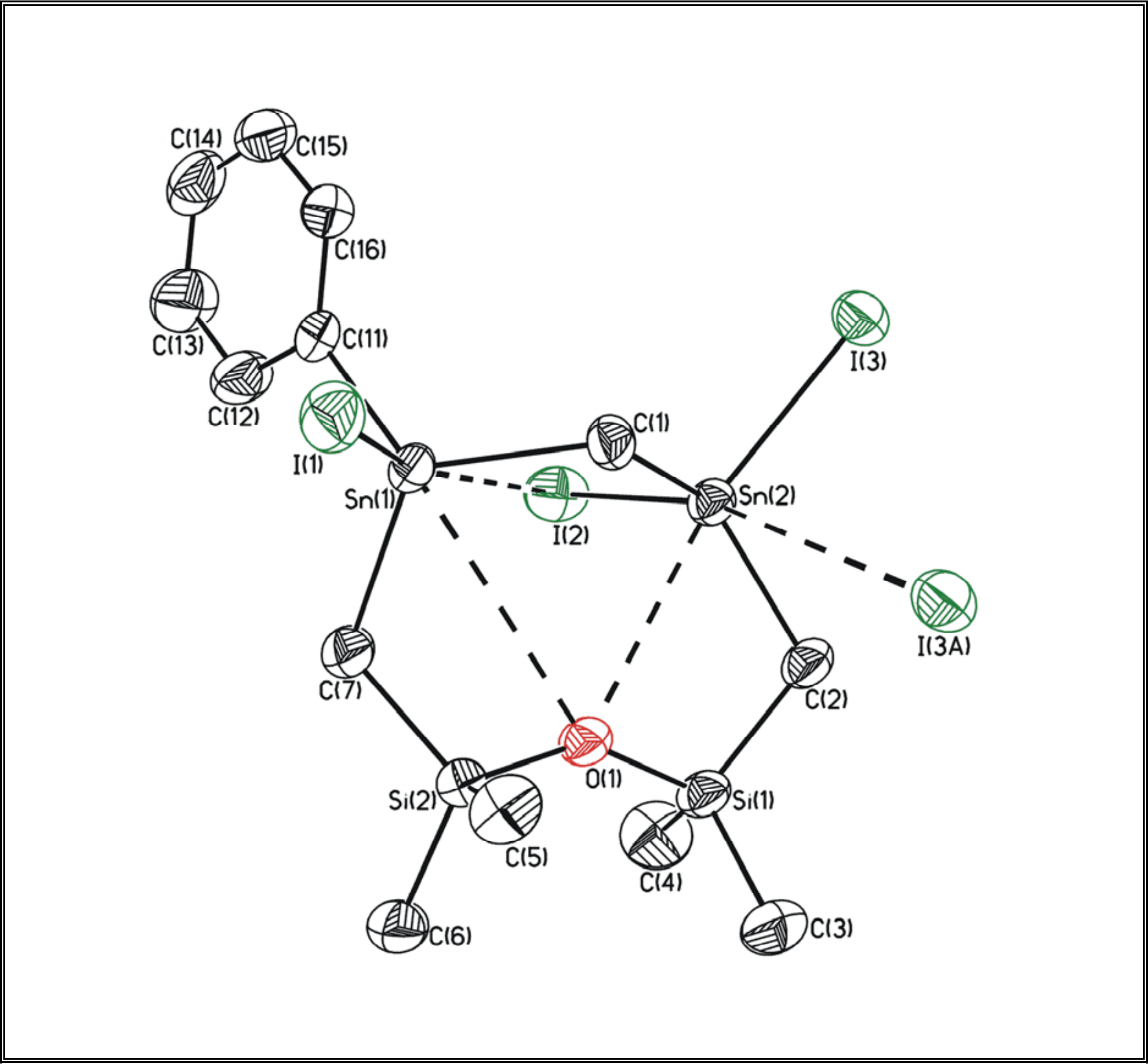


**Figure 11** Molecular structure (SHELXTL-PLUS) of **11** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 4** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **11**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.123(3) | Sn(2)-C(2) | 2.123(5) |
| Sn(1)-C(7) | 2.127(5) | Sn(2)-I(2) | 2.6935(5) |
| Sn(1)-C(11) | 2.148(5) | Sn(2)-I(3) | 2.7311(5) |
| Sn(1)-I(1) | 2.7271(6) | Sn(2)-O(1) | 3.039(3) |
| Sn(1)-I(2) | 3.9875(6) | Sn(2)-I(3A) | 4.3096(6) |
| Sn(1)-O(1) | 3.627(3) | Si(1)-O(1) | 1.639(4) |
| Sn(2)-C(1) | 2.129(5) | Si(2)-O(1) | 1.641(4) |

**Table 4** continued.

| Bond angles [°] | | | |
|---|---|---|---|
| C(1)-Sn(1)-C(7) | 117.0(2) | I(2)-Sn(2)-O(1) | 83.92(7) |
| C(1)-Sn(1)-C(11) | 115.8(2) | I(3)-Sn(2)-I(3A) | 90.988(16) |
| C(1)-Sn(1)-I(1) | 100.33(13) | I(3)-Sn(2)-O(1) | 168.97(7) |
| C(1)-Sn(1)-I(2) | 70.08(13) | I(3A)-Sn(2)-O(1) | 81.58(7) |
| C(1)-Sn(1)-O(1) | 67.09(14) | C(2)-Si(1)-C(3) | 111.7(3) |
| C(7)-Sn(1)-C(11) | 111.4(2) | C(2)-Si(1)-C(4) | 111.4(3) |
| C(7)-Sn(1)-I(1) | 105.14(18) | C(3)-Si(1)-C(4) | 109.8(4) |
| C(7)-Sn(1)-I(2) | 83.89(18) | O(1)-Si(1)-C(2) | 103.7(2) |
| C(7)-Sn(1)-O(1) | 50.30(15) | O(1)-Si(1)-C(3) | 111.1(3) |
| C(11)-Sn(1)-I(1) | 105.09(14) | O(1)-Si(1)-C(4) | 109.0(3) |
| C(11)-Sn(1)-I(2) | 76.11(14) | C(5)-Si(2)-C(6) | 111.8(3) |
| C(11)-Sn(1)-O(1) | 132.85(15) | C(5)-Si(2)-C(7) | 112.5(3) |
| I(1)-Sn(1)-I(2) | 169.334(16) | C(6)-Si(2)-C(7) | 109.1(3) |
| I(1)-Sn(1)-O(1) | 121.10(6) | O(1)-Si(2)-C(5) | 109.0(3) |
| I(2)-Sn(1)-O(1) | 60.37(6) | O(1)-Si(2)-C(6) | 108.9(3) |
| C(1)-Sn(2)-C(2) | 127.6(2) | O(1)-Si(2)-C(7) | 105.3(2) |
| C(1)-Sn(2)-I(2) | 104.44(13) | Sn(1)-C(1)-Sn(2) | 118.0(2) |
| C(1)-Sn(2)-I(3) | 104.54(14) | Sn(1)-O(1)-Sn(2) | 65.69(6) |
| C(1)-Sn(2)-I(3A) | 70.33(14) | Sn(1)-I(2)-Sn(2) | 62.735(13) |
| C(1)-Sn(2)-O(1) | 80.71(15) | Sn(1)-C(7)-Si(2) | 115.3(3) |
| C(2)-Sn(2)-I(2) | 106.24(16) | Sn(2)-C(2)-Si(1) | 109.4(3) |
| C(2)-Sn(2)-I(3) | 108.01(15) | Sn(1)-O(1)-Si(1) | 148.23(18) |
| C(2)-Sn(2)-I(3A) | 69.17(16) | Sn(1)-O(1)-Si(2) | 68.26(12) |
| C(2)-Sn(2)-O(1) | 61.74(16) | Sn(2)-O(1)-Si(1) | 82.57(14) |
| I(2)-Sn(2)-I(3) | 103.787(19) | Sn(2)-O(1)-Si(2) | 133.14(17) |
| I(2)-Sn(2)-I(3A) | 165.200(16) | Si(1)-O(1)-Si(2) | 143.2(2) |

| Torsion angles [°] | | | |
|---|---|---|---|
| Sn(1)-C(1)-Sn(2)-C(2) | -98.9(3) | Si(1)-O(1)-Si(2)-C(7) | -157.2(4) |
| C(1)-Sn(2)-C(2)-Si(1) | 60.1(4) | O(1)-Si(2)-C(7)-Sn(1) | -56.3(4) |
| Sn(2)-C(2)-Si(1)-O(1) | -17.4(3) | Si(2)-C(7)-Sn(1)-C(1) | 20.3(4) |
| C(2)-Si(1)-O(1)-Si(2) | -156.3(4) | C(7)-Sn(1)-C(1)-Sn(2) | 54.5(4) |

In the molecular structure of the dichloro-substituted eight-membered ring **14** one tin atom is intermolecularly coordinated to a chlorine atom of a second molecule *via* Sn(2)···Cl(2A) interactions, producing in this way a polymeric structure (Figure12).

Sn(1) and Sn(2) have a bicapped distorted tetrahedral coordination geometry. This configuration is realized at Sn(1) and Sn(2) by Sn-C bond distances ranging from 2.113(3) to 2.132(3) Å and by Sn(1)-Cl(1), Sn(2)-Cl(2) bond lengths of 2.3840(10) and 2.4058(9) Å, respectively. Furthermore, the intramolecular Sn(1)···Cl(2), Sn(1)···O(1) and Sn(2)···O(1) interactions, which have distances of 3.5387(9), 3.556(2) and 3.208(2) Å, are accompanied by one intermolecular Sn(2)···Cl(2A) distance of 3.8421(10) Å. The intramolecular Sn···O and Sn···Cl distances as well as the intermolecular Sn(2)···Cl(2A) distance are shorter than the sum of the van der Waals radii of tin, oxygen and chlorine (1.70 Å).[104] The intramolecular Sn(1)···Cl(2) distance is shorter than the intermolecular Sn(2)···Cl(2A) distance and furthermore the intramolecular Sn(1)···O(1) distance is longer than the other intramolecular Sn(2)···O(1) distance, as already observed for compound **9**. The two Sn(1)-C(1) and Sn(2)-C(1) distances are only slightly asymmetric.

The Cl(1)-Sn(1)-Cl(2), C(11)-Sn(1)-O(1), Cl(2)-Sn(2)-Cl(2A) and C(21)-Sn(2)-O(1) angles amount to 175.75(3)°, 136.96(10)°, 174.47(4)° and 176.05(9)°, respectively. The first and the last two angles differ only slightly from the ideal value of 180°. The Si(1)-O(1)-Si(2) angle of 147.78(15)° is greater than the corresponding angle of compound **11**, this being related to the long Sn(1)···O(1) and Sn(2)···O(1) contacts. Both silicon atoms have an almost ideal tetrahedral coordination geometry. Also in this case the Si(1)-O(1) and Si(2)-O(1) bond lengths with 1.636(2) and 1.640(2) Å are within the standard Si-O bond lengths reported in the literature.[112-114]

Moreover, the two tin atoms in the eight-membered ring **14** are chiral.

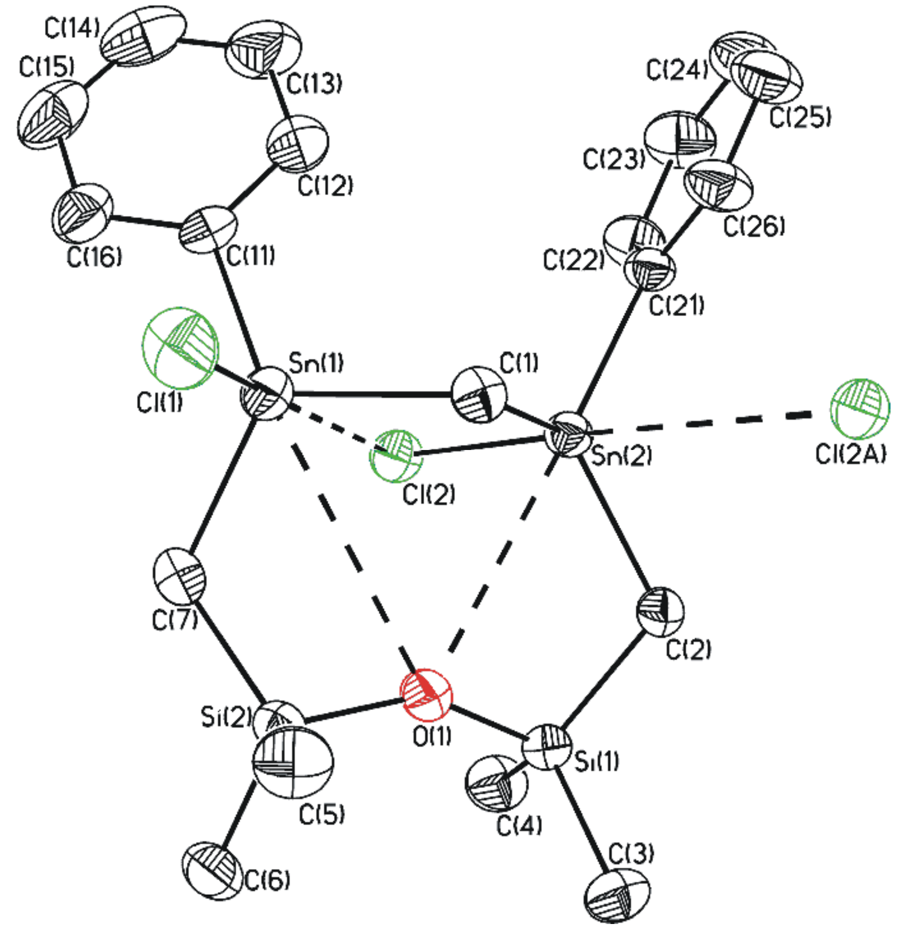


**Figure 12** Molecular structure (SHELXTL-PLUS) of **14** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 5** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **14**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.123(3) | Sn(2)-C(2) | 2.124(3) |
| Sn(1)-C(7) | 2.125(3) | Sn(2)-C(21) | 2.132(3) |
| Sn(1)-C(11) | 2.130(3) | Sn(2)-Cl(2) | 2.4058(9) |
| Sn(1)-Cl(1) | 2.3840(10) | Sn(2)-O(1) | 3.208(2) |
| Sn(1)-Cl(2) | 3.5387(9) | Sn(2)-Cl(2A) | 3.8421(10) |
| Sn(1)-O(1) | 3.556(2) | Si(1)-O(1) | 1.636(2) |
| Sn(2)-C(1) | 2.113(3) | Si(2)-O(1) | 1.640(2) |

**Table 5** continued.

| Bond angles [°] | | | |
|---|---|---|---|
| C(1)-Sn(1)-C(7) | 115.99(13) | C(21)-Sn(2)-O(1) | 176.05(9) |
| C(1)-Sn(1)-C(11) | 110.49(14) | Cl(2)-Sn(2)-Cl(2A) | 174.47(4) |
| C(1)-Sn(1)-Cl(1) | 103.24(8) | Cl(2)-Sn(2)-O(1) | 75.23(5) |
| C(1)-Sn(1)-Cl(2) | 72.70(8) | Cl(2A)-Sn(2)-O(1) | 100.20(4) |
| C(1)-Sn(1)-O(1) | 64.05(10) | C(2)-Si(1)-C(3) | 112.70(16) |
| C(7)-Sn(1)-C(11) | 117.33(14) | C(2)-Si(1)-C(4) | 109.05(17) |
| C(7)-Sn(1)-Cl(1) | 103.28(10) | C(3)-Si(1)-C(4) | 109.61(17) |
| C(7)-Sn(1)-Cl(2) | 77.82(10) | O(1)-Si(1)-C(2) | 105.16(13) |
| C(7)-Sn(1)-O(1) | 52.04(10) | O(1)-Si(1)-C(3) | 108.30(15) |
| C(11)-Sn(1)-Cl(1) | 104.41(10) | O(1)-Si(1)-C(4) | 111.99(16) |
| C(11)-Sn(1)-Cl(2) | 78.46(9) | C(5)-Si(2)-C(6) | 110.16(19) |
| C(11)-Sn(1)-O(1) | 136.96(10) | C(5)-Si(2)-C(7) | 110.06(18) |
| Cl(1)-Sn(1)-Cl(2) | 175.75(3) | C(6)-Si(2)-C(7) | 111.75(17) |
| Cl(1)-Sn(1)-O(1) | 118.52(5) | O(1)-Si(2)-C(5) | 109.19(16) |
| Cl(2)-Sn(1)-O(1) | 58.84(4) | O(1)-Si(2)-C(6) | 108.93(16) |
| C(1)-Sn(2)-C(2) | 113.82(13) | O(1)-Si(2)-C(7) | 106.66(14) |
| C(1)-Sn(2)-C(21) | 109.99(13) | Sn(1)-C(1)-Sn(2) | 113.80(13) |
| C(1)-Sn(2)-Cl(2) | 103.11(8) | Sn(1)-O(1)-Sn(2) | 63.05(4) |
| C(1)-Sn(2)-Cl(2A) | 72.24(8) | Sn(1)-Cl(2)-Sn(2) | 70.39(2) |
| C(1)-Sn(2)-O(1) | 71.89(10) | Sn(1)-C(7)-Si(2) | 114.42(16) |
| C(2)-Sn(2)-C(21) | 122.13(12) | Sn(2)-C(2)-Si(1) | 111.65(15) |
| C(2)-Sn(2)-Cl(2) | 103.92(9) | Sn(1)-O(1)-Si(1) | 141.66(11) |
| C(2)-Sn(2)-Cl(2A) | 75.82(9) | Sn(1)-O(1)-Si(2) | 69.26(8) |
| C(2)-Sn(2)-O(1) | 58.96(9) | Sn(2)-O(1)-Si(1) | 78.86(8) |
| C(21)-Sn(2)-Cl(2) | 100.88(9) | Sn(2)-O(1)-Si(2) | 132.12(11) |
| C(21)-Sn(2)-Cl(2A) | 83.72(9) | Si(1)-O(1)-Si(2) | 147.78(15) |
| Torsion angles [°] | | | |
| Sn(1)-C(1)-Sn(2)-C(2) | -111.1(2) | Si(1)-O(1)-Si(2)-C(7) | -139.5(3) |
| C(1)-Sn(2)-C(2)-Si(1) | 63.2(2) | O(1)-Si(2)-C(7)-Sn(1) | -51.1(2) |
| Sn(2)-C(2)-Si(1)-O(1) | -26.2(2) | Si(2)-C(7)-Sn(1)-C(1) | 22.0(2) |
| C(2)-Si(1)-O(1)-Si(2) | -178.3(3) | C(7)-Sn(1)-C(1)-Sn(2) | 66.0(2) |

The lattice of **15** is composed of discrete *cyclo*-$CH_2[Sn(I_2)CH_2Si(Me_2)]_2O$ molecules with no intermolecular coordination. Furthermore, compound **15** crystallises with two different conformers in the unit cell (Figure13).

All tin atoms of **15** Sn(1), Sn(2), Sn(3) and Sn(4) have a [4+1] coordination with a monocapped strongly distorted tetrahedral coordination geometry, where $\Delta(\sum\vartheta)$[105-107] = 19.4° for Sn(1), $\Delta(\sum\vartheta)$ = 24.3° for Sn(2), $\Delta(\sum\vartheta)$ = 21.9° for Sn(3) and $\Delta(\sum\vartheta)$ = 24.6° for Sn(4). This configuration is realised by intramolecular Sn(1)···O(1), Sn(2)···O(1), Sn(3)···O(2) and Sn(4)···O(2) distances of 3.211(3), 3.175(4), 3.179(4) and 3.196(4) Å, respectively. The Sn···O distances are shorter than the sum of the van der Waals radii of tin and oxygen.[104] The Sn-C bonds have lengths within the range 2.116(6)-2.137(6) Å and the Sn-I bonds have distances ranging from 2.6798(6) to 2.7269(6) Å.

The I(1)-Sn(1)-O(1), I(4)-Sn(2)-O(1), I(6)-Sn(3)-O(2), I(7)-Sn(4)-O(2) angles amount, respectively, to 169.05(7)°, 165.49(6)°, 167.79(7)° and 164.24(7)°, the deviation of these angles from the ideal value of 180° being, also in this case, the result of ring constraints. The Si(1)-O(1)-Si(2) and Si(3)-O(2)-Si(4) angles of 142.2(2)° and 140.3(3)°, respectively, are slightly smaller than the Si-O-Si angles of compounds **11** and **9** and significantly smaller than that of derivative **14**.

All silicon atoms have almost ideal tetrahedral coordination geometries.

All Si-O bond lengths with values of 1.642(4)-1.656(4) Å are within the typical range for Si-O bonds reported in the literature.[112-114]

Notably, the eight-membered ring **15**, comparably to the tetraiodo methylene-bridged ditin compound **7**, consists of discrete molecules however, contrary to the latter no intramolecular Sn···I interactions are observed. In addition, the Sn-I bonds distances of **15** are, as it could be expected, comparable with those of derivative **7**.

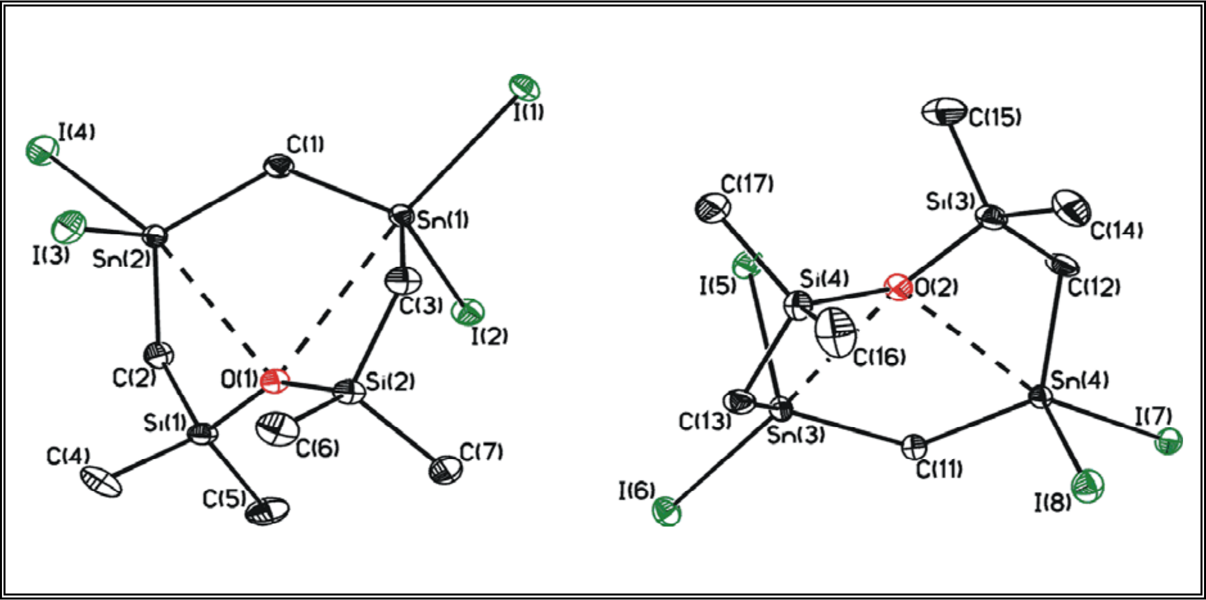


**Figure 13** Molecular structure (SHELXTL-PLUS) of **15** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 6** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **15**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.124(5) | Sn(3)-C(11) | 2.130(5) |
| Sn(1)-C(3) | 2.116(6) | Sn(3)-C(13) | 2.119(6) |
| Sn(1)-I(1) | 2.7070(5) | Sn(3)-I(5) | 2.6910(6) |
| Sn(1)-I(2) | 2.6798(6) | Sn(3)-I(6) | 2.7105(5) |
| Sn(1)-O(1) | 3.211(3) | Sn(3)-O(2) | 3.179(4) |
| Sn(2)-C(1) | 2.125(5) | Sn(4)-C(11) | 2.127(5) |
| Sn(2)-C(2) | 2.137(6) | Sn(4)-C(12) | 2.127(5) |
| Sn(2)-I(3) | 2.6843(6) | Sn(4)-I(7) | 2.7212(5) |
| Sn(2)-I(4) | 2.7269(6) | Sn(4)-I(8) | 2.6912(6) |
| Sn(2)-O(1) | 3.175(4) | Sn(4)-O(2) | 3.196(4) |
| Si(1)-O(1) | 1.656(4) | Si(3)-O(2) | 1.656(4) |
| Si(2)-O(1) | 1.642(4) | Si(4)-O(2) | 1.653(4) |
| **Bond angles [°]** | | | |
| C(1)-Sn(1)-C(3) | 122.3(2) | C(11)-Sn(3)-C(13) | 123.9(2) |
| C(1)-Sn(1)-I(1) | 104.39(15) | C(11)-Sn(3)-I(5) | 106.86(16) |
| C(1)-Sn(1)-I(2) | 105.37(17) | C(11)-Sn(3)-I(6) | 103.36(14) |

**Table 6** continued.

| | | | |
|---|---|---|---|
| C(1)-Sn(1)-O(1) | 84.97(16) | C(11)-Sn(3)-O(2) | 85.34(15) |
| C(3)-Sn(1)-I(1) | 110.88(15) | C(13)-Sn(3)-I(5) | 107.82(16) |
| C(3)-Sn(1)-I(2) | 109.52(17) | C(13)-Sn(3)-I(6) | 108.64(14) |
| C(3)-Sn(1)-O(1) | 58.57(16) | C(13)-Sn(3)-O(2) | 59.15(16) |
| I(1)-Sn(1)-I(2) | 102.530(19) | I(5)-Sn(3)-I(6) | 104.757(19) |
| I(1)-Sn(1)-O(1) | 169.05(7) | I(5)-Sn(3)-O(2) | 80.39(7) |
| I(2)-Sn(1)-O(1) | 79.97(7) | I(6)-Sn(3)-O(2) | 167.79(7) |
| C(1)-Sn(2)-C(2) | 120.0(2) | C(11)-Sn(4)-C(12) | 123.9(2) |
| C(1)-Sn(2)-I(3) | 106.58(18) | C(11)-Sn(4)-I(7) | 103.59(15) |
| C(1)-Sn(2)-I(4) | 104.48(15) | C(11)-Sn(4)-I(8) | 107.05(16) |
| C(1)-Sn(2)-O(1) | 85.87(16) | C(11)-Sn(4)-O(2) | 84.94(16) |
| C(2)-Sn(2)-I(3) | 113.26(18) | C(12)-Sn(4)-I(7) | 105.55(15) |
| C(2)-Sn(2)-I(4) | 106.48(15) | C(12)-Sn(4)-I(8) | 109.10(19) |
| C(2)-Sn(2)-O(1) | 59.11(16) | C(12)-Sn(4)-O(2) | 58.96(17) |
| I(3)-Sn(2)-I(4) | 104.62(2) | I(7)-Sn(4)-I(8) | 106.310(18) |
| I(3)-Sn(2)-O(1) | 81.54(7) | I(7)-Sn(4)-O(2) | 164.24(7) |
| I(4)-Sn(2)-O(1) | 165.49(6) | I(8)-Sn(4)-O(2) | 83.24(7) |
| C(2)-Si(1)-C(4) | 110.2(3) | C(12)-Si(3)-C(14) | 110.6(3) |
| C(2)-Si(1)-C(5) | 111.0(3) | C(12)-Si(3)-C(15) | 109.8(3) |
| C(4)-Si(1)-C(5) | 111.6(3) | C(14)-Si(3)-C(15) | 111.0(3) |
| O(1)-Si(1)-C(2) | 103.8(2) | O(2)-Si(3)-C(12) | 104.4(2) |
| O(1)-Si(1)-C(4) | 109.8(3) | O(2)-Si(3)-C(14) | 110.4(3) |
| O(1)-Si(1)-C(5) | 111.2(3) | O(2)-Si(3)-C(15) | 110.5(3) |
| C(3)-Si(2)-C(6) | 111.6(3) | C(13)-Si(4)-C(16) | 110.7(3) |
| C(3)-Si(2)-C(7) | 110.2(3) | C(13)-Si(4)-C(17) | 110.6(3) |
| C(6)-Si(2)-C(7) | 110.6(3) | C(16)-Si(4)-C(17) | 110.5(3) |
| O(1)-Si(2)-C(3) | 104.2(2) | O(2)-Si(4)-C(13) | 104.1(2) |
| O(1)-Si(2)-C(6) | 109.4(3) | O(2)-Si(4)-C(16) | 110.0(3) |
| O(1)-Si(2)-C(7) | 110.8(3) | O(2)-Si(4)-C(17) | 110.9(3) |
| Sn(1)-C(1)-Sn(2) | 119.1(3) | Sn(3)-C(11)-Sn(4) | 119.3(3) |
| Sn(1)-O(1)-Sn(2) | 69.99(7) | Sn(3)-O(2)-Sn(4) | 70.39(8) |
| Sn(1)-C(3)-Si(2) | 112.4(3) | Sn(3)-C(13)-Si(4) | 112.4(3) |
| Sn(2)-C(2)-Si(1) | 111.1(3) | Sn(4)-C(12)-Si(3) | 112.8(3) |

**Table 6** continued.

| | | | |
|---|---|---|---|
| Sn(1)-O(1)-Si(1) | 136.33(19) | Sn(3)-O(2)-Si(3) | 137.4(2) |
| Sn(1)-O(1)-Si(2) | 78.99(13) | Sn(3)-O(2)-Si(4) | 79.62(13) |
| Sn(2)-O(1)-Si(1) | 79.42(14) | Sn(4)-O(2)-Si(3) | 79.63(14) |
| Sn(2)-O(1)-Si(2) | 135.54(18) | Sn(4)-O(2)-Si(4) | 137.27(18) |
| Si(1)-O(1)-Si(2) | 142.2(2) | Si(3)-O(2)-Si(4) | 140.3(3) |
| Torsion angles [°] | | | |
| Sn(1)-C(1)-Sn(2)-C(2) | -53.6(4) | Sn(3)-C(11)-Sn(4)-C(12) | -47.2(4) |
| C(1)-Sn(2)-C(2)-Si(1) | 80.1(4) | C(11)-Sn(4)-C(12)-Si(3) | 71.4(4) |
| Sn(2)-C(2)-Si(1)-O(1) | -28.5(3) | Sn(4)-C(12)-Si(3)-O(2) | -23.2(4) |
| C(2)-Si(1)-O(1)-Si(2) | 178.4(4) | C(12)-Si(3)-O(2)-Si(4) | 175.8(4) |
| Si(1)-O(1)-Si(2)-C(3) | 178.4(4) | Si(3)-O(2)-Si(4)-C(13) | 176.8(4) |
| O(1)-Si(2)-C(3)-Sn(1) | -27.2(4) | O(2)-Si(4)-C(13)-Sn(3) | -24.3(3) |
| Si(2)-C(3)-Sn(1)-C(1) | 74.9(4) | Si(4)-C(13)-Sn(3)-C(11) | 73.0(4) |
| C(3)-Sn(1)-C(1)-Sn(2) | -44.5(4) | C(13)-Sn(3)-C(11)-Sn(4) | -47.3(4) |

The unit cell of compound **16** contains four different molecules, each of them being connected to another molecule by four intermolecular Sn(2)···Br(11A), Sn(12)···Br(3B), Sn(22)···Br(33C) and Sn(32)···Br(23C) coordinations (Figure14).

The tin atoms of derivative **16** have a bicapped distorted tetrahedral coordination geometry.

The Sn-C bond distances are as expected and fall in the range between 2.098(12) and 2.136(12) Å while the Sn-Br bonds have lengths ranging from 2.4750(16) to 2.5111(16) Å. The intramolecular Sn···Br distances are within the range 3.9212(18)-4.1015(18) Å while the intermolecular Sn···Br distances range from 3.8240(18)-3.9011(18) Å. The intramolecular Sn···O distances are as expected and fall in the range 3.020(8)-3.351(8) Å. The Sn···O as well as the Sn···Br distances are shorter than the sum of the van der Waals radii of tin, oxygen and bromine.[104]

At Sn(1) and Sn(2) the Br(1)-Sn(1)-Br(4), O(1)-Sn(1)-Br(2), Br(4)-Sn(2)-Br(11A) and O(1)-Sn(2)-Br(3) angles amount to 164.43(5)°, 148.84(16)°, 178.17(16)° and 172.45(17)°, respectively. At Sn(11) and Sn(12) the Br(12)-Sn(11)-Br(13), O(11)-Sn(11)-Br(14), Br(3B)-Sn(12)-Br(12) and O(11)-Sn(12)-Br(11) angles amount to

155.47(6)°, 158.56(16)°, 175.11(5)° and 171.61(16)°, respectively. For the shorter Sn(2)···Br(11A) relative to Sn(1)···Br(4), Sn(2)···O(1) relative to Sn(1)···O(1), Sn(12)···Br(3B) relative to Sn(11)···Br(12) and Sn(12)···O(11) relative to Sn(11)···O(11) contacts, there is a smaller deviation from the ideal value of 180°. These deviations can be explained as result of ring constraints.

At Sn(21) and Sn(22) the Br(21)-Sn(21)-Br(24), O(21)-Sn(21)-Br(22), Br(24)-Sn(22)-Br(33C) and O(21)-Sn(22)-Br(23) angles amount to 150.45(5)°, 163.38(11)°, 175.64(5)° and 171.02(16)°, respectively. The latter angles deviate only lightly deviated from the ideal value of 180°. Again the deviation is a result of ring constraints.

At Sn(31) and Sn(32) the Br(31)-Sn(31)-Br(34), O(31)-Sn(31)-Br(32), Br(23C)-Sn(32)-Br(34) and O(31)-Sn(32)-Br(33) angles amount to 159.57(5)°, 154.24(16)°, 176.92(6)° and 171.96(17)°, respectively.

Also in this case the latter angles are closer to the ideal vaue of 180°, and again this deviation can be explained as a result of ring constraints.

Furthermore the Si(1)-O(1)-Si(2), Si(11)-O(11)-Si(12), Si(21)-O(21)-Si(22) and Si(31)-O(31)-Si(32) angles amounting to 143.2(6)°, 140.5(5)°, 140.7(5)° and 143.7(6)°, respectively, are slightly smaller than the Si-O-Si angles of derivatives **11**, **14** and *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O]$ (**9**),[87,91] but slightly greater than those of compound **15**.

All silicon atoms have an almost ideal tetrahedral coordination geometry.

All the Si-O bond lengths ranging from 1.642(9)-1.670(9) Å are within the standard Si-O bond lengths reported in the literature.[112-114]

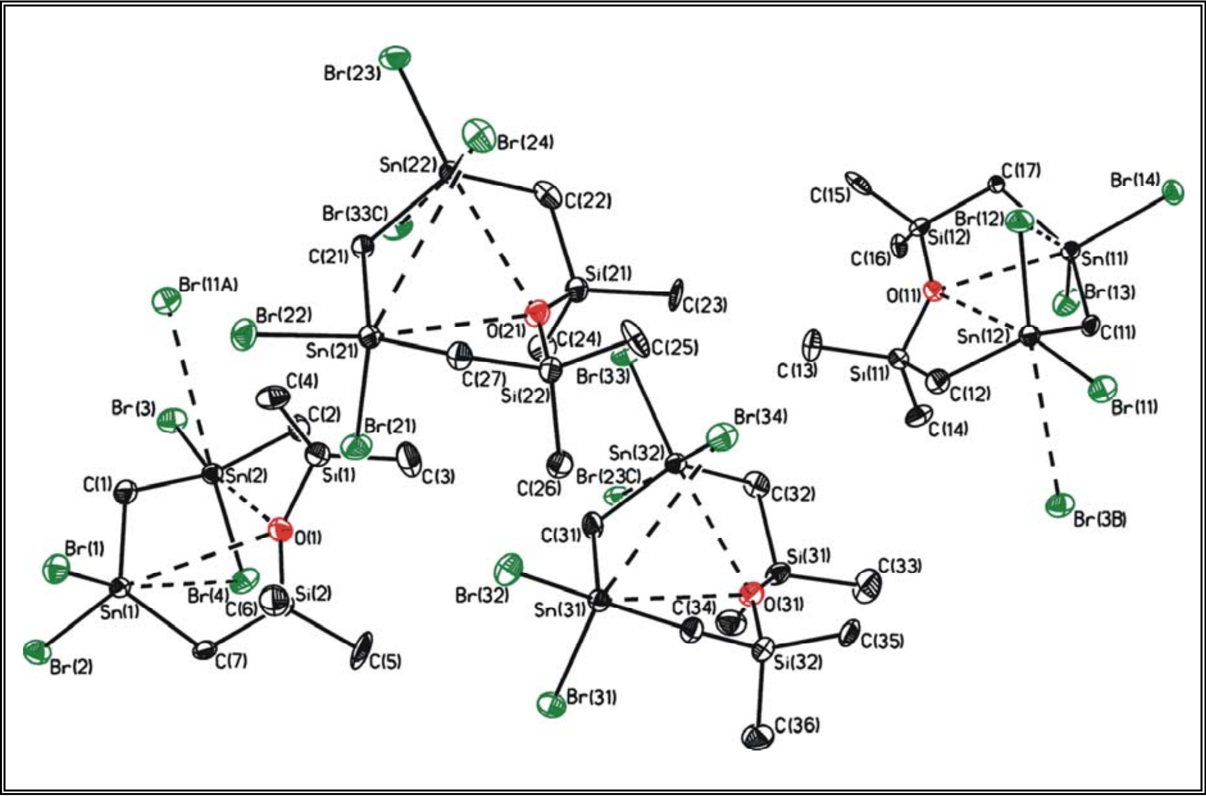


**Figure 14** Molecular structure (SHELXTL-PLUS) of **16** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 7** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **16**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.133(13) | Sn(21)-C(21) | 2.134(11) |
| Sn(1)-C(7) | 2.098(12) | Sn(21)-C(27) | 2.109(11) |
| Sn(1)-Br(1) | 2.4750(16) | Sn(21)-Br(21) | 2.4855(16) |
| Sn(1)-Br(2) | 2.4911(16) | Sn(21)-Br(22) | 2.4895(16) |
| Sn(1)-Br(4) | 3.9212(18) | Sn(21)-Br(24) | 4.1015(18) |
| Sn(1)-O(1) | 3.351(8) | Sn(21)-O(21) | 3.156(8) |
| Sn(2)-C(1) | 2.108(13) | Sn(22)-C(21) | 2.099(12) |
| Sn(2)-C(2) | 2.102(12) | Sn(22)-C(22) | 2.119(13) |
| Sn(2)-Br(3) | 2.5088(16) | Sn(22)-Br(23) | 2.5075(16) |
| Sn(2)-Br(4) | 2.4885(17) | Sn(22)-Br(24) | 2.4846(16) |
| Sn(2)-Br(11A) | 3.8240(18) | Sn(22)-Br(33C) | 3.8733(17) |
| Sn(2)-O(1) | 3.020(8) | Sn(22)-O(21) | 3.058(8) |
| Si(1)-O(1) | 1.663(10) | Si(21)-O(21) | 1.646(9) |

**Table 7** continued.

| | | | |
|---|---|---|---|
| Si(2)-O(1) | 1.642(9) | Si(22)-O(21) | 1.670(9) |
| Sn(11)-C(11) | 2.134(12) | Sn(31)-C(31) | 2.136(12) |
| Sn(11)-C(17) | 2.133(11) | Sn(31)-C(37) | 2.111(12) |
| Sn(11)-Br(12) | 4.0808(17) | Sn(31)-Br(31) | 2.4777(16) |
| Sn(11)-Br(13) | 2.4842(16) | Sn(31)-Br(32) | 2.4825(16) |
| Sn(11)-Br(14) | 2.4909(15) | Sn(31)-Br(34) | 3.9886(18) |
| Sn(11)-O(11) | 3.169(8) | Sn(31)-O(31) | 3.336(8) |
| Sn(12)-C(11) | 2.112(12) | Sn(32)-C(31) | 2.101(12) |
| Sn(12)-C(12) | 2.105(13) | Sn(32)-C(32) | 2.121(12) |
| Sn(12)-Br(3B) | 3.9011(18) | Sn(32)-Br(23C) | 3.8813(17) |
| Sn(12)-Br(11) | 2.5103(16) | Sn(32)-Br(33) | 2.5111(16) |
| Sn(12)-Br(12) | 2.4860(17) | Sn(32)-Br(34) | 2.4813(16) |
| Sn(12)-O(11) | 3.045(8) | Sn(32)-O(31) | 3.044(9) |
| Si(11)-O(11) | 1.666(9) | Si(31)-O(31) | 1.656(9) |
| Si(12)-O(11) | 1.644(9) | Si(32)-O(31) | 1.662(9) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(7) | 124.9(5) | C(21)-Sn(21)-C(27) | 126.0(5) |
| C(1)-Sn(1)-Br(1) | 105.9(4) | C(21)-Sn(21)-Br(21) | 103.4(4) |
| C(1)-Sn(1)-Br(2) | 104.2(4) | C(21)-Sn(21)-Br(22) | 104.7(3) |
| C(1)-Sn(1)-Br(4) | 66.7(4) | C(21)-Sn(21)-Br(24) | 61.7(3) |
| C(1)-Sn(1)-O(1) | 73.3(4) | C(21)-Sn(21)-O(21) | 77.9(3) |
| C(7)-Sn(1)-Br(1) | 107.5(4) | C(27)-Sn(21)-Br(21) | 109.3(4) |
| C(7)-Sn(1)-Br(2) | 108.6(3) | C(27)-Sn(21)-Br(22) | 108.6(3) |
| C(7)-Sn(1)-Br(4) | 69.4(4) | C(27)-Sn(21)-Br(24) | 68.8(4) |
| C(7)-Sn(1)-O(1) | 55.9(4) | C(27)-Sn(21)-O(21) | 59.1(4) |
| Br(1)-Sn(1)-Br(2) | 103.96(6) | Br(21)-Sn(21)-Br(22) | 102.34(6) |
| Br(1)-Sn(1)-Br(4) | 164.43(5) | Br(21)-Sn(21)-Br(24) | 150.45(5) |
| Br(1)-Sn(1)-O(1) | 106.56(17) | Br(21)-Sn(21)-O(21) | 92.82(16) |
| Br(2)-Sn(1)-Br(4) | 91.33(5) | Br(22)-Sn(21)-Br(24) | 106.10(5) |
| Br(2)-Sn(1)-O(1) | 148.84(17) | Br(22)-Sn(21)-O(21) | 163.38(11) |
| Br(4)-Sn(1)-O(1) | 58.67(16) | Br(24)-Sn(21)-O(21) | 60.20(16) |
| C(1)-Sn(2)-C(2) | 125.2(6) | C(21)-Sn(22)-C(22) | 124.6(5) |

**Table 7** continued.

| | | | |
|---|---|---|---|
| C(1)-Sn(2)-Br(3) | 104.7(4) | C(21)-Sn(22)-Br(23) | 104.7(3) |
| C(1)-Sn(2)-Br(4) | 104.8(4) | C(21)-Sn(22)-Br(24) | 103.9(4) |
| C(1)-Sn(2)-Br(11A) | 77.0(4) | C(21)-Sn(22)-Br(33C) | 72.2(3) |
| C(1)-Sn(2)-O(1) | 81.4(4) | C(21)-Sn(22)-O(21) | 80.7(4) |
| C(2)-Sn(2)-Br(3) | 111.2(4) | C(22)-Sn(22)-Br(23) | 109.5(4) |
| C(2)-Sn(2)-Br(4) | 106.9(4) | C(22)-Sn(22)-Br(24) | 110.3(4) |
| C(2)-Sn(2)-Br(11A) | 71.6(4) | C(22)-Sn(22)-Br(33C) | 73.8(4) |
| C(2)-Sn(2)-O(1) | 61.3(4) | C(22)-Sn(22)-O(21) | 61.6(4) |
| Br(3)-Sn(2)-Br(4) | 101.48(6) | Br(23)-Sn(22)-Br(24) | 101.43(6) |
| Br(3)-Sn(2)-Br(11A) | 78.23(5) | Br(23)-Sn(22)-Br(33C) | 78.10(4) |
| Br(3)-Sn(2)-O(1) | 172.45(17) | Br(23)-Sn(22)-O(21) | 171.02(16) |
| Br(4)-Sn(2)-Br(11A) | 178.17(6) | Br(24)-Sn(22)-Br(33C) | 175.64(5) |
| Br(4)-Sn(2)-O(1) | 80.91(18) | Br(24)-Sn(22)-O(21) | 83.93(16) |
| Br(11A)-Sn(2)-O(1) | 99.15(18) | Br(33C)-Sn(22)-O(21) | 97.09(16) |
| C(2)-Si(1)-C(3) | 111.3(7) | C(22)-Si(21)-C(23) | 110.2(6) |
| C(2)-Si(1)-C(4) | 110.5(6) | C(22)-Si(21)-C(24) | 110.9(6) |
| C(3)-Si(1)-C(4) | 113.0(7) | C(23)-Si(21)-C(24) | 110.7(6) |
| O(1)-Si(1)-C(2) | 101.9(5) | O(21)-Si(21)-C(22) | 104.2(5) |
| O(1)-Si(1)-C(3) | 112.1(7) | O(21)-Si(21)-C(23) | 112.5(6) |
| O(1)-Si(1)-C(4) | 107.4(6) | O(21)-Si(21)-C(24) | 108.1(6) |
| C(5)-Si(2)-C(6) | 113.3(8) | C(25)-Si(22)-C(26) | 111.5(7) |
| C(5)-Si(2)-C(7) | 110.5(7) | C(25)-Si(22)-C(27) | 112.5(6) |
| C(6)-Si(2)-C(7) | 107.7(7) | C(26)-Si(22)-C(27) | 111.3(6) |
| O(1)-Si(2)-C(5) | 109.5(7) | O(21)-Si(22)-C(25) | 109.2(6) |
| O(1)-Si(2)-C(6) | 110.9(6) | O(21)-Si(22)-C(26) | 110.0(6) |
| O(1)-Si(2)-C(7) | 104.7(5) | O(21)-Si(22)-C(27) | 101.9(5) |
| Sn(1)-C(1)-Sn(2) | 116.3(6) | Sn(21)-C(21)-Sn(22) | 117.7(5) |
| Sn(1)-O(1)-Sn(2) | 68.65(17) | Sn(21)-O(21)-Sn(22) | 71.31(17) |
| Sn(1)-Br(4)-Sn(2) | 63.88(4) | Sn(21)-Br(24)-Sn(22) | 61.03(4) |
| Sn(1)-C(7)-Si(2) | 115.2(6) | Sn(21)-C(27)-Si(22) | 110.8(6) |
| Sn(2)-C(2)-Si(1) | 109.2(7) | Sn(22)-C(22)-Si(21) | 109.1(6) |
| Si(1)-O(1)-Si(2) | 143.2(6) | Si(21)-O(21)-Si(22) | 140.7(5) |
| C(11)-Sn(11)-C(17) | 126.7(5) | C(31)-Sn(31)-C(37) | 124.8(5) |

**Table 7** continued.

| | | | |
|---|---|---|---|
| C(11)-Sn(11)-Br(12) | 62.6(3) | C(31)-Sn(31)-Br(31) | 105.5(4) |
| C(11)-Sn(11)-Br(13) | 104.2(4) | C(31)-Sn(31)-Br(32) | 106.8(4) |
| C(11)-Sn(11)-Br(14) | 102.3(3) | C(31)-Sn(31)-Br(34) | 65.0(4) |
| C(11)-Sn(11)-O(11) | 77.2(3) | C(31)-Sn(31)-O(31) | 74.5(4) |
| C(17)-Sn(11)-Br(12) | 69.8(4) | C(37)-Sn(31)-Br(31) | 106.8(4) |
| C(17)-Sn(11)-Br(13) | 109.8(3) | C(37)-Sn(31)-Br(32) | 108.4(3) |
| C(17)-Sn(11)-Br(14) | 108.2(3) | C(37)-Sn(31)-Br(34) | 69.3(4) |
| C(17)-Sn(11)-O(11) | 59.0(4) | C(37)-Sn(31)-O(31) | 55.9(4) |
| Br(12)-Sn(11)-Br(13) | 155.47(6) | Br(31)-Sn(31)-Br(32) | 102.53(6) |
| Br(12)-Sn(11)-Br(14) | 99.91(5) | Br(31)-Sn(31)-Br(34) | 159.57(5) |
| Br(12)-Sn(11)-O(11) | 60.43(15) | Br(31)-Sn(31)-O(31) | 101.80(16) |
| Br(13)-Sn(11)-Br(14) | 103.23(6) | Br(32)-Sn(31)-Br(34) | 97.64(5) |
| Br(13)-Sn(11)-O(11) | 97.59(16) | Br(32)-Sn(31)-O(31) | 154.24(16) |
| Br(14)-Sn(11)-O(11) | 158.56(16) | Br(34)-Sn(31)-O(31) | 58.87(16) |
| C(11)-Sn(12)-C(12) | 124.2(5) | C(31)-Sn(32)-C(32) | 126.0(6) |
| C(11)-Sn(12)-Br(3B) | 72.4(4) | C(31)-Sn(32)-Br(23C) | 78.1(4) |
| C(11)-Sn(12)-Br(11) | 104.1(3) | C(31)-Sn(32)-Br(33) | 104.1(4) |
| C(11)-Sn(12)-Br(12) | 104.0(4) | C(31)-Sn(32)-Br(34) | 105.0(4) |
| C(11)-Sn(12)-O(11) | 80.4(4) | C(31)-Sn(32)-O(31) | 81.9(4) |
| C(12)-Sn(12)-Br(3B) | 74.0(4) | C(32)-Sn(32)-Br(23C) | 69.9(4) |
| C(12)-Sn(12)-Br(11) | 109.9(4) | C(32)-Sn(32)-Br(33) | 109.9(3) |
| C(12)-Sn(12)-Br(12) | 110.9(4) | C(32)-Sn(32)-Br(34) | 107.7(4) |
| C(12)-Sn(12)-O(11) | 62.0(4) | C(32)-Sn(32)-O(31) | 62.0(4) |
| Br(3B)-Sn(12)-Br(11) | 76.66(4) | Br(23C)-Sn(32)-Br(33) | 77.90(4) |
| Br(3B)-Sn(12)-Br(12) | 175.11(5) | Br(23C)-Sn(32)-Br(34) | 176.92(6) |
| Br(3B)-Sn(12)-O(11) | 98.34(16) | Br(23C)-Sn(32)-O(31) | 98.49(17) |
| Br(11)-Sn(12)-Br(12) | 101.28(6) | Br(33)-Sn(32)-Br(34) | 101.36(6) |
| Br(11)-Sn(12)-O(11) | 171.61(16) | Br(33)-Sn(32)-O(31) | 171.96(17) |
| Br(12)-Sn(12)-O(11) | 84.22(16) | Br(34)-Sn(32)-O(31) | 81.86(17) |
| C(12)-Si(11)-C(13) | 112.6(6) | C(32)-Si(31)-C(33) | 110.9(7) |
| C(12)-Si(11)-C(14) | 110.0(6) | C(32)-Si(31)-C(34) | 111.0(7) |
| C(13)-Si(11)-C(14) | 113.4(6) | C(33)-Si(31)-C(34) | 112.3(8) |
| O(11)-Si(11)-C(12) | 103.4(5) | O(31)-Si(31)-C(32) | 103.4(5) |

**Table 7** continued.

| | | | |
|---|---|---|---|
| O(11)-Si(11)-C(13) | 109.0(6) | O(31)-Si(31)-C(33) | 111.0(6) |
| O(11)-Si(11)-C(14) | 107.8(6) | O(31)-Si(31)-C(34) | 107.8(6) |
| C(15)-Si(12)-C(16) | 110.8(7) | C(35)-Si(32)-C(36) | 111.0(7) |
| C(15)-Si(12)-C(17) | 111.8(6) | C(35)-Si(32)-C(37) | 112.8(6) |
| C(16)-Si(12)-C(17) | 110.9(6) | C(36)-Si(32)-C(37) | 112.2(7) |
| O(11)-Si(12)-C(15) | 109.2(6) | O(31)-Si(32)-C(35) | 107.5(6) |
| O(11)-Si(12)-C(16) | 110.9(6) | O(31)-Si(32)-C(36) | 108.6(6) |
| O(11)-Si(12)-C(17) | 103.1(5) | O(31)-Si(32)-C(37) | 104.3(5) |
| Sn(11)-C(11)-Sn(12) | 117.3(5) | Sn(31)-C(31)-Sn(32) | 117.0(5) |
| Sn(11)-O(11)-Sn(12) | 71.34(17) | Sn(31)-O(31)-Sn(32) | 68.80(17) |
| Sn(11)-Br(12)-Sn(12) | 61.47(4) | Sn(31)-Br(34)-Sn(32) | 62.91(4) |
| Sn(11)-C(17)-Si(12) | 109.0(6) | Sn(31)-C(37)-Si(32) | 115.0(6) |
| Sn(12)-C(12)-Si(11) | 109.1(7) | Sn(32)-C(32)-Si(31) | 108.0(6) |
| Si(11)-O(11)-Si(12) | 140.5(5) | Si(31)-O(31)-Si(32) | 143.7(6) |
| Torsion angles [°] | | | |
| Sn(1)-C(1)-Sn(2)-C(2) | -90.2(9) | Sn(21)-C(21)-Sn(22)-C(22) | 79.6(8) |
| C(1)-Sn(2)-C(2)-Si(1) | 37.5(10) | C(21)-Sn(22)-C(22)-Si(21) | -41.3(9) |
| Sn(2)-C(2)-Si(1)-O(1) | 26.8(8) | Sn(22)-C(22)-Si(21)-O(21) | -20.9(7) |
| C(2)-Si(1)-O(1)-Si(2) | 153.6(10) | C(22)-Si(21)-O(21)-Si(22) | -148.2(9) |
| Si(1)-O(1)-Si(2)-C(7) | 172.7(10) | Si(21)-O(21)-Si(22)-C(27) | -177.8(9) |
| O(1)-Si(2)-C(7)-Sn(1) | -33.9(8) | O(21)-Si(22)-C(27)-Sn(21) | 33.4(7) |
| Si(2)-C(7)-Sn(1)-C(1) | 44.9(10) | Si(22)-C(27)-Sn(21)-C(21) | -61.9(9) |
| C(7)-Sn(1)-C(1)-Sn(2) | 18.4(10) | C(27)-Sn(21)-C(21)-Sn(22) | 3.4(10) |
| Sn(11)-C(11)-Sn(12)-C(12) | 82.1(8) | Sn(31)-C(31)-Sn(32)-C(32) | 88.2(9) |
| C(11)-Sn(12)-C(12)-Si(11) | -40.1(9) | C(31)-Sn(32)-C(32)-Si(31) | -39.8(9) |
| Sn(12)-C(12)-Si(11)-O(11) | -23.2(8) | Sn(32)-C(32)-Si(31)-O(31) | -24.6(7) |
| C(12)-Si(11)-O(11)-Si(12) | -151.9(9) | C(32)-Si(31)-O(31)-Si(32) | -154.0(10) |
| Si(11)-O(11)-Si(12)-C(17) | -175.5(9) | Si(31)-O(31)-Si(32)-C(37) | -174.1(10) |
| O(11)-Si(12)-C(17)-Sn(11) | 35.6(7) | O(31)-Si(32)-C(37)-Sn(31) | 35.3(8) |
| Si(12)-C(17)-Sn(11)-C(11) | -59.5(8) | Si(32)-C(37)-Sn(31)-C(31) | -49.9(10) |
| C(17)-Sn(11)-C(11)-Sn(12) | -0.7(10) | C(37)-Sn(31)-C(31)-Sn(32) | -13.1(11) |

The Sn(1) and Sn(2) atoms in compound **17** are both [5+1] coordinated with a monocapped distorted trigonal bipyramidal coordination geometry (Figure 15).

The Sn-C bond distances range from 2.12(2) to 2.14(3) Å. The equatorial Sn(1)-Cl(2) and Sn(2)-Cl(4) bonds have distances of 2.372(7) and 2.377(7) Å, respectively, while the axial Sn(1)-Cl(1) and Sn(2)-Cl(3) bond distances amount to 2.481(7) and 2.481(7) Å. The Sn(1)···O(2) and Sn(2)···O(3) interactions have distances of 2.287(19) and 2.379(18) Å, respectively, while the Sn(1)···O(1) and Sn(2)···O(1) distances amount to 3.378(15) and 3.470(16) Å. The intramolecular Sn···O(1) distances are rather long but still within the sum of the van der Waals radii of tin and oxygen.[104] Furthermore the bond lengths of tin to the equatorial chlorine atoms are shorter than those to the axial chlorine atoms.

The Sn(1)···O(2) and Sn(2)···O(3) distances are particularly short and reflect the strong donor capacity of DMSO. For the complex $[MeSn(Cl_2)]_2CH_2 \cdot 2DMSO$ the average Sn···O distance amounts to 2.588(6) Å.[33]

One of the two DMSO molecules is connected with another *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ molecule by one H(8B)···Cl(1A) interaction with a C(8)-Cl(1A) distance of 3.69(4) Å. The last distance is rather long and at the borderline of the sum of the van der waals radii of chlorine and carbon (3.35-3.60 Å).[104]

Notably, while the Sn-C, Sn-Cl and Sn(1)···O(1) distances are almost of the same value of those of *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**), the Sn(2)···O(1) distance is significantly longer than that of compound **9**.[87,91]

The Cl(1)-Sn(1)-O(2) and Cl(3)-Sn(2)-O(3) angles amount to 175.6(5)° and 172.8(4)°, while the Cl(2)-Sn(1)-O(1) and Cl(4)-Sn(2)-O(1) angles amount to 149.8(3)° and 139.7(3)°. The first two angles differ only slightly from the ideal value of 180° while for the longer Sn(1)···O(1) and Sn(2)···O(1) distances the deviation from the ideal value is greater.

The Si(1)-O(1)-Si(2) angle amounting to 144.9(11)° is smaller than the Si-O-Si angles of *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**)[87,91] and derivative **14**, but greater than those of compounds **11**, **15** and **16**.

The silicon atoms have an almost ideal tetrahedral coordination geometry.

The Si(1)-O(1) and Si(2)-O(1) bonds have distances of 1.609(17) and 1.669(19) Å, thus being within the standard Si-O bond lengths reported in the literature.[112-114]

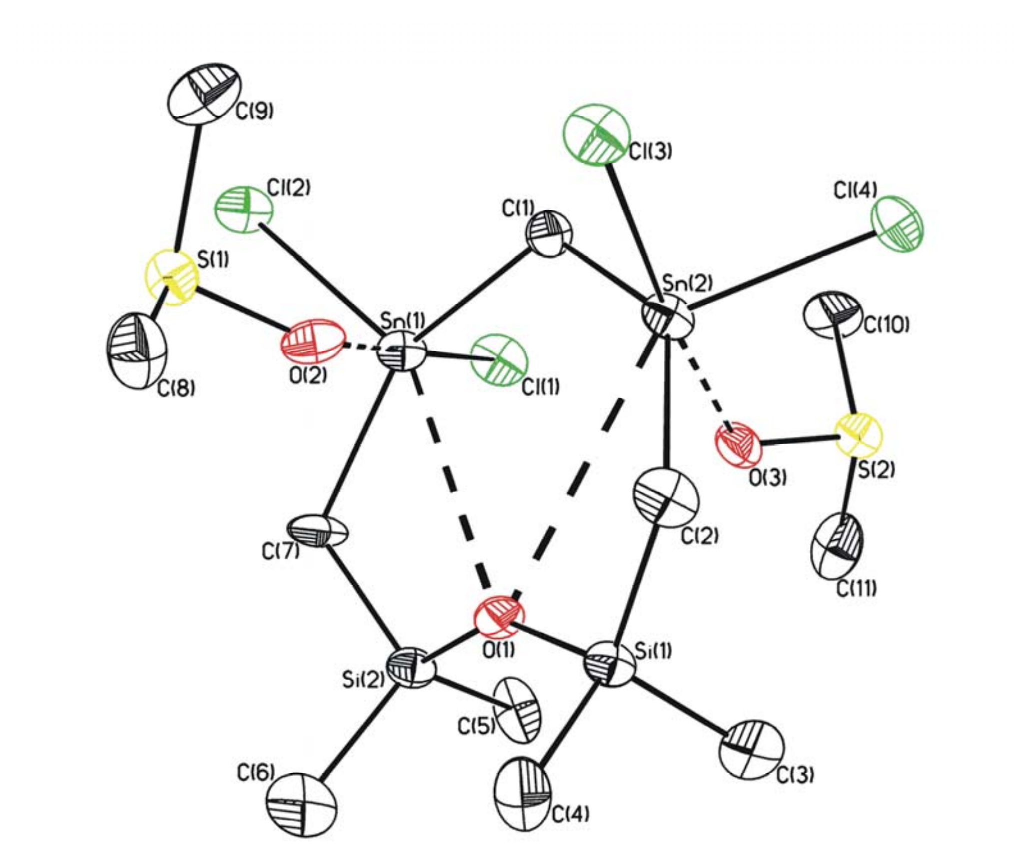


**Figure 15** Molecular structure (SHELXTL-PLUS) of **17** showing 30% probability displacement ellipsoids and the atom numbering scheme. The H(8B)-Cl(1A) is omitted.

**Table 8** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **17**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.13(3) | Sn(2)-Cl(4) | 2.377(7) |
| Sn(1)-C(7) | 2.12(2) | Sn(2)-O(1) | 3.470(16) |
| Sn(1)-Cl(1) | 2.481(7) | Sn(2)-O(3) | 2.379(18) |
| Sn(1)-Cl(2) | 2.372(7) | Si(1)-O(1) | 1.609(17) |
| Sn(1)-O(1) | 3.378(15) | Si(2)-O(1) | 1.669(19) |
| Sn(1)-O(2) | 2.287(19) | O(2)-S(1) | 1.539(18) |
| Sn(2)-C(1) | 2.12(3) | C(8)-Cl(1A) | 3.69(4) |
| Sn(2)-C(2) | 2.14(3) | O(3)-S(2) | 1.506(18) |
| Sn(2)-Cl(3) | 2.481(7) | | |

**Table 8** continued.

| Bond angles [°] | | | |
|---|---|---|---|
| C(1)-Sn(1)-C(7) | 145.9(10) | O(3)-Sn(2)-Cl(4) | 83.7(4) |
| C(1)-Sn(1)-Cl(1) | 95.3(8) | C(2)-Si(1)-C(3) | 113.1(14) |
| C(1)-Sn(1)-Cl(2) | 105.2(7) | C(2)-Si(1)-C(4) | 109.9(15) |
| C(7)-Sn(1)-Cl(1) | 96.2(9) | C(3)-Si(1)-C(4) | 108.2(13) |
| C(7)-Sn(1)-Cl(2) | 105.6(7) | O(1)-Si(1)-C(2) | 106.6(10) |
| Cl(1)-Sn(1)-Cl(2) | 95.1(3) | O(1)-Si(1)-C(3) | 110.5(12) |
| O(1)-Sn(1)-C(1) | 90.6(8) | O(1)-Si(1)-C(4) | 108.4(11) |
| O(1)-Sn(1)-C(7) | 55.3(8) | C(5)-Si(2)-C(6) | 110.9(14) |
| O(1)-Sn(1)-Cl(1) | 109.1(3) | C(5)-Si(2)-C(7) | 109.3(16) |
| O(1)-Sn(1)-Cl(2) | 149.8(3) | C(6)-Si(2)-C(7) | 110.0(14) |
| O(1)-Sn(1)-O(2) | 68.5(5) | O(1)-Si(2)-C(5) | 110.7(11) |
| O(2)-Sn(1)-C(1) | 81.2(9) | O(1)-Si(2)-C(6) | 110.6(11) |
| O(2)-Sn(1)-C(7) | 85.5(10) | O(1)-Si(2)-C(7) | 105.2(11) |
| O(2)-Sn(1)-Cl(1) | 175.6(5) | Sn(1)-C(1)-Sn(2) | 116.8(12) |
| O(2)-Sn(1)-Cl(2) | 88.3(4) | Sn(1)-O(1)-Sn(2) | 63.8(3) |
| C(1)-Sn(2)-C(2) | 138.9(9) | Sn(1)-C(7)-Si(2) | 116.4(14) |
| C(1)-Sn(2)-Cl(3) | 95.3(8) | Sn(2)-C(2)-Si(1) | 117.3(13) |
| C(1)-Sn(2)-Cl(4) | 110.3(7) | Sn(1)-O(1)-Si(1) | 138.6(8) |
| C(2)-Sn(2)-Cl(3) | 94.5(8) | Sn(1)-O(1)-Si(2) | 75.2(6) |
| C(2)-Sn(2)-Cl(4) | 109.2(7) | Sn(2)-O(1)-Si(1) | 74.8(6) |
| Cl(3)-Sn(2)-Cl(4) | 91.4(2) | Sn(2)-O(1)-Si(2) | 136.6(8) |
| O(1)-Sn(2)-C(1) | 88.3(7) | Si(1)-O(1)-Si(2) | 144.9(11) |
| O(1)-Sn(2)-C(2) | 53.6(7) | O(2)-S(1)-C(8) | 102.9(12) |
| O(1)-Sn(2)-Cl(3) | 123.2(3) | O(2)-S(1)-C(9) | 106.5(12) |
| O(1)-Sn(2)-Cl(4) | 139.7(3) | C(8)-S(1)-C(9) | 100.8(15) |
| O(1)-Sn(2)-O(3) | 63.4(5) | O(3)-S(2)-C(10) | 106.8(12) |
| O(3)-Sn(2)-C(1) | 81.5(9) | O(3)-S(2)-C(11) | 104.0(12) |
| O(3)-Sn(2)-C(2) | 92.1(9) | C(10)-S(2)-C(11) | 94.1(16) |
| O(3)-Sn(2)-Cl(3) | 172.8(4) | | |
| **Torsion angles [°]** | | | |
| Sn(1)-C(1)-Sn(2)-C(2) | -13(2) | Si(1)-O(1)-Si(2)-C(7) | 175(2) |

**Table 8** continued.

| | | | |
|---|---|---|---|
| C(1)-Sn(2)-C(2)-Si(1) | 43(2) | O(1)-Si(2)-C(7)-Sn(1) | 33.3(19) |
| Sn(2)-C(2)-Si(1)-O(1) | -33.6(17) | Si(2)-C(7)-Sn(1)-C(1) | -19(3) |
| C(2)-Si(1)-O(1)-Si(2) | 175.9(19) | C(7)-Sn(1)-C(1)-Sn(2) | -8(3) |

In the molecular structure of compound **18** the *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$-unit is coordinated by one chelating DMSO molecule (Figure 16). The Sn(1)···O(11) and Sn(2)···O(11) distances amount to 2.419(2) and 2.672(2) Å, respectively. A further stabilization of this configuration is given by two Cl(3)···H(11A) and Cl(2)···H(12A) interactions with Cl(3)···C(11) and Cl(2)···C(12) distances of 3.589(4) and 3.615(4) Å. The tin atoms Sn(1) and Sn(2) are both [5+1] coordinated with a monocapped distorted trigonal bipyramidal coordination geometry.

The Sn-C bond distances are as expected and fall in the range 2.100(4)-2.114(4) Å. At Sn(1) and Sn(2) the equatorial Sn(1)-Cl(2) and Sn(2)-Cl(3) bonds have lengths of 2.3630(9) and 2.3549(11) Å, respectively, while the axial Sn(1)-Cl(1) and Sn(2)-Cl(4) bond have distances of 2.4348(10) and 2.3863(11) Å, respectively. In addition the Sn(1)···O(1) and Sn(2)···O(1) distances amount to 3.456(2) and 3.460(3) Å, respectively. The Sn···O(1) distances are rather long but shorter than the sum of the van der Waals radii of tin and oxygen.[104] Also in this case as well as for compound **17**, the bond lengths of tin to the equatorial chlorine atoms are shorter than those to the axial chlorine atoms. The Sn···O(11) distances are particularly short but slightly longer than those of compound **17**, nevertheless in the typical range for such bonds in DMSO adducts.[33] The two Sn(1)-C(1) and Sn(2)-C(1) bonds are only slightly asymmetric. Furthermore the Cl(2)···C(12) and Cl(3)···C(11) distances are at the borderline of the sum of the van der Waals radii of chlorine and carbon (3.35-3.60 Å).[104] Notably, as already observed for derivative **17**, while the Sn-C, Sn-Cl bonds and the Sn(1)···O(1) distances are only slightly different from those of *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**),[87,91] the Sn(2)···O(1) contact is significantly longer than the corresponding distance of compound **9**.[87,91]

The Cl(1)-Sn(1)-O(11) and Cl(4)-Sn(2)-O(11) angles amount to 171.86(7)° and 168.48(6)°, while the Cl(2)-Sn(1)-O(1) and Cl(3)-Sn(2)-O(1) angles amount to

157.01(5)° and 150.13(5)°. The first two angles are smaller than the corresponding angles of compound **17**.

The Si(1)-O(1)-Si(2) angle amounting to 152.52(18)° is greater than the corresponding angle of derivative **17** and in general greater than the corresponding angles of all the ring species presented in this work until now, including the *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**).[87,91]

The silicon atoms have an almost ideal tetrahedral coordination geometry. The Si(1)-O(1) and Si(2)-O(1) bonds have lengths of 1.645(3) and 1.636(3) Å, in agreement with the standard bond lengths reported in the literature.[112-114]

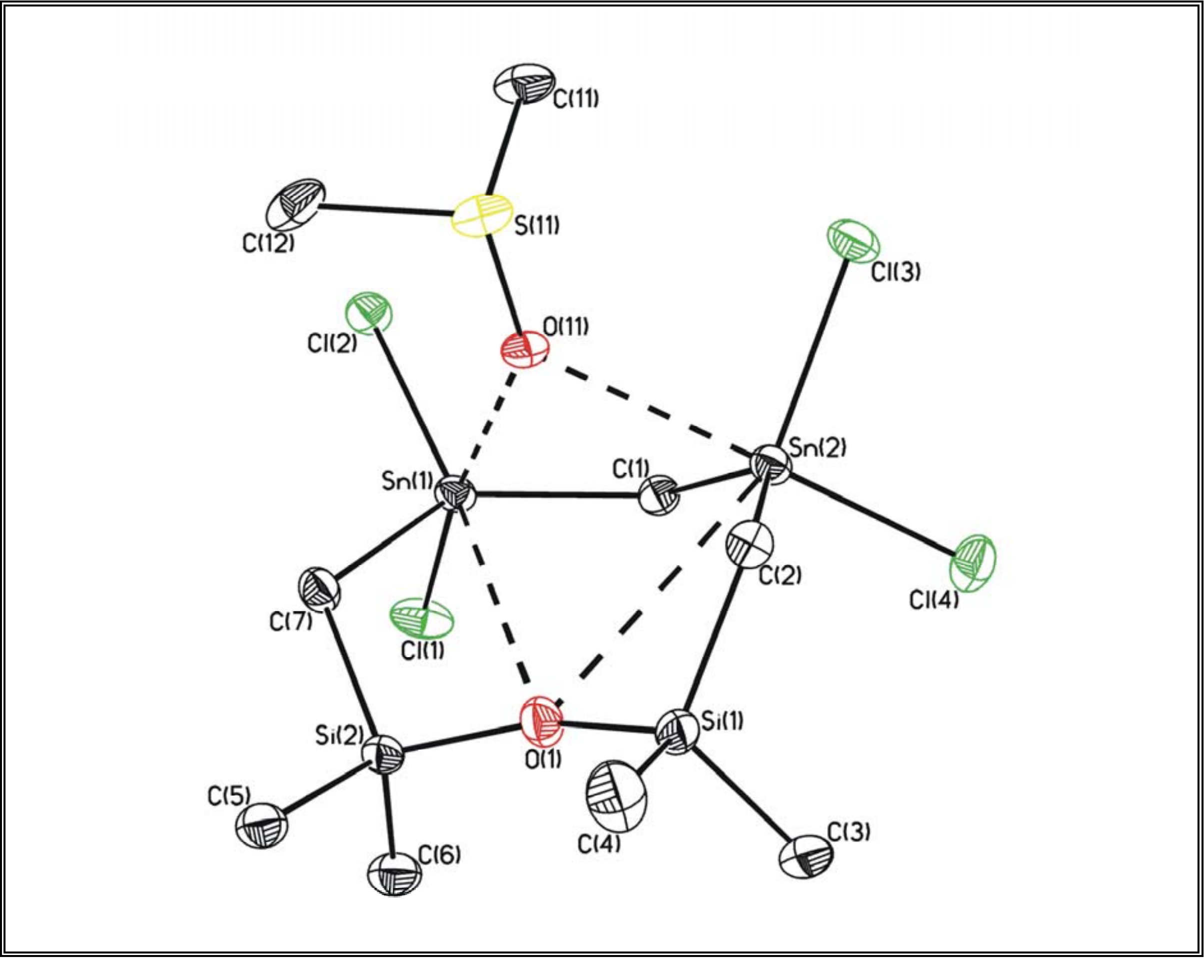


**Figure 16** Molecular structure (SHELXTL-PLUS) of **18** showing 30% probability displacement ellipsoids and the atom numbering scheme. The two Cl(2)-H(12A) and Cl(3)-H(11A) are omitted.

**Table 9** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **18**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.114(4) | Sn(2)-Cl(4) | 2.3863(11) |
| Sn(1)-C(7) | 2.100(4) | Sn(2)-O(1) | 3.460(3) |
| Sn(1)-Cl(1) | 2.4348(10) | Sn(2)-O(11) | 2.672(2) |
| Sn(1)-Cl(2) | 2.3630(9) | Si(1)-O(1) | 1.645(3) |
| Sn(1)-O(1) | 3.456(2) | Si(2)-O(1) | 1.636(3) |
| Sn(1)-O(11) | 2.419(2) | O(11)-S(11) | 1.537(2) |
| Sn(2)-C(1) | 2.106(3) | Cl(2)-C(12) | 3.615(4) |
| Sn(2)-C(2) | 2.100(3) | Cl(3)-C(11) | 3.589(4) |
| Sn(2)-Cl(3) | 2.3549(11) | | |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(7) | 131.68(14) | O(11)-Sn(2)-Cl(3) | 84.13(6) |
| C(1)-Sn(1)-Cl(1) | 95.98(10) | O(11)-Sn(2)-Cl(4) | 168.48(6) |
| C(1)-Sn(1)-Cl(2) | 111.88(11) | C(2)-Si(1)-C(3) | 112.3(2) |
| C(7)-Sn(1)-Cl(1) | 98.42(11) | C(2)-Si(1)-C(4) | 109.96(19) |
| C(7)-Sn(1)-Cl(2) | 112.76(10) | C(3)-Si(1)-C(4) | 111.2(2) |
| Cl(1)-Sn(1)-Cl(2) | 94.04(4) | O(1)-Si(1)-C(2) | 104.62(15) |
| O(1)-Sn(1)-C(1) | 78.23(11) | O(1)-Si(1)-C(3) | 107.36(17) |
| O(1)-Sn(1)-C(7) | 53.49(11) | O(1)-Si(1)-C(4) | 111.20(18) |
| O(1)-Sn(1)-Cl(1) | 105.68(5) | C(5)-Si(2)-C(6) | 110.33(19) |
| O(1)-Sn(1)-Cl(2) | 157.01(5) | C(5)-Si(2)-C(7) | 110.42(18) |
| O(1)-Sn(1)-O(11) | 75.56(7) | C(6)-Si(2)-C(7) | 110.64(18) |
| O(11)-Sn(1)-C(1) | 76.30(11) | O(1)-Si(2)-C(5) | 111.59(16) |
| O(11)-Sn(1)-C(7) | 88.78(12) | O(1)-Si(2)-C(6) | 108.73(17) |
| O(11)-Sn(1)-Cl(1) | 171.86(7) | O(1)-Si(2)-C(7) | 105.02(16) |
| O(11)-Sn(1)-Cl(2) | 86.61(6) | Sn(1)-C(1)-Sn(2) | 114.80(16) |
| C(1)-Sn(2)-C(2) | 131.20(15) | Sn(1)-O(1)-Sn(2) | 61.87(4) |
| C(1)-Sn(2)-Cl(3) | 112.24(11) | Sn(1)-O(11)-Sn(2) | 88.45(7) |
| C(1)-Sn(2)-Cl(4) | 98.15(10) | Sn(1)-C(7)-Si(2) | 114.58(19) |
| C(2)-Sn(2)-Cl(3) | 107.91(11) | Sn(2)-C(2)-Si(1) | 113.99(17) |
| C(2)-Sn(2)-Cl(4) | 103.37(11) | Sn(1)-O(1)-Si(1) | 132.75(14) |
| Cl(3)-Sn(2)-Cl(4) | 97.02(4) | Sn(1)-O(1)-Si(2) | 72.00(9) |

**Table 9** continued.

| | | | |
|---|---|---|---|
| O(1)-Sn(2)-C(1) | 78.22(12) | Sn(2)-O(1)-Si(1) | 71.50(10) |
| O(1)-Sn(2)-C(2) | 53.44(11) | Sn(2)-O(1)-Si(2) | 133.72(12) |
| O(1)-Sn(2)-Cl(3) | 150.13(5) | Si(1)-O(1)-Si(2) | 152.52(18) |
| O(1)-Sn(2)-Cl(4) | 109.44(5) | O(11)-S(11)-C(11) | 105.85(17) |
| O(1)-Sn(2)-O(11) | 72.75(7) | O(11)-S(11)-C(12) | 106.32(18) |
| O(11)-Sn(2)-C(1) | 70.96(11) | C(11)-S(11)-C(12) | 98.1(2) |
| O(11)-Sn(2)-C(2) | 87.07(11) | | |
| Torsion angles [°] | | | |
| Sn(1)-C(1)-Sn(2)-C(2) | 42.0(3) | Si(1)-O(1)-Si(2)-C(7) | 132.5(4) |
| C(1)-Sn(2)-C(2)-Si(1) | 34.6(3) | O(1)-Si(2)-C(7)-Sn(1) | 46.2(2) |
| Sn(2)-C(2)-Si(1)-O(1) | -48.4(2) | Si(2)-C(7)-Sn(1)-C(1) | -26.8(3) |
| C(2)-Si(1)-O(1)-Si(2) | -133.5(4) | C(7)-Sn(1)-C(1)-Sn(2) | -47.5(3) |

In compound **19** the *cyclo*-CH$_2$[Sn(Cl$_2$)CH$_2$Si(Me$_2$)]$_2$O-fragment (**9**) is coordinated by two DMF molecules with Sn(1)···O(2) and Sn(2)···O(3) distances of 2.3116(15) and 2.2774(15) Å, respectively (Figure 17).

Both tin atoms have a monocapped distorted trigonal bipyramidal coordination geometry.

The Sn-C bond distances range from 2.1096(19) to 2.1246(18) Å. The equatorial Sn(1)-Cl(2) and Sn(2)-Cl(4) bonds have legths of 2.3692(6) and 2.3724(5) Å, while the axial Sn(1)-Cl(1) and Sn(2)-Cl(3) bond distances amount to 2.4807(6) and 2.4877(6) Å, respectively. Furthermore, the Sn(1)···O(1) and Sn(2)···O(1) distances amounting to 3.3542(17) and 3.3425(14) Å, respectively, are rather long but shorter than the sum of the van der Waals radii of tin and oxygen.[104] Otherwise, the Sn(1)···O(2) and Sn(2)···O(3) distances are particularly short and in the typical range for Sn···O distances (2.116-2.710 Å) in DMF adducts.[124-127] Also in this case as well as for compounds **17** and **18**, the bond distances of tin to the equatorial chlorine atoms are shorter than those to the axial chlorine atoms.

Noteworthily, as already reported for derivatives **17** and **18**, the Sn(2)···O(1) distance is significantly longer than that of compound **9**.[87,91]

The Cl(1)-Sn(1)-O(2) and Cl(3)-Sn(2)-O(3) angles amounting to 178.64(4)° and 174.20(4)° differ only slightly from the ideal value of 180°, while for the Cl(2)-Sn(1)-O(1) and Cl(4)-Sn(2)-O(1) angles of 160.11(3)° and 148.72(3)° the deviation is considerably greater. The Cl(1)-Sn(1)-O(2) and Cl(3)-Sn(2)-O(3) angles are closer to the ideal value of 180° than those of derivative **18** and particularly of the corresponding DMSO adduct **17**.

The Si(1)-O(1)-Si(2) angle amounting to 143.35(11)° is smaller than those of compounds **17**, **18** and *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**).[87,91]

The silicon atoms have an almost ideal tetrahedral coordination geometry.

The Si(1)-O(1) and Si(2)-O(1) bonds have distances of 1.6339(18) and 1.6539(16) Å, respectively, within the standard values for Si-O bonds reported in the literature.[112-114]

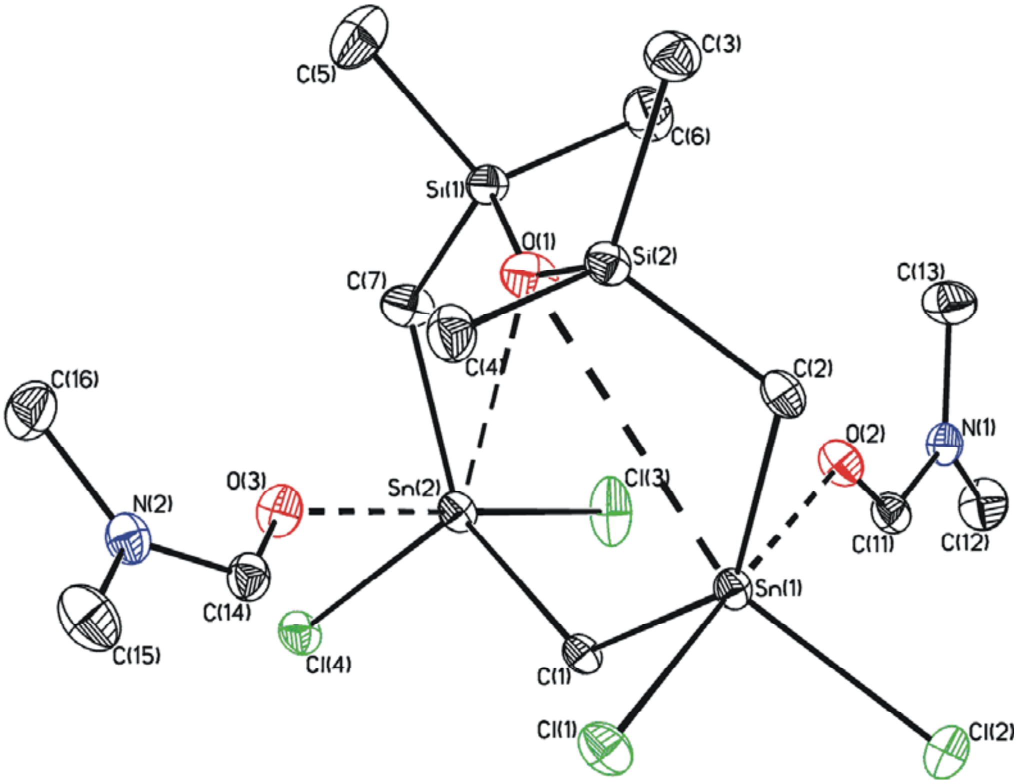


**Figure 17** Molecular structure (SHELXTL-PLUS) of **19** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 10** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **19**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.1246(18) | Sn(2)-Cl(3) | 2.4877(6) |
| Sn(1)-C(2) | 2.1096(19) | Sn(2)-Cl(4) | 2.3724(5) |
| Sn(1)-Cl(1) | 2.4807(6) | Sn(2)-O(1) | 3.3425(14) |
| Sn(1)-Cl(2) | 2.3692(6) | Sn(2)-O(3) | 2.2774(15) |
| Sn(1)-O(1) | 3.3542(17) | Si(1)-O(1) | 1.6339(18) |
| Sn(1)-O(2) | 2.3116(15) | Si(2)-O(1) | 1.6539(16) |
| Sn(2)-C(1) | 2.115(2) | O(2)-C(11) | 1.253(3) |
| Sn(2)-C(7) | 2.114(2) | O(3)-C(14) | 1.243(3) |
| **Bond angles [°]** | | | |
| C(1)-Sn(1)-C(2) | 139.86(9) | O(3)-Sn(2)-Cl(3) | 174.20(4) |
| C(1)-Sn(1)-Cl(1) | 94.32(6) | O(3)-Sn(2)-Cl(4) | 83.78(4) |
| C(1)-Sn(1)-Cl(2) | 107.08(6) | C(5)-Si(1)-C(6) | 110.16(4) |
| C(2)-Sn(1)-Cl(1) | 94.87(6) | C(5)-Si(1)-C(7) | 111.54(12) |
| C(2)-Sn(1)-Cl(2) | 111.39(6) | C(6)-Si(1)-C(7) | 109.87(12) |
| Cl(1)-Sn(1)-Cl(2) | 92.75(2) | O(1)-Si(1)-C(5) | 108.89(12) |
| O(1)-Sn(1)-C(1) | 84.08(6) | O(1)-Si(1)-C(6) | 109.32(11) |
| O(1)-Sn(1)-C(2) | 55.78(7) | O(1)-Si(1)-C(7) | 106.97(10) |
| O(1)-Sn(1)-Cl(1) | 102.97(3) | C(2)-Si(2)-C(3) | 110.29(10) |
| O(1)-Sn(1)-Cl(2) | 160.11(3) | C(2)-Si(2)-C(4) | 111.96(11) |
| O(1)-Sn(1)-O(2) | 78.32(5) | C(3)-Si(2)-C(4) | 109.47(11) |
| O(2)-Sn(1)-C(1) | 86.23(7) | O(1)-Si(2)-C(2) | 104.87(9) |
| O(2)-Sn(1)-C(2) | 85.49(7) | O(1)-Si(2)-C(3) | 112.09(11) |
| O(2)-Sn(1)-Cl(1) | 178.64(4) | O(1)-Si(2)-C(4) | 108.10(9) |
| O(2)-Sn(1)-Cl(2) | 85.90(4) | Sn(1)-C(1)-Sn(2) | 121.77(10) |
| C(1)-Sn(2)-C(7) | 140.41(8) | Sn(1)-O(1)-Sn(2) | 67.16(3) |
| C(1)-Sn(2)-Cl(3) | 93.64(6) | Sn(1)-C(2)-Si(2) | 113.27(10) |
| C(1)-Sn(2)-Cl(4) | 108.28(5) | Sn(2)-C(7)-Si(1) | 115.66(12) |
| C(7)-Sn(2)-Cl(3) | 96.58(8) | Sn(1)-O(1)-Si(1) | 132.68(8) |
| C(7)-Sn(2)-Cl(4) | 109.57(6) | Sn(1)-O(1)-Si(2) | 74.24(6) |
| Cl(3)-Sn(2)-Cl(4) | 91.47(2) | Sn(2)-O(1)-Si(1) | 76.73(5) |
| O(1)-Sn(2)-C(1) | 84.51(6) | Sn(2)-O(1)-Si(2) | 138.96(9) |

**Table 10** continued.

| | | | |
|---|---|---|---|
| O(1)-Sn(2)-C(7) | 56.79(7) | Si(1)-O(1)-Si(2) | 143.35(11) |
| O(1)-Sn(2)-Cl(3) | 116.70(3) | O(2)-C(11)-N(1) | 124.6(2) |
| O(1)-Sn(2)-Cl(4) | 148.72(3) | C(11)-N(1)-C(12) | 121.7(2) |
| O(1)-Sn(2)-O(3) | 67.18(5) | O(3)-C(14)-N(2) | 122.6(2) |
| O(3)-Sn(2)-C(1) | 91.02(7) | C(14)-N(2)-C(15) | 121.9(2) |
| O(3)-Sn(2)-C(7) | 81.95(9) | | |
| Torsion angles [°] | | | |
| Sn(1)-C(1)-Sn(2)-C(7) | -4.0(2) | Si(1)-O(1)-Si(2)-C(2) | -120.42(19) |
| C(1)-Sn(2)-C(7)-Si(1) | -1.2(2) | O(1)-Si(2)-C(2)-Sn(1) | -40.13(14) |
| Sn(2)-C(7)-Si(1)-O(1) | -23.11(17) | Si(2)-C(2)-Sn(1)-C(1) | 22.0(2) |
| C(7)-Si(1)-O(1)-Si(2) | -177.82(18) | C(2)-Sn(1)-C(1)-Sn(2) | 15.39(19) |

In compound **20** both Sn(1) and Sn(2) coordinate to the O(2) of the 1,3-dimethylimidazolidin-2-one molecule (Figure 18). The five-membered imidazolidine ring is perpendicular to the plane defined by Sn(1), Sn(2), O(2) and this arrangement is stabilized by a Cl(2)···H(17A) interaction with Cl(2)-C(17) distance of 3.529(3) Å.

The Sn(1) and Sn(2) tin atoms are both [5+1] coordinated with a monocapped distorted trigonal bipyramidal coordination geometry.

The Sn-C bond distances are as expected and range from 2.104(2) to 2.111(2) Å. In addition, the equatorial Sn(1)-Cl(2) and Sn(2)-Cl(3) bond distances of 2.3424(6) and 2.3440(6) Å, respectively, are shorter than the axial Sn(1)-Cl(1) and Sn(2)-Cl(4) bond distances which amount to 2.4024(6) and 2.4159(6) Å, respectively. The Sn(1)···O(2) and Sn(2)···O(2) interactions have distances of 2.6687(15) and 2.5545(15) Å, while the Sn(1)···O(1) and Sn(2)···O(1) distances amount to 3.4396(15) and 3.3466(15) Å. The Sn···O(1) distances are rather long but shorter than the sum of the van der Waals radii of tin and oxygen.[104] Notably, the Sn···O(2) distances are longer than the corresponding distances of compound **19** however, they are comparable with standard Sn···O distances (2.116-2.710 Å) in adducts with molecules containing C=O- groups.[124-127] The two Sn(1)-C(1) and Sn(2)-C(1) bonds are practically symmetric. Furthermore, the Cl(2)···H(17A) distance is rather long but at the borderline of the sum of the van der Waals radii of carbon and chlorine (3.35-

3.60 Å).[104] As already discussed for derivatives **17, 18** and **19**, the Sn(2)···O(1) contact is significantly longer than that of compound **9**.[87,91]

The Cl(1)-Sn(1)-O(2) and Cl(4)-Sn(2)-O(2) angles amounting to 173.27(3)° and 173.30(4)° differ only slightly from the ideal value of 180°, while the Cl(2)-Sn(1)-O(1) and Cl(3)-Sn(2)-O(1) angles amounting to 148.53(3)° and 151.39(3)° differ considerably from the ideal value.

The Si(1)-O(1)-Si(2) angle amounts to 150.55(11)°, which is smaller only than that of derivative **18**, but greater than the other Si-O-Si angles of all the ring species here presented, including also compound **9**.[87,91]

The silicon atoms have an almost ideal tetrahedral coordination geometry. The Si(1)-O(1) and Si(2)-O(1) bonds have lenghts of 1.6454(15) and 1.6380(15) Å, respectively, within the standard values for Si-O bonds reported in the literature.[112-114]

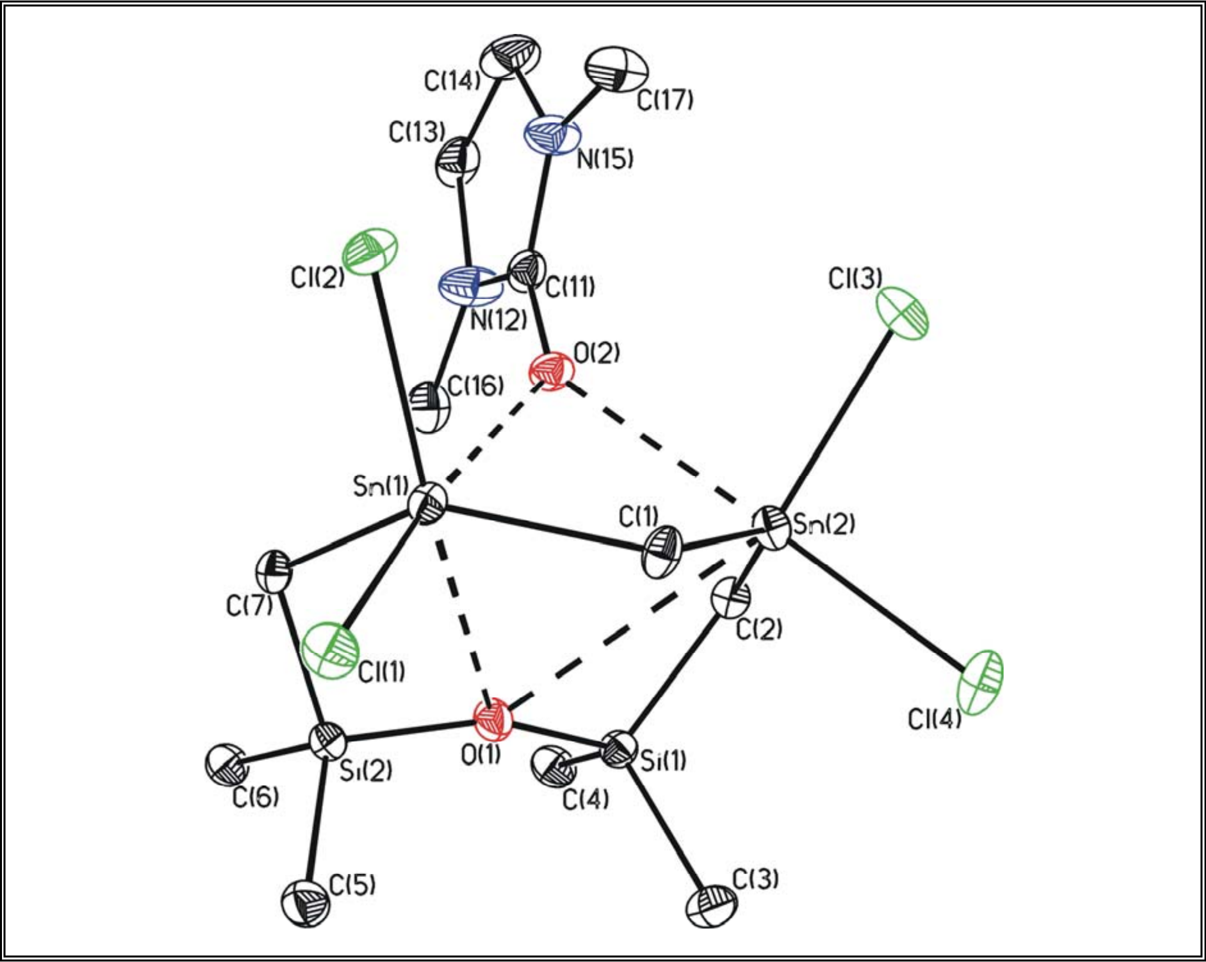


**Figure 18** Molecular structure (SHELXTL-PLUS) of **20** showing 30% probability displacement ellipsoids and the atom numbering scheme, the Cl(2)···H(17A) being omitted.

**Table 11** Selected bond lengths [Å], bond angles [°] and torsion angles [°] of **20**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.104(2) | Sn(2)-Cl(4) | 2.4159(6) |
| Sn(1)-C(7) | 2.111(2) | Sn(2)-O(1) | 3.3466(15) |
| Sn(1)-Cl(1) | 2.4024(6) | Sn(2)-O(2) | 2.5545(15) |
| Sn(1)-Cl(2) | 2.3424(6) | Si(1)-O(1) | 1.6454(15) |
| Sn(1)-O(1) | 3.4396(15) | Si(2)-O(1) | 1.6380(15) |
| Sn(1)-O(2) | 2.6687(15) | O(2)-C(11) | 1.263(3) |
| Sn(2)-C(1) | 2.104(2) | N(12)-C(11) | 1.347(3) |
| Sn(2)-C(2) | 2.110(2) | N(15)-C(11) | 1.342(3) |
| Sn(2)-Cl(3) | 2.3440(6) | Cl(2)-C(17) | 3.529(3) |

| Bond angles [°] | | | |
|---|---|---|---|
| C(1)-Sn(1)-C(7) | 129.95(9) | O(2)-Sn(2)-Cl(3) | 85.66(4) |
| C(1)-Sn(1)-Cl(1) | 99.31(6) | O(2)-Sn(2)-Cl(4) | 173.30(4) |
| C(1)-Sn(1)-Cl(2) | 111.52(7) | C(2)-Si(1)-C(3) | 110.35(11) |
| C(7)-Sn(1)-Cl(1) | 100.11(7) | C(2)-Si(1)-C(4) | 111.38(11) |
| C(7)-Sn(1)-Cl(2) | 111.19(6) | C(3)-Si(1)-C(4) | 111.15(12) |
| Cl(1)-Sn(1)-Cl(2) | 97.08(2) | O(1)-Si(1)-C(2) | 104.44(9) |
| O(1)-Sn(1)-C(1) | 75.84(7) | O(1)-Si(1)-C(3) | 108.09(10) |
| O(1)-Sn(1)-C(7) | 54.11(6) | O(1)-Si(1)-C(4) | 111.19(10) |
| O(1)-Sn(1)-Cl(1) | 112.23(3) | C(5)-Si(2)-C(6) | 110.40(12) |
| O(1)-Sn(1)-Cl(2) | 148.53(3) | C(5)-Si(2)-C(7) | 110.09(11) |
| O(1)-Sn(1)-O(2) | 66.76(4) | C(6)-Si(2)-C(7) | 111.09(10) |
| O(2)-Sn(1)-C(1) | 73.96(7) | O(1)-Si(2)-C(5) | 109.76(10) |
| O(2)-Sn(1)-C(7) | 84.69(7) | O(1)-Si(2)-C(6) | 110.19(10) |
| O(2)-Sn(1)-Cl(1) | 173.27(3) | O(1)-Si(2)-C(7) | 105.19(9) |
| O(2)-Sn(1)-Cl(2) | 85.44(4) | Sn(1)-C(1)-Sn(2) | 116.98(10) |
| C(1)-Sn(2)-C(2) | 133.98(9) | Sn(1)-O(1)-Sn(2) | 63.81(3) |
| C(1)-Sn(2)-Cl(3) | 110.35(7) | Sn(1)-O(2)-Sn(2) | 86.73(5) |
| C(1)-Sn(2)-Cl(4) | 96.90(6) | Sn(1)-C(7)-Si(2) | 112.39(10) |
| C(2)-Sn(2)-Cl(3) | 110.88(6) | Sn(2)-C(2)-Si(1) | 111.85(10) |
| C(2)-Sn(2)-Cl(4) | 98.57(6) | Sn(1)-O(1)-Si(1) | 137.83(8) |
| Cl(3)-Sn(2)-Cl(4) | 95.64(3) | Sn(1)-O(1)-Si(2) | 71.56(5) |

**Table 11** continued.

| | | | |
|---|---|---|---|
| O(1)-Sn(2)-C(1) | 78.08(7) | Sn(2)-O(1)-Si(1) | 74.04(5) |
| O(1)-Sn(2)-C(2) | 55.90(6) | Sn(2)-O(1)-Si(2) | 135.37(8) |
| O(1)-Sn(2)-Cl(3) | 151.39(3) | Si(1)-O(1)-Si(2) | 150.55(11) |
| O(1)-Sn(2)-Cl(4) | 110.79(3) | O(2)-C(11)-N(12) | 124.5(2) |
| O(1)-Sn(2)-O(2) | 69.40(4) | O(2)-C(11)-N(15) | 126.4(2) |
| O(2)-Sn(2)-C(1) | 76.51(7) | N(12)-C(11)-N(15) | 109.1(2) |
| O(2)-Sn(2)-C(2) | 87.06(7) | | |
| Torsion angles [°] | | | |
| Sn(1)-C(1)-Sn(2)-C(2) | -50.16(19) | Si(1)-O(1)-Si(2)-C(7) | -150.5(2) |
| C(1)-Sn(2)-C(2)-Si(1) | -22.05(18) | O(1)-Si(2)-C(7)-Sn(1) | -48.43(13) |
| Sn(2)-C(2)-Si(1)-O(1) | 42.99(13) | Si(2)-C(7)-Sn(1)-C(1) | 26.24(18) |
| C(2)-Si(1)-O(1)-Si(2) | 153.0(2) | C(7)-Sn(1)-C(1)-Sn(2) | 47.14(18) |

**Table 7** Sn-C-Sn and Si-O-Si angles [°] of **11**, **14**, **15**, **16**, **17**, **18**, **19** and **20**.

| Compounds | Sn-C-Sn | Si-O-Si |
|---|---|---|
| *cyclo*-$[Sn(I_2)CH_2Sn(I)Ph\{CH_2Si(Me_2)\}_2O]$ (**11**) | 118.0(2) | 143.2(2) |
| *cyclo*-$CH_2[Sn(Cl)PhCH_2Si(Me_2)]_2O]$ (**14**) | 113.80(13) | 147.78(15) |
| *cyclo*-$CH_2[Sn(I_2)CH_2Si(Me_2)]_2O$ (**15**) | 119.1(3)/119.3(3) | 140.3(3)/142.2(2) |
| *cyclo*-$CH_2[Sn(Br_2)CH_2Si(Me_2)]_2O$ (**16**) | 116.3(6)-117.7(5) | 140.5(5)-143.7(6) |
| *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2$° · 2DMSO (**17**) | 116.8(12) | 144.9(11) |
| *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2$° · DMSO (**18**) | 114.80(16) | 152.52(18) |
| *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2$° · 2DMF (**19**) | 121.77(10) | 143.35(11) |
| *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2$° · 1,3-dimethyl-imidazolidin-2-one (**20**) | 116.98(10) | 150.55(11) |

## 1.3 Novel bis(triiodostannyl)alkanes and their complexes

### 1.3.1 Introduction

Since they were first described in 1957,[115,116] distannylated derivatives have received increasingly attention. 1,*n*-haloorganodistannylated species have been mainly studied as Lewis acids due to their ability to complex anions,[8,22-27,32-41,58,87,88,117,118] as well as neutral donor molecules forming DMSO,[33,34,82-84,119] HMPA,[8,33,35,37,82-84,120] pyridine[32] or water[117,121] adducts.

Although 1,*n*-haloorganodistannylated compounds are well known, methylene-bridged ditin hexahalides have only recently been reported. In 2001 Zobel et al. described the reaction of various polymethylene-bridged ditin hexahalides with anions,[117,118] and in 2002 Jousseaume et al. reported on the preparation of oligomethylene-, arylene- and benzylene-bridged ditin hexachlorides.[122]

Here it will be presented the synthesis of the first bis(triiodostannyl)alkanes $I_3Sn(CH_2)_nSnI_3$ (n = 1, 3) and their DMSO and DMF complexes.

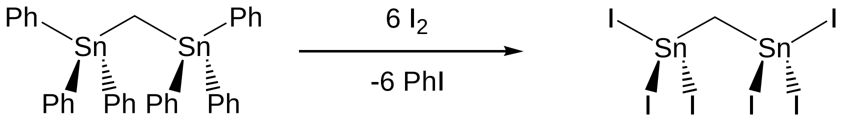
### 1.3.2 Synthesis of $I_3Sn(CH_2)_nSnI_3$ (n = 1, 3) and their complexes

The reaction of bis(triphenylstannyl)methane (**1**) with six molar equivalents of iodine led to the electrophilic cleavage of all phenyl groups in the starting material **1**, affording bis(triiodostannyl)methane (**21**) in almost quantitative yield (equation 13). Compound **21** was isolated as a yellow crystalline solid from $CH_2Cl_2$/*n*-hexane (1:1). It is well soluble in chlorinated solvents, diethyl ether, acetone, and water but almost insoluble in *n*-hexane.

The $^{119}Sn$-NMR spectrum ($CH_2Cl_2$) of **21** shows a single resonance at $\delta$ -835.2 ($^2J(^{119}Sn-^{117}Sn)$ = 474 Hz) ppm. The chemical shift at high field is to be expected. For instance, $MeSnI_3$ shows in the $^{119}Sn$-NMR spectrum ($CCl_4$) a single resonance at $\delta$ -699.5 ppm.[101]

In Figure 19 the time-dependent $^{119}Sn$-NMR spectra ($CH_2Cl_2$) of derivative **21** are reported.

The molecular structure of **21** will be discussed in chapter 1.3.3.



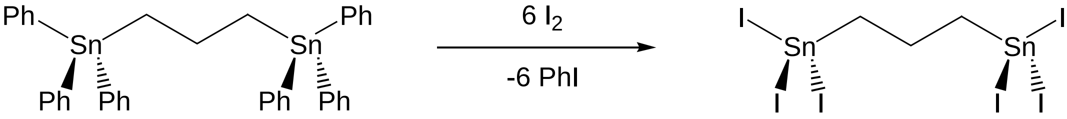
**1** **21**

(13)

In a similar manner treatment of bis(triphenylstannyl)propane (**22**) with six molar equivalents of iodine provided bis(triiodostannyl)propane (**23**) in almost quantitative yield (equation 14). Derivative **23** was crystallised from $CH_2Cl_2$/*n*-hexane (1:1) as a yellow solid. The hexaiodo-substituted organotin compounds **23** and **21** are well soluble in chlorinated solvents, acetone and diethyl ether but almost insoluble in *n*-hexane.

The $^{119}$Sn-NMR spectrum of **23** ($CH_2Cl_2$) shows a signal at $\delta$ -622.4 ($^{4}J(^{119}Sn-^{117}Sn)$ = 432 Hz) ppm.

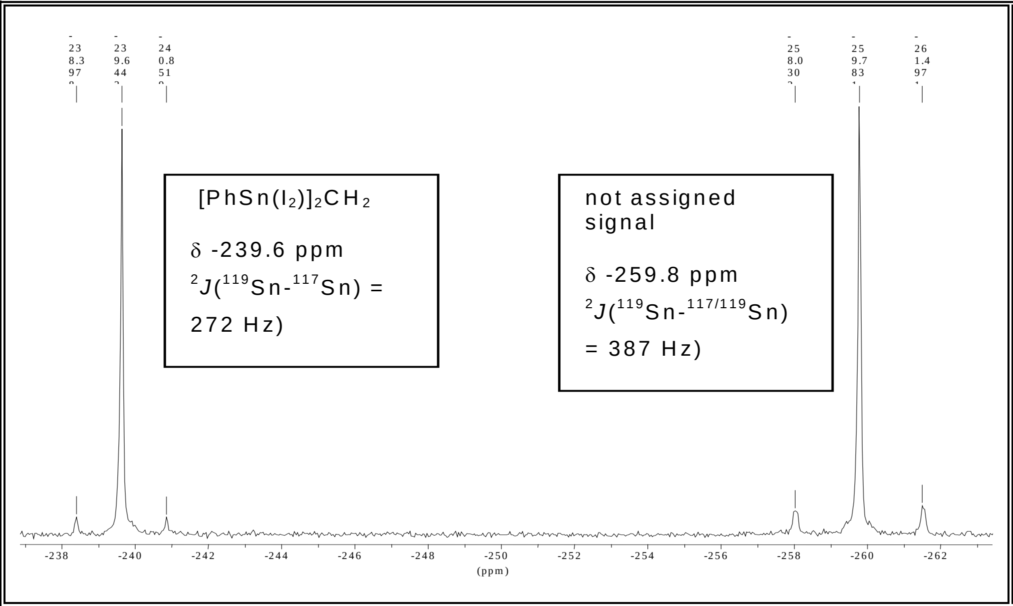
The molecular structure of **23** will be discussed in chapter 1.3.3.



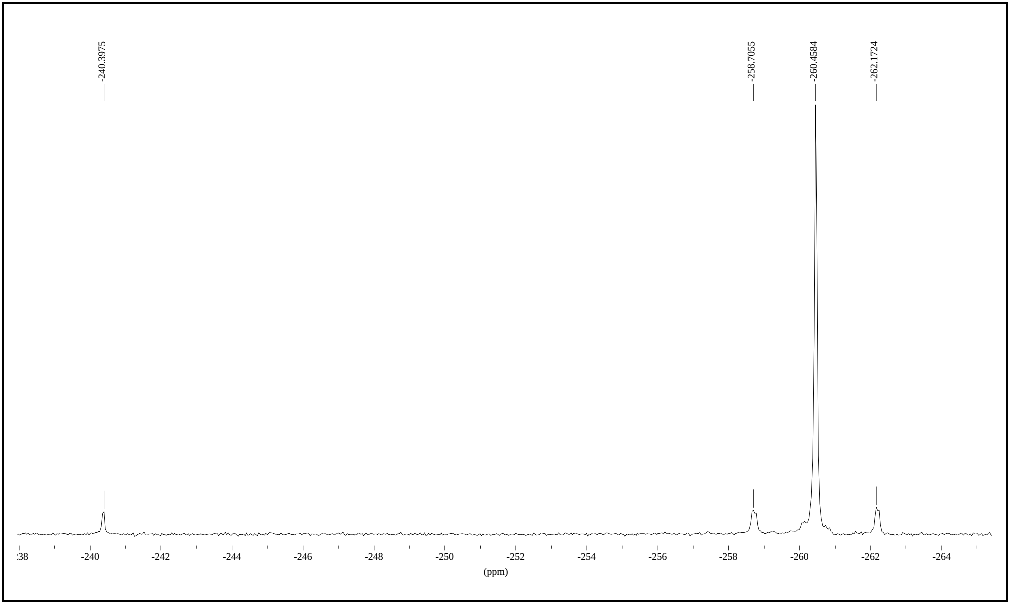
**22** **23**

(14)

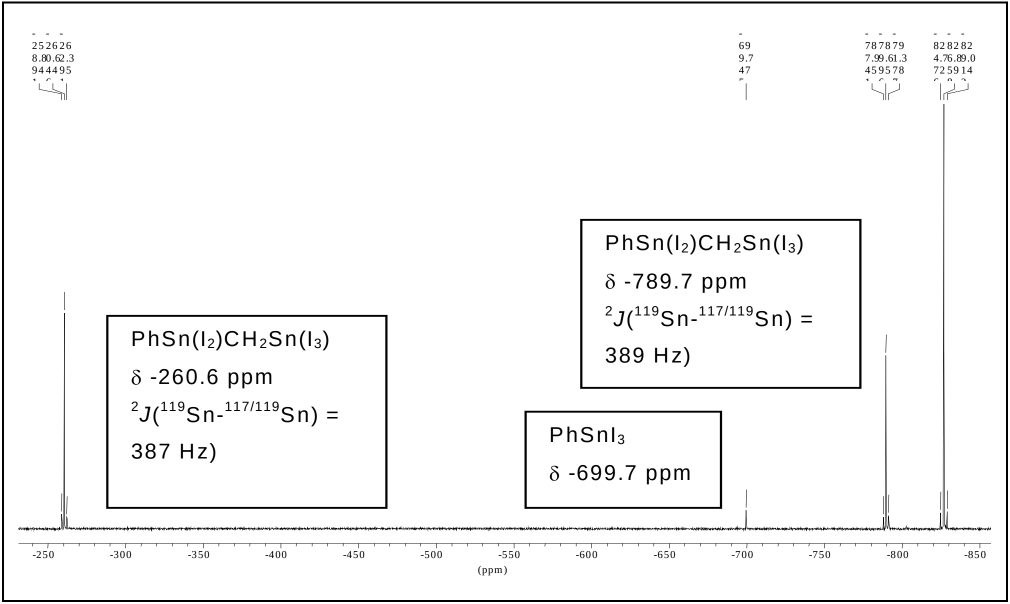
The cleavage of all phenyl groups in $(Ph_3Sn_2)_2(CH_2)_n$ (n = 1, 3) species can be considered a general route to alkylidene-bridged ditin hexaiodides; for this reason other investigations should be carried out on $(Ph_3Sn_2)_2(CH_2)_n$ (n = 2, 4, …).



(**a**) After 2 h

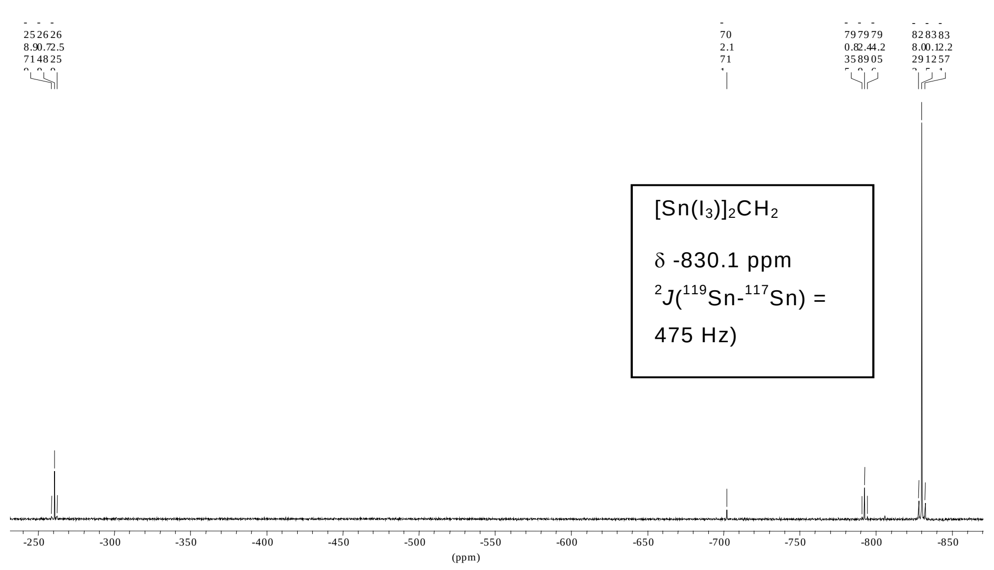


(**b**) After 24 h

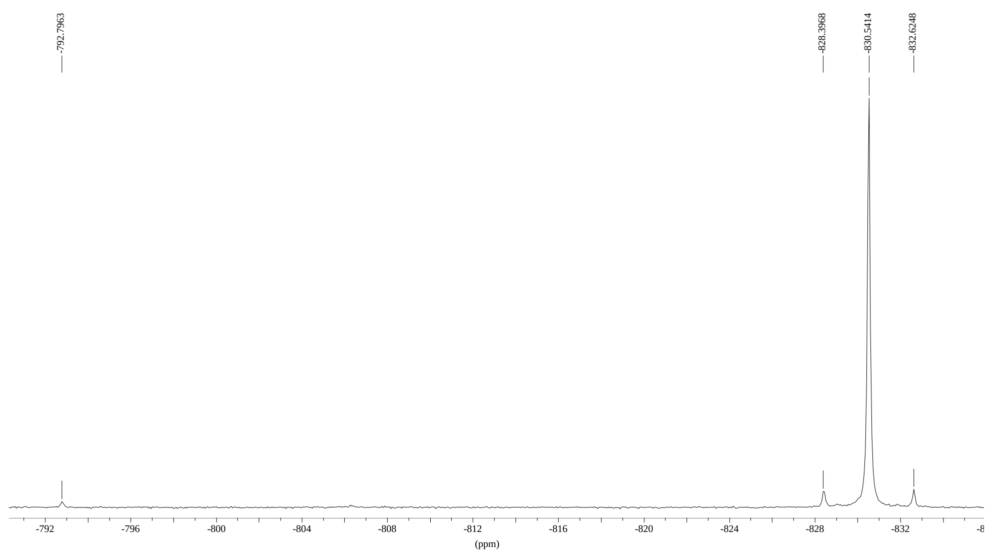


(**c**) After 48 h

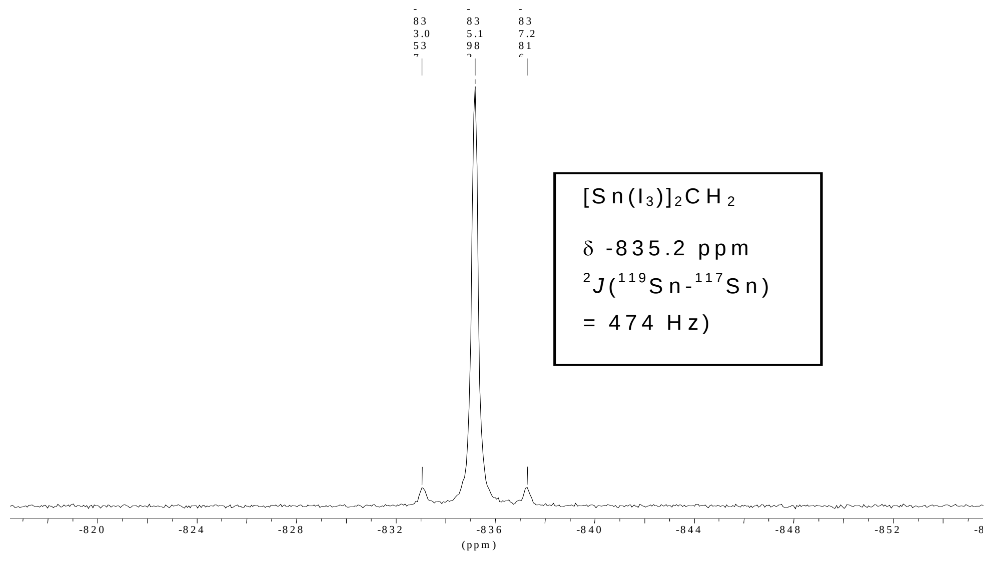
**Figure 19 (a, b, c)** Time-dependent $^{119}$Sn-NMR spectra ($CH_2Cl_2$) of compound **21**.



(**d**) After 72 h



(**e**) After 96 h



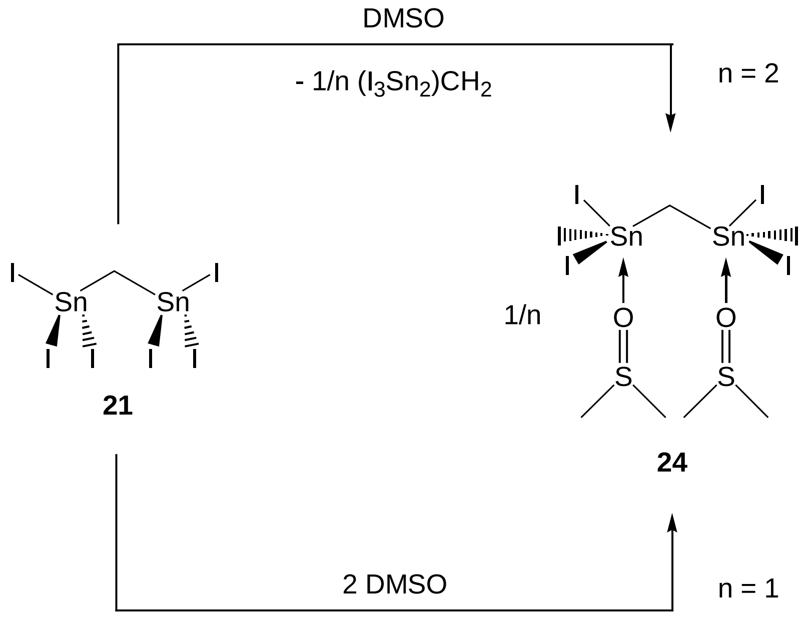
(**f**) After 120 h

**Figure 19 (d, e, f)** Time-depending $^{119}$Sn-NMR spectra (CH$_2$Cl$_2$) of compound **21**.

Replacing organo substituents at the tin atoms in alkylidene-bridged ditin species by halides appears to increase the Lewis acidity of each of the two tin centers. In 1982 Kuivila reported on the first bis(trichlorostannyl)methane-tetrakis-(dimethylsulfoxide) in which the bis(trichlorostannyl)methane react as tetra(monodentate) Lewis acid.[33,34] Somewhat surprisingly, $\alpha,\omega$-bis(trichlorostannyl)alkanes act only as bis(monodentate) Lewis acids without any evidence for the ditin acting as a chelate.[118]

To check if this observation is also valid for alkylidene-bridged ditin hexaiodides some experiments were carried out.

Derivative **21** was treated with one and two molar equivalents of DMSO (scheme 2) affording only adduct **24**.



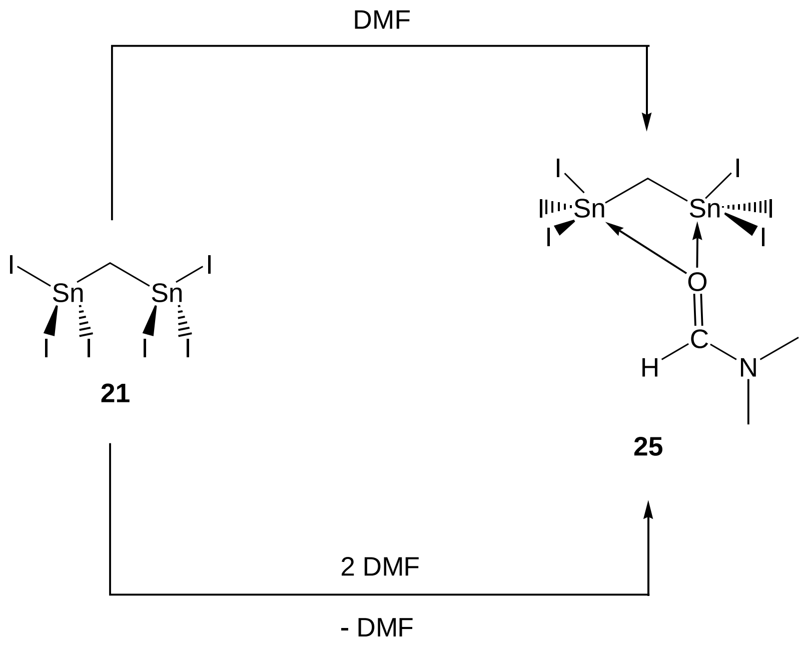
**Scheme 2** Reaction of **21** with 1 and 2 molar equivalents of DMSO.

Complex **24** was isolated as a yellow crystalline solid from $CH_2Cl_2$ in good yield. It is well soluble in chlorinated solvents and acetone but it is almost insoluble in *n*-hexane.

In $CDCl_3$ the $^{119}$Sn-NMR spectrum of **24** shows a single resonance at $\delta$ –878.3 ppm ($\nu^{1}/_{2}$ = 127 Hz), which is in agreement with the expectation of equivalent atoms. The complexation of **21** by DMSO, as expected, moves the chemical shift of the tin atoms to higher field. Additional NMR-investigations at lower temperature were not performed. The molecular structure of adduct **24** will be discussed in chapter 1.3.3.

When bis(triiodostannyl)methane (**21**) is reacted with one and two molar equivalents of DMF only adduct **25** is obtained (scheme 3).

Derivative **25** was recrystallised from $CH_2Cl_2$ as a yellow solid in good yield. It is well soluble in chlorinated solvents and acetone but almost insoluble in *n*-hexane.



**Scheme 3** Reaction of **21** with 1 and 2 molar equivalents of DMF.

The $^{119}$Sn-NMR spectrum of **25** ($CDCl_3$) shows a single resonance at $\delta$ –876.7 ppm ($\nu^{1}/_{2}$ = 86 Hz), indicating both tin atoms to be equivalent on the $^{119}$Sn-NMR

timescale. This fact is probably due to a rapid exchange of DMF between the two tin centers. No additional NMR investigations at lower temperature were carried out.
The molecular structure of adduct **25** will be discussed in chapter 1.3.3.

### 1.3.3 Molecular structures of bis(triiodostannyl)methane (21), bis(triiodostannyl)propane (23), bis(triiodostannyl)methane-bis(dimethylsulfoxide) (24), bis(triiodostannyl)methane-dimethylformamide (25)

Suitable crystals for the molecular structure determination of compounds **21** and **23** were obtained by slow evaporation of $CH_2Cl_2$ from a 1:1 $CH_2Cl_2$/*n*-hexane solution and of compounds **24** and **25** in a $CH_2Cl_2$ solution by slow evaporation of the solvent at room temperature.
Bis(triiodostannyl)methane (**21**) crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Compound **23** crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Derivative **24** crystallises in the orthorhombic space group *Pbca* with eight molecules in the unit cell. **25** crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecular structures of **21**, **23**, **24** and **25** are illustrated in Figures 20, 21, 22 and 23. Selected bond lengths and angles for **21**, **23**, **24** and **25** are listed in Tables 12, 13, 14 and 15.

Compound **21** is monomeric with no intra- or intermolecular coordination (Figure 20). The two tin centers are equivalent and tetracoordinated.
The Sn-I bond lengths fall in the range 2.6535(10) - 2.6683(11) Å. The Sn(1)-C(1) and Sn(2)-C(1) bond distances amounting to 2.125(8) and 2.143(8) Å, respectively, are slightly asymmetric.
The Sn(1)-C(1)-Sn(2) bond angle amount to 116.4(4)°, the deviation of this angle from the ideal value of 109° being the result of the sterically demanding iodine atoms.

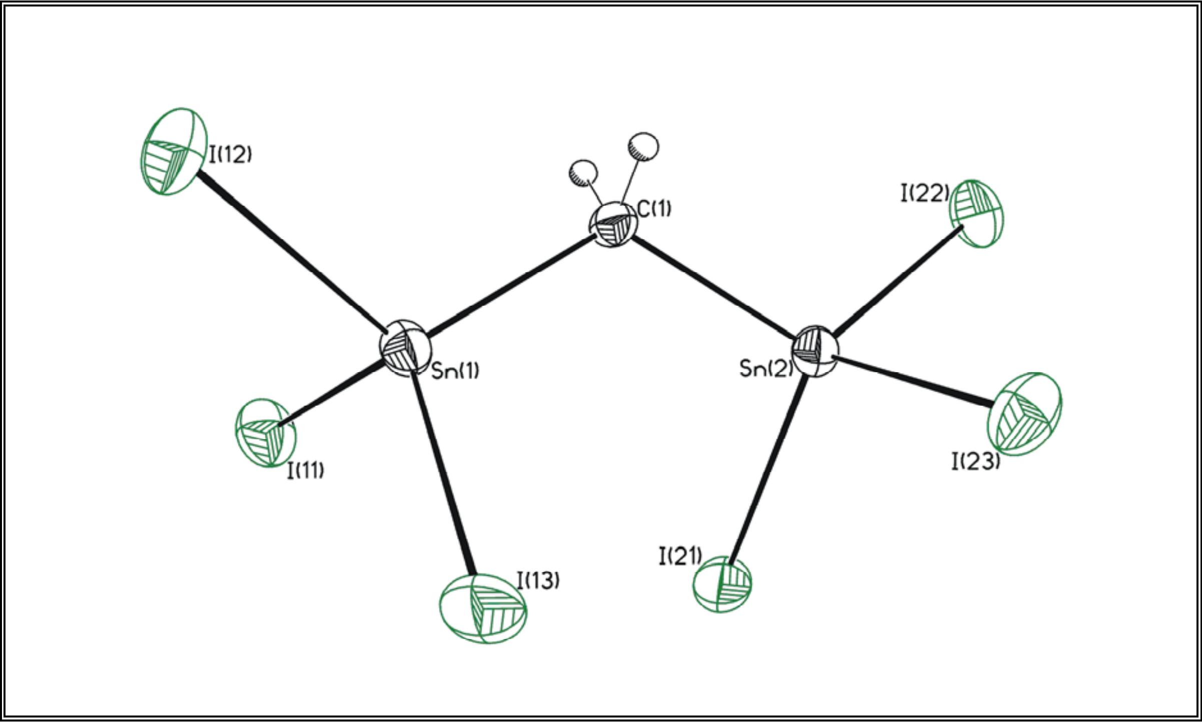


**Figure 20** Molecular structure (SHELXL-97) of **21** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 12** Selected bond lengths [Å] and bond angles [°] of **21**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.125(8) | Sn(2)-C(1) | 2.143(8) |
| Sn(1)-I(11) | 2.6683(11) | Sn(2)-I(21) | 2.6535(10) |
| Sn(1)-I(12) | 2.6669(11) | Sn(2)-I(22) | 2.6644(11) |
| Sn(1)-I(13) | 2.6557(11) | Sn(2)-I(23) | 2.6659(11) |
| **Bond angles [°]** | | | |
| C(1)-Sn(1)-I(11) | 110.3(2) | C(1)-Sn(2)-I(21) | 109.2(2) |
| C(1)-Sn(1)-I(12) | 109.9(2) | C(1)-Sn(2)-I(22) | 112.0(2) |
| C(1)-Sn(1)-I(13) | 111.7(2) | C(1)-Sn(2)-I(23) | 109.7(2) |
| I(11)-Sn(1)-I(12) | 106.01(3) | I(21)-Sn(2)-I(22) | 110.08(4) |
| I(11)-Sn(1)-I(13) | 110.57(4) | I(21)-Sn(2)-I(23) | 110.38(4) |
| I(12)-Sn(1)-I(13) | 108.21(4) | I(22)-Sn(2)-I(23) | 105.38(3) |
| | | Sn(1)-C(1)-Sn(2) | 116.4(4) |

Bis(triiodostannyl)propane (**23**) is monomeric as well (Figure 21).

The Sn-I bond lengths fall in the range between 2.6667(8) and 2.6862(9) Å. The Sn(1)-C(1) and Sn(2)-C(3) bond lengths, which amount to 2.133(8) and 2.139(7) Å, differ slightly. Both tin atoms have tetrahedral coordination geometries with average angles of 109.3° for Sn(1) and 109.4° for Sn(2). Notably, there is a significant deviation of the ideal value of 109° for the C(1)-Sn(1)-I(3) with 117.2(2)°, I(1)-Sn(1)-I(2) with 105.27(3)°, C(3)-Sn(2)-I(6) with 112.9(2)° and I(6)-Sn(2)-I(5) with 102.94(3)°. The Sn(1)-C(1)-C(2) and Sn(2)-C(3)-C(2) angles amount to 113.5(5)° and 112.2(6)° with a deviation of these angles from the ideal value of 109°.

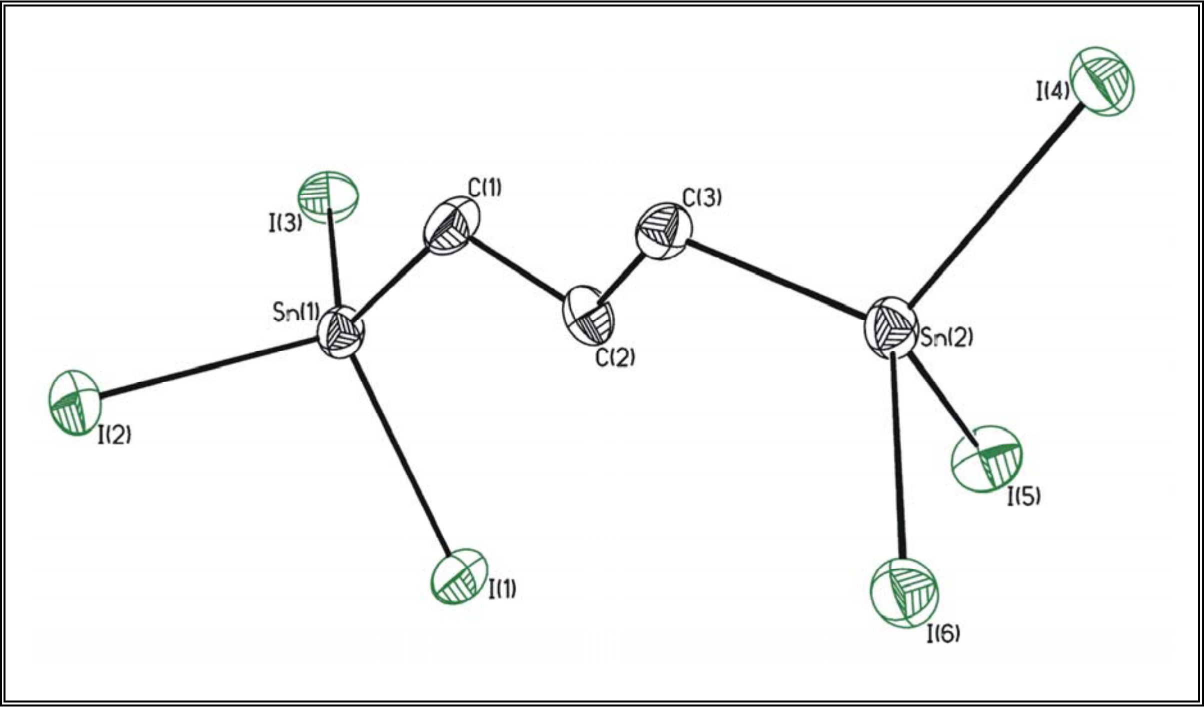


**Figure 21** Molecular structure (SHELXL-97) of **23** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 13** Selected bond lengths [Å] and bond angles [°] of **23**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.133(8) | Sn(2)-C(3) | 2.139(7) |
| Sn(1)-I(1) | 2.6703(9) | Sn(2)-I(4) | 2.6667(8) |
| Sn(1)-I(2) | 2.6855(8) | Sn(2)-I(5) | 2.6862(9) |
| Sn(1)-I(3) | 2.6720(9) | Sn(2)-I(6) | 2.6684(9) |

**Table 13** continued.

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.541(10) | C(2)-C(3) | 1.559(10) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-I(1) | 109.2(2) | C(3)-Sn(2)-I(6) | 112.9(2) |
| C(1)-Sn(1)-I(2) | 111.2(2) | I(4)-Sn(2)-I(5) | 107.08(3) |
| C(1)-Sn(1)-I(3) | 117.2(2) | I(4)-Sn(2)-I(6) | 111.37(3) |
| I(1)-Sn(1)-I(2) | 105.27(3) | I(5)-Sn(2)-I(6) | 102.94(3) |
| I(1)-Sn(1)-I(3) | 106.22(3) | Sn(1)-C(1)-C(2) | 113.5(5) |
| I(2)-Sn(1)-I(3) | 107.05(3) | Sn(2)-C(3)-C(2) | 112.2(6) |
| C(3)-Sn(2)-I(4) | 110.5(2) | C(1)-C(2)-C(3) | 108.4(7) |
| C(3)-Sn(2)-I(5) | 111.7(2) | | |

In the molecular structure of complex **24** each tin atom is coordinated by one DMSO molecule. The Sn(1)···O(1) and Sn(2)···O(2) distances are 2.266(6) and 2.520(7) Å, respectively (Figure 22). The coordination geometry at both tin atoms can be best described as a distorted trigonal bipyramid where $\Delta(\sum\vartheta)$[105-107] = 62.0° for Sn(1) and $\Delta(\sum\vartheta)$ = 61.4° for Sn(2).

At Sn(1) the equatorial positions are occupied by C(1), I(1) and I(2), the axial positions by O(1) and I(3). At Sn(2) C(1), I(4), I(6) occupy the equatorial and O(2), I(5) the axial positions. The equatorial Sn(1)-C(1), Sn(1)-I(1), Sn(1)-I(2), Sn(2)-C(1), Sn(2)-I(4) and Sn(2)-I(6) distances are 2.140(7), 2.7551(9), 2.7109(9), 2.128(7), 2.6885(8) and 2.6817(9) Å, respectively. The axial Sn(1)-I(3) and Sn(2)-I(5) of 2.8046(9) and 2.7777(9) Å, respectively, are longer than those to the equatorial iodine atoms. The two Sn-C bond distances are slightly asymmetric, with the Sn(2)-C(1) bond shorter than the Sn(2)-C(1) bond. The two Sn(1)···O(1) and Sn(2)···O(2) distances are particularly short. Sn-O distances within the range of 2.109(5)-2.621(6) Å are found in the literature for $(CH3)_{3-n}Sn(Cl)_n$-$CH_2(Cl)_nSn(CH3)_{3-n}$ · DMSO (n = 1-3) adducts.[33,34] Noteworthily, while the Sn-C bond lengths are not influenced by the presence of the DMSO molecules, the Sn-I bonds are longer than those of compound **21**.

The I(3)-Sn(1)-O(1) and I(5)-Sn(2)-O(2) angles amounting to 168.84(16)° and 173.90(17)°, respectively, differ slightly fron the ideal value of 180°. The Sn(1)-C(1)-

Sn(2) bond angle amounting to 115.0(3)° differ significantly from the ideal value of 109°.

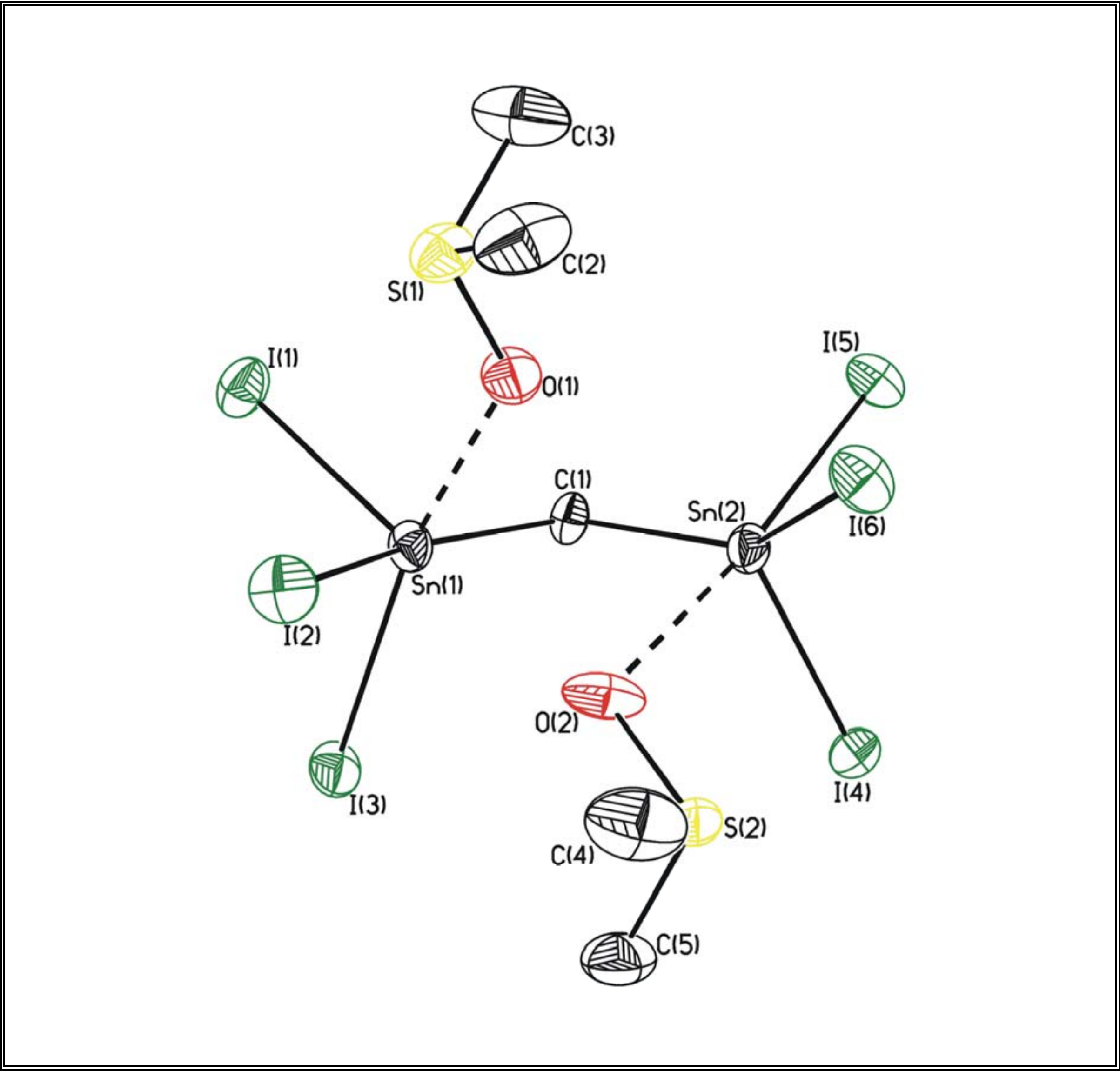


**Figure 22** Molecular structure (SHELXL-97) of **24** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 14** Selected bond lengths [Å] and bond angles [°] of **24**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.140(7) | Sn(2)-I(4) | 2.6885(8) |
| Sn(1)-I(1) | 2.7551(9) | Sn(2)-I(5) | 2.7777(9) |
| Sn(1)-I(2) | 2.7109(9) | Sn(2)-I(6) | 2.6817(9) |

**Table 14** continued.

| | | | |
|---|---|---|---|
| Sn(1)-I(3) | 2.8046(9) | Sn(2)-O(2) | 2.520(7) |
| Sn(1)-O(1) | 2.266(6) | O(1)-S(1) | 1.537(6) |
| Sn(2)-C(1) | 2.128(7) | O(2)-S(2) | 1.687(8) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-I(1) | 101.9(2) | C(1)-Sn(2)-I(6) | 131.3(2) |
| C(1)-Sn(1)-I(2) | 152.22(19) | I(4)-Sn(2)-I(5) | 97.24(3) |
| C(1)-Sn(1)-I(3) | 96.5(2) | I(4)-Sn(2)-I(6) | 110.39(3) |
| I(1)-Sn(1)-I(2) | 100.00(3) | I(5)-Sn(2)-I(6) | 96.13(3) |
| I(1)-Sn(1)-I(3) | 98.85(3) | O(2)-Sn(2)-C(1) | 75.8(3) |
| I(2)-Sn(1)-I(3) | 96.73(3) | O(2)-Sn(2)-I(4) | 88.35(16) |
| O(1)-Sn(1)-C(1) | 78.3(3) | O(2)-Sn(2)-I(5) | 173.90(17) |
| O(1)-Sn(1)-I(1) | 91.94(17) | O(2)-Sn(2)-I(6) | 84.14(14) |
| O(1)-Sn(1)-I(2) | 84.11(16) | Sn(1)-C(1)-Sn(2) | 115.0(3) |
| O(1)-Sn(1)-I(3) | 168.84(16) | O(1)-S(1)-C(2) | 104.2(5) |
| C(1)-Sn(2)-I(4) | 112.8(2) | O(2)-S(2A)-C(4) | 101.0(6) |
| C(1)-Sn(2)-I(5) | 99.7(2) | | |

In the molecular structure of compound **25** the two tin atoms are not equivalent. In fact, one DMF molecule is asymmetrically coordinated to the tin atoms (Sn(2)···O(1) 2.353(5) Å, Sn(1)···O(1) 3.038(5) Å) (Figure 23). As already observed for compound **24**, in derivative **25** the bis(triiodostannyl)methane (**21**) reacts as bidentate chelate even though the two Sn···O contacts have not comparable distances as in derivative **24** (Figure 22). Sn(1) is [4+1] coordinated with a monocapped distorted tetrahedral coordination geometry, while Sn(2) is pentacoordinated with a distorted trigonal bipyramidal coordination geometry ($\Delta(\sum\vartheta)$[105-107] = 66.5° for Sn(2)).

Interestingly, the coordination of DMF has only little influence on the Sn(1)-I(1), Sn(1)-I(2) and Sn(1)-I(3) bond lengths which amount to 2.6687(7), 2.6654(8) and 2.7062(9) Å, respectively. At Sn(2) the equatorial positions are occupied by C(1), I(4) and I(6), while I(5) and O(1) occupy the axial positions of the trigonal bipyramid. The bond lengths of Sn(2) to the equatorial iodine atoms are Sn(2)-I(4) 2.6914(7) and Sn(2)-I(6) 2.6807(8) Å and therefore shorter than those to the axial iodine atom

Sn(2)-I(5) 2.7906(8) Å. Notably, the Sn-I bond lengths of Sn(1) are not influenced from the presence of the DMF molecule and for this reason are almost of the same value of those of **21**. On the other side the Sn-I bonds of Sn(2) are longer than those of compound **21** and almost of the same value of those of derivative **24**. Furthermore, as already mentioned, the two Sn(1)···O(1) and Sn(2)···O(1) contacts do not have identical distances, with the former being shorter than the sum of the van der Waals radii of tin and oxygen[104] and the latter within the range 2.116-2.710 Å for Sn···O contacts in DMF adducts.[124-127] The tin atom Sn(1) has an almost ideal tetrahedral coordination geometry with an average angle of 109.1°. The O(1)-Sn(1)-I(3) and O(1)-Sn(2)-I(5) angles amount to 170.04° and 172.31°, respectively. The Sn(1)-C(1)-Sn(2) bond angle amounting to 121.1(3)° is the largest of these angles in the bis(triiodostannyl)methane derivatives series, with a significant deviation from the ideal value of 109°.

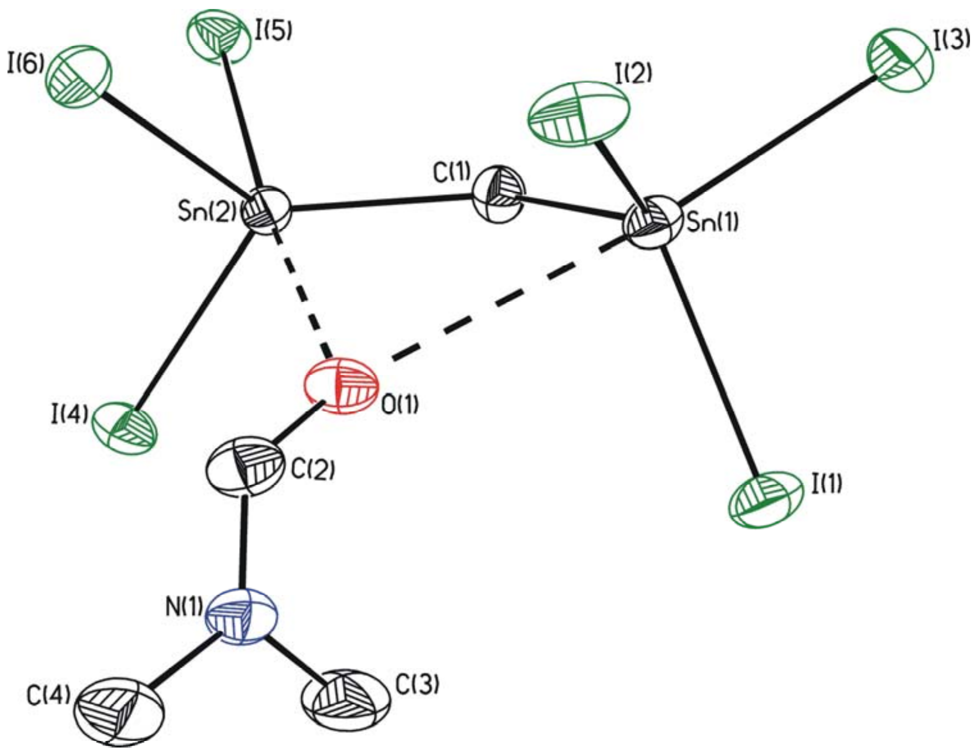


**Figure 23** Molecular structure (SHELXL-97) of **25** showing 30% probability displacement ellipsoids and the atom numbering scheme.

**Table 15** Selected bond lengths [Å] and bond angles [°] of **25**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.106(6) | Sn(2)-I(4) | 2.6914(7) |
| Sn(1)-I(1) | 2.6687(7) | Sn(2)-I(5) | 2.7906(8) |
| Sn(1)-I(2) | 2.6654(8) | Sn(2)-I(6) | 2.6807(8) |
| Sn(1)-I(3) | 2.7062(9) | Sn(2)-O(1) | 2.353(5) |
| Sn(1)-O(1) | 3.038(5) | O(1)-C(2) | 1.272(9) |
| Sn(2)-C(1) | 2.119(6) | N(1)-C(2) | 1.284(9) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-I(1) | 113.2(2) | C(1)-Sn(2)-I(6) | 126.40(19) |
| C(1)-Sn(1)-I(2) | 118.94(18) | I(4)-Sn(2)-I(5) | 96.37(3) |
| C(1)-Sn(1)-I(3) | 105.59(18) | I(4)-Sn(2)-I(6) | 108.64(2) |
| I(1)-Sn(1)-I(2) | 110.61(3) | I(5)-Sn(2)-I(6) | 98.75(2) |
| I(1)-Sn(1)-I(3) | 102.61(3) | O(1)-Sn(2)-C(1) | 79.1(2) |
| I(2)-Sn(1)-I(3) | 103.93(3) | O(1)-Sn(2)-I(4) | 83.41(12) |
| O(1)-Sn(1)-C(1) | 64.5(2) | O(1)-Sn(2)-I(5) | 172.31(13) |
| O(1)-Sn(1)-I(1) | 82.91(9) | O(1)-Sn(2)-I(6) | 88.57(12) |
| O(1)-Sn(1)-I(2) | 81.46(9) | Sn(1)-C(1)-Sn(2) | 121.1(3) |
| O(1)-Sn(1)-I(3) | 170.04(9) | Sn(1)-O(1)-Sn(2) | 85.07(14) |
| C(1)-Sn(2)-I(4) | 121.1(2) | O(1)-C(2)-N(1) | 124.7(8) |
| C(1)-Sn(2)-I(5) | 94.52(17) | C(2)-N(1)-C(3) | 122.2(7) |

## 1.4 Unexpected reaction of the 20-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$

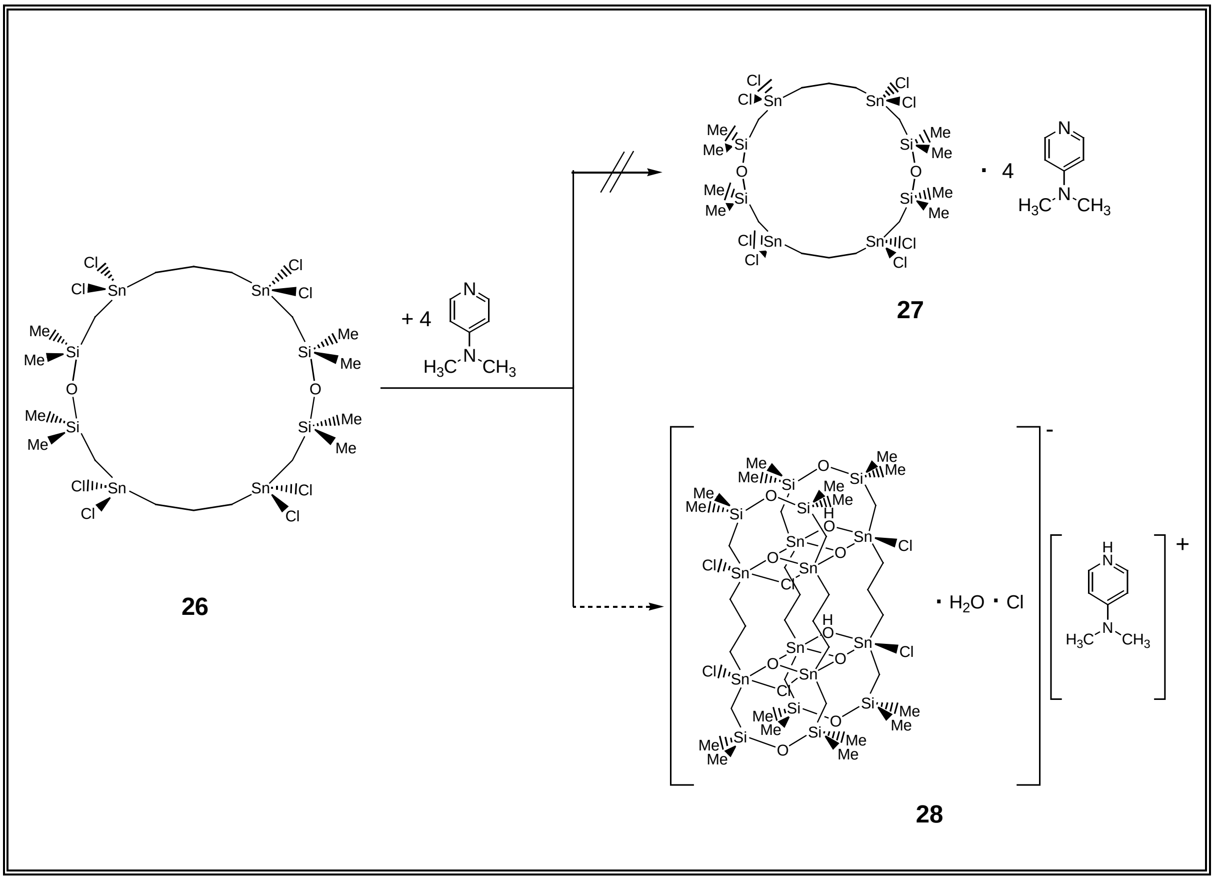
### 1.4.1 Introduction

In 2000 Schulte presented the synthesis of the first 20-membered ring with the -SnCSiO- unit in *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$.[88,91] The *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ has been characterized by Schulte by standard analytical methods such as elemental analysis and multinuclear NMR spectroscopy. Furthermore, the identity of the 20-membered ring structure in solution has been additionally confirmed by molecular weight measurements and electrospray mass spectroscopy. However, attempts to obtain single crystals suitable for X-ray diffraction analysis failed. In order to demonstrate the identity of the 20-membered ring structure some experiments were carried out.

### 1.4.2 Reaction of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ with 4-dimethylaminopyridine

The 20-membered ring compound *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)$-$CH_2Sn(Cl_2)$-$CH_2]_2CH_2$ was reacted with four molar equivalents of 4-dimethylaminopyridine (Scheme 4) with the intention to obtain the 1:4 complex **27**. Complex **27** could not be obtained from the reaction mixture. Instead, a few crystals were obtained, the X-ray diffraction analysis of which proved these to be the partially hydrolyzed 20-membered-ring **28** with a ladder-type structure.

The molecular structure of compound **28** will be discussed in paragraph 1.4.3.



**Scheme 4** Reaction of *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)$-$CH_2]_2CH_2$ with 4-dimethylaminopyridine.

### 1.4.3 Molecular structure of 4-dimethylaminopyridinium $\{\{[Sn(Cl)CH_2Si(Me_2)$-$OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\{\{[Sn(OH)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)]$-$(CH_2)_3\}_2O_2\}.H_2O.Cl]^-$ (28)

Suitable crystals for the molecular structure determination of compound **28** are obtained by slow evaporation of the solvent in a $CH_2Cl_2$ solution at room temperature. Derivative **28** crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecular structure of compound **28**, as well as its dimeric crystal structure are illustrated in Figures 24 and 25. Selected bond lengths and angles for **28** are listed in Table 16.

Compound **28** crystallises with two $CH_2Cl_2$ molecules and exists in the crystal lattice as $[\{\{[Sn(Cl)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\{\{[Sn(OH)CH_2Si(Me_2)OSi$-$(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}^{\cdot}H_2O^{\cdot}Cl]^-$ anion and 4-dimethylaminopyridinium cation connected by one Cl(7)···H(44) contact of 2.23(4) Å, being shorter than the sum of the van der Waals radii of chlorine and hydrogen (2.90-3.35 Å).[104] The molecular structure of compound **28** is characterized by two 20-membered rings linked together to form a double ladder structure (Figure 24). The double ladder is intermolecularly coordinated to one $H_2O$ molecule and to one chloride *via* Sn-O-H(3)···O(11) and Sn-O-H(6)···Cl(7) hydrogen bonds of 1.92(3) and 2.43(3) Å, respectively. Furthermore, the O(11)···Cl(7) distance of 3.153(2) Å suggests hydrogen bonding between the coordinated $H_2O$ molecule and chloride.

Compound **28** consists of two, to first approximation planar $Sn_4O_3Cl_3$ layers, linked together by four trimethylene groups. The four exocyclic as well as the four endocyclic tin atoms are pentacoordinated with a distorted trigonal bipyramidal geometry. The equatorial positions are occupied by C(1), C(10), O(1) for Sn(1), C(2), C(3), O(1) for Sn(2), C(11), C(20), O(2) for Sn(3), C(12), C(13), O(2) for Sn(4), C(7), C(8), O(4) for Sn(5), C(5), C(6), O(4) for Sn(6), C(17), C(18), O(5) for Sn(7) and C(15), C(16), O(5) for Sn(8). The Sn-C bonds have lengths ranging from 2.112(3)-2.140(3) Å, the Sn-Cl bonds from 2.4631(8)-2.7304(9) Å while the Sn-O bonds have distances within the range of 2.012(2)-2.2043(19) Å.

The Cl(1)-Sn(1)-Cl(2), Cl(3)-Sn(4)-O(3), Cl(4)-Sn(5)-Cl(5), Cl(6)-Sn(8)-O(6) angles relative to the exocyclic tin atoms amount to 169.99(3)°, 158.04(7)°, 169.52(3)° and 156.32(7)°. The Cl(2)-Sn(2)-O(2), O(1)-Sn(3)-O(3), Cl(5)-Sn(6)-O(5), O(4)-Sn(7)-O(6) angles relative to the endocyclic tin atoms amount to 152.83(6)°, 145.36(8)°, 151.87(6)° and 144.73(8)°. The former as well as the latter angles present a deviation from the ideal value of 180°, this deviation being greater for the endocyclic tin atoms.

The Si(1)-O(7)-Si(2), Si(3)-O(8)-Si(4), Si(5)-O(9)-Si(6) and Si(7)-O(10)-Si(8) angles amounting to 149.87(13)°, 151.25(14)°, 153.82(15)° and 155.88(15)° are significantly greater than the Si-O-Si angle in the related 10-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)]_2O$.[88,91]

The Si-O bond distances ranging from 1.624(2)-1.648(2) Å are within the standard range for Si-O bond lengths reported in literature.[112-114] Furthermore all the silicon atoms have an almost ideal tetrahedral coordination geometry.

In addition, the crystal lattice of compound **28** is characterized by a dimeric structure in which the two entities are connected by a combination of two Cl(7)···O(11A) and

Cl(7A)···O(11) interactions, creating in this way a central 4-membered $Cl_2O_4$ ring (Figure 25).

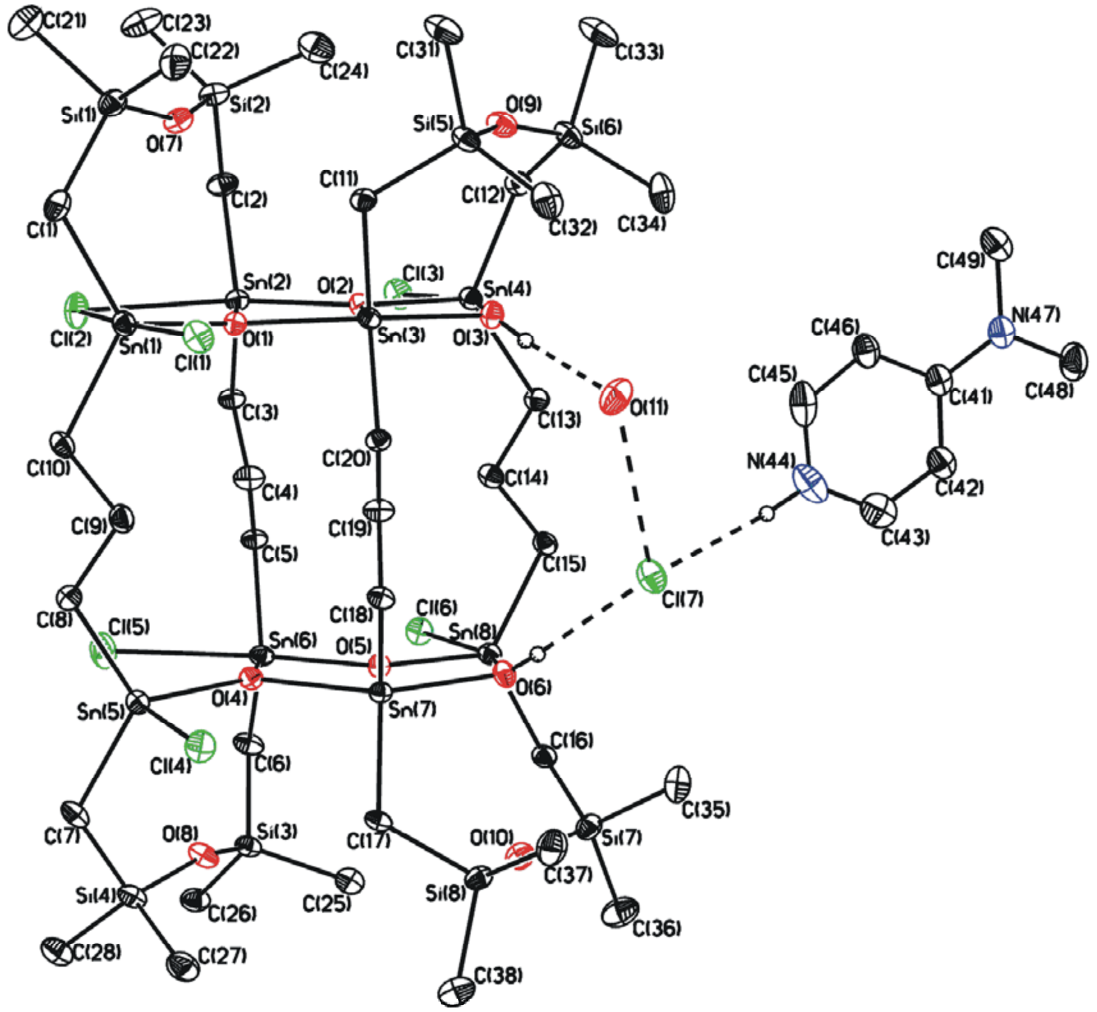


**Figure 24** Molecular structure (SHELXL-97) of **28** showing 30% probability displacement ellipsoids and the atom numbering scheme. The $CH_2Cl_2$ molecules are omitted.

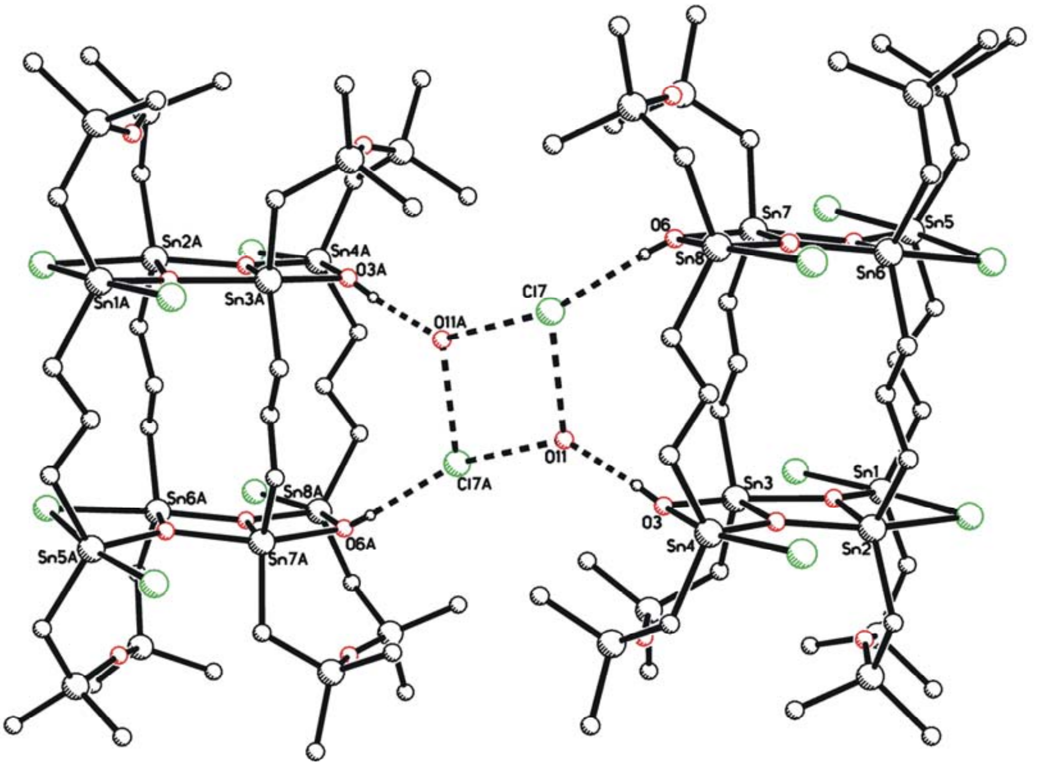


**Figure 25** Dimeric crystal structure of **25**.

**Table 16** Selected bond lengths [Å] and bond angles [°] of **28**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.122(3) | Sn(6)-C(6) | 2.114(3) |
| Sn(1)-C(10) | 2.134(3) | Sn(6)-Cl(5) | 2.6757(10) |
| Sn(1)-Cl(1) | 2.4631(8) | Sn(6)-O(4) | 2.060(2) |
| Sn(1)-Cl(2) | 2.7304(9) | Sn(6)-O(5) | 2.0930(19) |
| Sn(1)-O(1) | 2.012(2) | Sn(7)-C(17) | 2.112(3) |
| Sn(2)-C(2) | 2.129(3) | Sn(7)-C(18) | 2.130(3) |
| Sn(2)-C(3) | 2.128(3) | Sn(7)-O(4) | 2.2043(19) |
| Sn(2)-Cl(2) | 2.6612(9) | Sn(7)-O(5) | 2.055(2) |
| Sn(2)-O(1) | 2.052(2) | Sn(7)-O(6) | 2.136(2) |
| Sn(2)-O(2) | 2.0936(19) | Sn(8)-C(15) | 2.139(3) |
| Sn(3)-C(11) | 2.113(3) | Sn(8)-C(16) | 2.131(3) |

**Table 16** continued.

| | | | |
|---|---|---|---|
| Sn(3)-C(20) | 2.139(3) | Sn(8)-Cl(6) | 2.5243(8) |
| Sn(3)-O(1) | 2.2014(19) | Sn(8)-O(5) | 2.036(2) |
| Sn(3)-O(2) | 2.060(2) | Sn(8)-O(6) | 2.172(2) |
| Sn(3)-O(3) | 2.109(2) | Si(1)-O(7) | 1.626(2) |
| Sn(4)-C(12) | 2.119(3) | Si(2)-O(7) | 1.648(2) |
| Sn(4)-C(13) | 2.135(3) | Si(3)-O(8) | 1.639(2) |
| Sn(4)-Cl(3) | 2.4928(8) | Si(4)-O(8) | 1.633(2) |
| Sn(4)-O(2) | 2.040(2) | Si(5)-O(9) | 1.629(2) |
| Sn(4)-O(3) | 2.171(2) | Si(6)-O(9) | 1.625(2) |
| Sn(5)-C(7) | 2.119(3) | Si(7)-O(10) | 1.624(3) |
| Sn(5)-C(8) | 2.140(3) | Si(8)-O(10) | 1.624(2) |
| Sn(5)-Cl(4) | 2.4662(8) | H(3)-O(11) | 1.92(3) |
| Sn(5)-Cl(5) | 2.6739(9) | H(6)-Cl(7) | 2.43(3) |
| Sn(5)-O(4) | 2.015(2) | O(11)-Cl(7) | 3.153(2) |
| Sn(6)-C(5) | 2.125(3) | Cl(7)-H(44) | 2.23(4) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(10) | 123.89(12) | C(15)-Sn(8)-C(16) | 124.35(12) |
| C(1)-Sn(1)-Cl(1) | 96.92(9) | C(15)-Sn(8)-Cl(6) | 94.77(9) |
| C(1)-Sn(1)-Cl(2) | 88.17(9) | C(15)-Sn(8)-O(5) | 119.26(10) |
| C(1)-Sn(1)-O(1) | 119.46(11) | C(15)-Sn(8)-O(6) | 94.53(11) |
| C(10)-Sn(1)-Cl(1) | 96.30(9) | C(16)-Sn(8)-Cl(6) | 95.53(8) |
| C(10)-Sn(1)-Cl(2) | 87.91(9) | C(16)-Sn(8)-O(5) | 116.16(10) |
| C(10)-Sn(1)-O(1) | 113.88(10) | C(16)-Sn(8)-O(6) | 97.09(10) |
| Cl(1)-Sn(1)-Cl(2) | 169.99(3) | Cl(6)-Sn(8)-O(5) | 84.01(6) |
| Cl(1)-Sn(1)-O(1) | 93.20(6) | Cl(6)-Sn(8)-O(6) | 156.32(7) |
| Cl(2)-Sn(1)-O(1) | 76.69(6) | O(5)-Sn(8)-O(6) | 72.44(8) |
| C(2)-Sn(2)-C(3) | 121.51(11) | Sn(5)-O(4)-Sn(6) | 120.84(9) |
| C(2)-Sn(2)-Cl(2) | 91.16(10) | Sn(5)-Cl(5)-Sn(6) | 83.00(2) |
| C(2)-Sn(2)-O(1) | 121.49(10) | Sn(5)-O(4)-Sn(7) | 134.09(10) |
| C(2)-Sn(2)-O(2) | 103.82(11) | Sn(5)-C(8)-C(9) | 116.6(2) |
| C(3)-Sn(2)-Cl(2) | 90.59(9) | Sn(6)-O(4)-Sn(7) | 104.09(9) |
| C(3)-Sn(2)-O(1) | 115.96(9) | Sn(6)-O(5)-Sn(7) | 108.38(10) |

**Table 16** continued.

| | |
|---|---|
| C(3)-Sn(2)-O(2) | 100.27(10) |
| Cl(2)-Sn(2)-O(1) | 77.83(6) |
| Cl(2)-Sn(2)-O(2) | 152.83(6) |
| O(1)-Sn(2)-O(2) | 75.01(8) |
| C(11)-Sn(3)-C(20) | 126.17(12) |
| C(11)-Sn(3)-O(1) | 95.99(9) |
| C(11)-Sn(3)-O(2) | 112.08(10) |
| C(11)-Sn(3)-O(3) | 100.82(10) |
| C(20)-Sn(3)-O(1) | 97.18(9) |
| C(20)-Sn(3)-O(2) | 121.68(9) |
| C(20)-Sn(3)-O(3) | 96.93(11) |
| O(1)-Sn(3)-O(2) | 72.56(8) |
| O(1)-Sn(3)-O(3) | 145.36(8) |
| O(2)-Sn(3)-O(3) | 73.09(8) |
| C(12)-Sn(4)-C(13) | 123.14(12) |
| C(12)-Sn(4)-Cl(3) | 97.09(8) |
| C(12)-Sn(4)-O(2) | 113.94(10) |
| C(12)-Sn(4)-O(3) | 95.68(10) |
| C(13)-Sn(4)-Cl(3) | 95.07(9) |
| C(13)-Sn(4)-O(2) | 122.15(10) |
| C(13)-Sn(4)-O(3) | 92.79(11) |
| Cl(3)-Sn(4)-O(2) | 86.29(6) |
| Cl(3)-Sn(4)-O(3) | 158.04(7) |
| O(2)-Sn(4)-O(3) | 72.20(8) |
| Sn(1)-O(1)-Sn(2) | 122.11(9) |
| Sn(1)-Cl(2)-Sn(2) | 82.52(2) |
| Sn(1)-O(1)-Sn(3) | 132.34(10) |
| Sn(1)-C(10)-C(9) | 115.6(2) |
| Sn(2)-O(1)-Sn(3) | 104.21(9) |
| Sn(2)-O(2)-Sn(3) | 107.86(10) |
| Sn(2)-O(2)-Sn(4) | 141.42(10) |
| Sn(2)-C(3)-C(4) | 116.12(19) |
| Sn(3)-O(2)-Sn(4) | 110.69(8) |
| Sn(6)-O(5)-Sn(8) | 140.23(10) |
| Sn(6)-C(5)-C(4) | 114.9(2) |
| Sn(7)-O(5)-Sn(8) | 111.31(8) |
| Sn(7)-O(6)-Sn(8) | 103.26(9) |
| Sn(7)-C(18)-C(19) | 114.4(2) |
| Sn(8)-C(15)-C(14) | 114.5(2) |
| C(1)-Si(1)-C(21) | 107.74(16) |
| C(1)-Si(1)-C(22) | 110.19(16) |
| C(21)-Si(1)-C(22) | 109.80(15) |
| O(7)-Si(1)-C(1) | 108.42(13) |
| O(7)-Si(1)-C(21) | 111.25(15) |
| O(7)-Si(1)-C(22) | 109.43(15) |
| C(2)-Si(2)-C(23) | 108.62(14) |
| C(2)-Si(2)-C(24) | 110.11(16) |
| C(23)-Si(2)-C(24) | 110.26(17) |
| O(7)-Si(2)-C(2) | 108.87(13) |
| O(7)-Si(2)-C(23) | 109.81(15) |
| O(7)-Si(2)-C(24) | 109.15(14) |
| C(6)-Si(3)-C(25) | 110.25(16) |
| C(6)-Si(3)-C(26) | 108.49(14) |
| C(25)-Si(3)-C(26) | 110.77(15) |
| O(8)-Si(3)-C(6) | 107.77(13) |
| O(8)-Si(3)-C(25) | 109.05(14) |
| O(8)-Si(3)-C(26) | 110.46(14) |
| C(7)-Si(4)-C(27) | 109.61(16) |
| C(7)-Si(4)-C(28) | 107.85(15) |
| C(27)-Si(4)-C(28) | 111.81(15) |
| O(8)-Si(4)-C(7) | 108.89(13) |
| O(8)-Si(4)-C(27) | 108.11(15) |
| O(8)-Si(4)-C(28) | 110.54(15) |
| C(11)-Si(5)-C(31) | 109.20(15) |
| C(11)-Si(5)-C(32) | 109.50(15) |
| C(31)-Si(5)-C(32) | 110.10(15) |

**Table 16** continued.

| | | | |
|---|---|---|---|
| Sn(3)-O(3)-Sn(4) | 103.99(10) | O(9)-Si(5)-C(11) | 108.93(13) |
| Sn(3)-C(20)-C(19) | 114.90(19) | O(9)-Si(5)-C(31) | 107.63(14) |
| Sn(4)-C(13)-C(14) | 116.3(2) | O(9)-Si(5)-C(32) | 111.42(15) |
| C(7)-Sn(5)-C(8) | 121.11(12) | C(12)-Si(6)-C(33) | 108.19(15) |
| C(7)-Sn(5)-Cl(4) | 97.11(9) | C(12)-Si(6)-C(34) | 111.91(15) |
| C(7)-Sn(5)-Cl(5) | 89.29(9) | C(33)-Si(6)-C(34) | 109.43(17) |
| C(7)-Sn(5)-O(4) | 120.47(11) | O(9)-Si(6)-C(12) | 109.63(14) |
| C(8)-Sn(5)-Cl(4) | 94.96(9) | O(9)-Si(6)-C(33) | 106.76(15) |
| C(8)-Sn(5)-Cl(5) | 88.76(9) | O(9)-Si(6)-C(34) | 110.75(15) |
| C(8)-Sn(5)-O(4) | 116.47(10) | C(16)-Si(7)-C(35) | 111.74(16) |
| Cl(4)-Sn(5)-Cl(5) | 169.52(3) | C(16)-Si(7)-C(36) | 108.59(15) |
| Cl(4)-Sn(5)-O(4) | 91.76(6) | C(35)-Si(7)-C(36) | 109.14(16) |
| Cl(5)-Sn(5)-O(4) | 77.82(6) | O(10)-Si(7)-C(16) | 108.07(14) |
| C(5)-Sn(6)-C(6) | 120.66(11) | O(10)-Si(7)-C(35) | 111.48(15) |
| C(5)-Sn(6)-Cl(5) | 87.18(9) | O(10)-Si(7)-C(36) | 107.70(15) |
| C(5)-Sn(6)-O(4) | 116.89(10) | C(17)-Si(8)-C(37) | 109.75(15) |
| C(5)-Sn(6)-O(5) | 103.61(10) | C(17)-Si(8)-C(38) | 109.04(15) |
| C(6)-Sn(6)-Cl(5) | 91.19(10) | C(37)-Si(8)-C(38) | 111.38(16) |
| C(6)-Sn(6)-O(4) | 120.38(10) | O(10)-Si(8)-C(17) | 108.54(13) |
| C(6)-Sn(6)-O(5) | 104.72(10) | O(10)-Si(8)-C(37) | 110.40(15) |
| Cl(5)-Sn(6)-O(4) | 77.07(6) | O(10)-Si(8)-C(38) | 107.66(15) |
| Cl(5)-Sn(6)-O(5) | 151.87(6) | Sn(1)-C(1)-Si(1) | 120.97(18) |
| O(4)-Sn(6)-O(5) | 74.88(8) | Sn(2)-C(2)-Si(2) | 120.31(16) |
| C(17)-Sn(7)-C(18) | 125.68(12) | Sn(3)-C(11)-Si(5) | 117.77(15) |
| C(17)-Sn(7)-O(4) | 97.81(9) | Sn(4)-C(12)-Si(6) | 119.60(16) |
| C(17)-Sn(7)-O(5) | 111.97(10) | Sn(5)-C(7)-Si(4) | 120.77(17) |
| C(17)-Sn(7)-O(6) | 101.39(10) | Sn(6)-C(6)-Si(3) | 119.88(16) |
| C(18)-Sn(7)-O(4) | 96.87(10) | Sn(7)-C(17)-Si(8) | 118.86(16) |
| C(18)-Sn(7)-O(5) | 122.33(9) | Sn(8)-C(16)-Si(7) | 119.62(16) |
| C(18)-Sn(7)-O(6) | 95.55(11) | C(3)-C(4)-C(5) | 112.3(2) |
| O(4)-Sn(7)-O(5) | 72.62(8) | C(8)-C(9)-C(10) | 110.7(3) |
| O(4)-Sn(7)-O(6) | 144.73(8) | C(13)-C(14)-C(15) | 111.6(3) |
| O(5)-Sn(7)-O(6) | 72.83(8) | C(18)-C(19)-C(20) | 112.6(2) |

## 1.5 Experimental section

### 1.5.1 General methods

The synthesis and working up of oxidation- and hydrolysis-sensitive compounds were carried out under an inert atmosphere of nitrogen. The latter was dried by a gas-cleaning equipment with molecular sieve 4 Å. The solvents were purified by distillation from appropriate drying agents under argon.[123]

### 1.5.2 Spectroscopic and analytical methods

The $^1$H-, $^{13}$C-, $^{29}$Si- and $^{119}$Sn-NMR spectra were recorded on Bruker DRX 400 and Bruker DPX 300 spectrometers with broad-band decoupling of $^1$H at 400.13 MHz, $^{13}$C at 100.63 MHz, $^{29}$Si at 59.63 and 79.49 MHz, $^{119}$Sn at 111.92 and 149.21 MHz. . The chemical shifts $\delta$ are given in ppm and referenced to external $Me_4Si$ ($^1$H, $^{13}$C, $^{29}$Si) and $Me_4Sn$ ($^{119}$Sn). The NMR spectra were recorded at room temperature (295-298 K) if not otherwise stated. The couplings $J$ are given in Hz. The $^{29}$Si- and $^{119}$Sn-NMR spectra were recorded on a DRX 300 spectrometer in non deuterated solvents with $D_2O$ capillaries.

Elemental analyses were performed on a LECO-CHNS-932 analyser.

The IR spectra were recorded on a Bruker IFS 28 spectrometer in the range 200-4000 cm$^{-1}$.

The melting point determination was performed on a Büchi 510, the observed melting points being uncorrected.

### 1.5.3 Synthesis of the new compounds

Bis(triphenylstannyl)methane,[33] bis(iododiphenylstannyl)methane,[35,36,56] bis(bromo-diphenylstannyl)methane,[35,36,56] bis{[(dimethylsilyl)methyl]diphenylstannyl}-methane,[87,91,99] bis{[(dimethylisopropoxysilyl)methyl]diphenylstannyl}methane,[87.91,99] 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane,[87,91] 5,5,7,7-tetramethyl-1,1,3,3,-tetraphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane[87,91] as well as all the other starting materials were synthesised according to literature methods. Iodine, bromine, mercuric chloride, bromobenzene, dimethylsulfoxide, dimethylformamide, (trimethylsilyl)methylchloride, 1,3-dimethylimidazolidin-2-one as well as all the other compounds mentioned in the experimental section were commercial products.

### Bis{diiodo[(trimethylsylil)methyl]stannyl}methane (7)

Iodine (5.36 g, 21.12 mmol) was added in small portions within 5 h to a solution of bis{[(trimethylsilyl)methyl]diphenylstannyl}methane (**6**) (3.88 g, 5.28 mmol) in dichloromethane (50 mL) at 0 °C. The resulting solution was stirred at room temperature in darkness for 16 h, the solvent as well as the iodobenzene were then removed at 10 and $10^{-3}$ Torr, respectively, leaving a green-yellow solid. The solid was then recrystallised from $CH_2Cl_2$/*n*-hexane (1:1) to give bis{diiodo[(trimethylsylil)-methyl]stannyl}methane (**7**) (4.27 g, 4.57 mmol, 87%) as a colourless solid with m.p. 83-84 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ ( (ppm) 0.22 (s, $^1J(^1H–^{13}C)$ = 119 Hz, $^2J(^1H–^{29}Si)$ = 19 Hz, 12H; $CH_3$), 1.56 (s, $^1J(^1H–^{13}C)$ = 119 Hz, $^2J(^1H–^{117/119}Sn)$ = 90/94 Hz, 4H; $SiCH_2Sn$), 2.60 (s, $^1J(^1H–^{13}C)$ = 116 Hz, $^2J(^1H–^{117/119}Sn)$ = 58 Hz, 2H; $SnCH_2Sn$). **$^{13}$C{$^1$H} NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 1.32 (s, $^1J(^{13}C–^{29}Si)$ = 52 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 28 Hz; $CH_3$), 14.47 (s, $^1J(^{13}C–^{117/119}Sn)$ = 271/284 Hz, $^1J(^{13}C–^{29}Si)$ = 43 Hz; $SiCH_2Sn$), 14.70 (s, $^1J(^{13}C–^{117/119}Sn)$ = 236/247 Hz; $SnCH_2Sn$). **$^{29}$Si{$^1$H} NMR** ($CDCl_3$, 59.63 MHz): $\delta$ (ppm) 3.8 (s, $^2J(^{29}Si–^{117/119}Sn)$ = 43 Hz, $^1J(^{29}Si-^{13}C)$ = 52 Hz). **$^{119}$Sn{$^1$H} NMR** ($CH_2Cl_2$, 111.92 MHz): $\delta$ (ppm) –201.3 (s, $^2J(^{119}Sn-^{117}Sn)$ = 313 Hz). Anal. Calc. for $C_9H_{24}I_4Sn_2Si_2$ (933.48): C, 11.6; H, 2.6. Found: C, 11.6; H, 2.4%.

### Bis{dichloro[(trimethylsylil)methyl]stannyl}methane (8)

To a solution of bis{[(trimethylsilyl)methyl]diphenylstannyl}methane (**6**) (4.55 g, 6.20 mmol) in acetone (75 mL) was added dropwise a solution of mercuric chloride

(6.74 g, 24.83 mmol) in acetone (50 mL) within 2 h at 0 °C. The resulting solution was stirred at room temperature for 16 h, and the precipitated phenylmercuric chloride filtered. The solvent was then removed in vacuo and the residue extracted with *n*-hexane (150 mL). A second portion of phenylmercuric chloride precipitated and was filtered. Part of the solvent was then removed in vacuo and the remaining solution left to give bis{dichloro[(trimethylsylil)methyl]-stannyl}methane (**8**) (2.96 g, 5.21 mmol, 84%) as a colourless solid with m.p. 58-62 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ ( (ppm) 0.20 (s, $^1J(^1H–^{13}C)$ = 119 Hz, $^2J(^1H–^{29}Si)$ = 40 Hz, 12H; $CH_3$), 1.09 (s, $^2J(^1H–^{117/119}Sn)$ = 99/104 Hz, 4H; $SiCH_2Sn$), 1.71 (s, $^2J(^1H–^{117/119}Sn)$ = 63 Hz, 2H; $SnCH_2Sn$). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 0.95 (s, $^1J(^{13}C–^{29}Si)$ = 53 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 31 Hz; $CH_3$), 14.09 (s; $SiCH_2Sn$), 20.4 (s; $SnCH_2Sn$). **$^{29}Si\{^1H\}$ NMR** ($CDCl_3$, 79.49 MHz): $\delta$ (ppm) 3.1 (s, $^2J(^{29}Si–^{117/119}Sn)$ = 47 Hz). **$^{119}Sn\{^1H\}$ NMR** ($CDCl_3$, 149.21 MHz): $\delta$ (ppm) 113.6 (s, $\nu\,^1/_2$ = 104 Hz). Anal. Calc. for $C_9H_{24}Cl_4Sn_2Si_2$ (567.69): C, 19.0; H, 4.3. Found: C, 17.9; H, 4.6%.

### 1,1,3-Triiodo-5,5,7,7-tetramethyl-3-phenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (11)

Iodine (1.38 g, 5.44 mmol) was added in small portions over a 1h-period to a solution of 5,5,7,7-tetramethyl-1,1,3,3,-tetraphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**10**) (1.94 g, 2.69 mmol) in dichloromethane (40 mL) at 0 °C. The resulting solution was stirred at room temperature in darkness for 16 h, the solvent and the iodobenzene were then removed at 10 and $10^{-3}$ Torr, respectively, leaving a crude product wich was recrystallised from $CH_2Cl_2$/*n*-hexane (1:1) to give 1,1,3-triiodo-5,5,7,7-tetramethyl-3-phenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**11**) (0.45 g, 0.52 mmol, 58%) as a colourless solid with m.p. 82-84 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 0.23 (s, $^1J(^1H–^{13}C)$ = 119 Hz, 6H; $CH_3$), 0.26 (s, $^1J(^1H–^{13}C)$ = 118 Hz, 6H; $CH_3$), 1.02 (s, $^2J(^1H–^{117/119}Sn)$ = 84 Hz, 2H; $SiCH_2Sn$), 1.48 (s, $^2J(^1H–^{117/119}Sn)$ = 103 Hz, 2H; $SiCH_2Sn$), 2.18 (s, $^2J(^1H–^{117/119}Sn)$ = 58/76 Hz, 2H; $SnCH_2Sn$), 7.40 (m, 3H; $H_{m/p}$), 7.58 (d, $^3J(^1H–^{117/119}Sn)$ = 62/65 Hz, 1H; $H_o$), 7.59 (d, $^{3}J(^{1}H–^{117/119}Sn)$ = 63/66 Hz, 1H; $H_o$). **$^{13}$C{$^{1}$H} NMR** ($CDCl_3$, 100.63 MHz): δ (ppm) 3.18 (s, $^{1}J(^{13}C–^{29}Si)$ = 60 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 19 Hz; $CH_3$), 3.39 (s, $^{1}J(^{13}C–^{29}Si)$ = 60 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 16 Hz; $CH_3$), 4.87 (s, $^{1}J(^{13}C–^{29}Si)$ = 57 Hz, $^{1}J(^{13}C–^{117/119}Sn)$ = 256/269 Hz; $SiCH_2Sn$), 9.31 (complex pattern; $SnCH_2Sn$), 16,16 (s, $^{1}J(^{13}C–^{29}Si)$ = 55 Hz, $^{1}J(^{13}C–^{117/119}Sn)$ = 248/259 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 19 Hz; $SiCH_2Sn$), 128.95 (s, $^{3}J(^{13}C–^{117/119}Sn)$ = 63 Hz; $C_m$), 130.23 (s, $^{4}J(^{13}C–^{117/119}Sn)$ = 14 Hz; $C_p$), 135.16 (s, $^{2}J(^{13}C–^{117/119}Sn)$ = 51 Hz; $C_o$), 139.16, (s, $^{3}J(^{13}C–^{117/119}Sn)$ = 21 Hz; $C_i$). **$^{29}$Si{$^{1}$H} NMR** ($CDCl_3$, 79.49 MHz): δ (ppm) 11.9 (s, $^{2}J(^{29}Si–^{117/119}Sn)$ = 54 Hz), 12.8 (s, $^{2}J(^{29}Si–^{117/119}Sn)$ = 48 Hz). **$^{119}$Sn{$^{1}$H} NMR** ($CDCl_3$, 149.21 MHz): δ (ppm) -40.0 (s, $^{2}J(^{119}Sn-^{117/119}Sn)$ = 115 Hz), –196.5 (s, $^{2}J(^{119}Sn-^{117/119}Sn)$ = 115 Hz). Anal. Calc. for $C_{13}H_{23}I_3OSn_2Si_2$ (869.62): C, 18.0; H, 2.7. Found: C, 18.7; H, 2.6%.

### 1,3-Dichloro-5,5,7,7-tetramethyl-1,3-diphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (14)

1,1,3,3,-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**9**) (190 mg, 0.34 mmol) was added to 5,5,7,7-tetramethyl-1,1,3,3,-tetraphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**10**) (247 mg, 0.34 mmol) and the resulting mixture was heated at 70 °C for 16 h. The suspension was then cooled to room temperature giving a crude product. It was recrystallised from $CH_2Cl_2$/*n*-hexane (1:1) to give 1,3-dichloro-5,5,7,7-tetramethyl-1,3-diphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**14**) (227 mg, 0.36 mmol, 52%) as a colourless solid with m.p. 77-79 °C.

**$^{1}$H NMR** ($CDCl_3$, 400.13 MHz): δ (ppm) 0.24 (s, $^{4}J(^{1}H–^{117/119}Sn)$ = 40 Hz, 6H; $CH_3$), 0.70 (s, $\nu^{1}/_{2}$ = 44 Hz, 2H; $SiCH_2Sn$), 1.32 (s, $^{1}J(^{1}H–^{13}C)$ = 129 Hz, $^{2}J(^{1}H–^{117/119}Sn)$ = 64 Hz, 2H; $SnCH_2Sn$), 7.40 (m, 6H; $H_{m/p}$), 7.60 (m, 4H; $H_o$). **$^{13}$C{$^{1}$H} NMR** ($CDCl_3$, 100.63 MHz): δ (ppm) 3.06 (complex pattern; $CH_3$), 5.29 (complex pattern; $SnCH_2Sn$), 5.63 (s, $^{3}J(^{13}C–^{117/119}Sn)$ = 13 Hz; $SiCH_2Sn$), 128.98 (s, $^{3}J(^{13}C–^{117/119}Sn)$ = 62 Hz; $C_m$), 130.17 (s, $^{4}J(^{13}C–^{117/119}Sn)$ = 14 Hz; $C_p$), 135.08 (s, $^{2}J(^{13}C–^{117/119}Sn)$ = 53 Hz; $C_o$). **$^{29}$Si{$^{1}$H} NMR** ($CDCl_3$, 79.49 MHz): δ (ppm) 12.2 (s, $^{2}J(^{29}Si–^{117/119}Sn)$ = 57 Hz), 13.2 (s, $^{2}J(^{29}Si–^{117/119}Sn)$ = 51 Hz). **$^{119}$Sn{$^{1}$H} NMR** ($CDCl_3$, 149.21 MHz):

$\delta$ (ppm) 89.4 (s, $\nu^{1}/_{2}$ = 145 Hz). Anal. Calc. for $C_{19}H_{28}Cl_2OSn_2Si_2$ (636.93): C, 35.8; H, 4.4. Found: C, 33.4; H, 4.1%.

### 1,1,3,3,-Tetraiodo-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (15)

Iodine (710 mg, 2.80 mmol) was added in small portions within 45 min to a solution of 5,5,7,7-tetramethyl-1,1,3,3,-tetraphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**10**) (500 mg, 0.69 mmol) in dichloromethane (30 mL) at 0 °C. The resulting solution was stirred at room temperature in darkness for 16 h before removing the solvent and the iodobenzene at 10 Torr and $10^{-3}$ Torr, respectively. The crude product was then recrystallised from $CH_2Cl_2$/*n*-hexane (1:1) to give 1,1,3,3,-tetraiodo-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**15**) (347 mg, 0.38 mmol, 54%) as a colourless solid with m.p. 88-89 °C.

**$^{1}$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 0.30 (s, $^{1}J(^{1}H–^{13}C)$ = 119 Hz, $^{2}J(^{1}H–^{29}Si)$ = 7 Hz, 12H; $CH_3$), 1.62 (s, $^{1}J(^{1}H–^{13}C)$ = 126 Hz, $^{2}J(^{1}H–^{117/119}Sn)$ = 102/106 Hz, 4H; $SiCH_2Sn$), 2.65 (s, $^{1}J(^{1}H–^{13}C)$ = 136 Hz, $^{2}J(^{1}H–^{117/119}Sn)$ = 68/71 Hz, 2H; $SnCH_2Sn$). **$^{13}$C{$^{1}$H} NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 3.30 (complex pattern; $CH_3$), 15.58 (complex pattern; $SiCH_2Sn$), 29.80 (s, $\nu^{1}/_{2}$ = 4 Hz; $SnCH_2Sn$). **$^{29}$Si{$^{1}$H} NMR** ($CH_2Cl_2$, 59.63 MHz): $\delta$ (ppm) 12.9 (s, $^{2}J(^{29}Si–^{117/119}Sn)$ = 56 Hz). **$^{119}$Sn{$^{1}$H} NMR** ($CH_2Cl_2$, 111.92 MHz): $\delta$ (ppm) –222.0 (s, $^{1}J(^{119}Sn–^{13}C)$ = 277 Hz). Anal. Calc. for $C_7H_{18}I_4OSn_2Si_2$ (919.41): C, 9.1; H, 2.0 %. Found: C, 9.3; H, 1.9%.

### 1,1,3,3,-Tetrabromo-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (16)

Bromine (560 mg, 3.50 mmol) was added dropwise within 1h to a solution of 5,5,7,7-tetramethyl-1,1,3,3,-tetraphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**10**) (630 mg, 0.88 mmol) in dichloromethane (20 mL) at 0 °C. The resulting solution was stirred at room temperature for 16 h, the solvent and the bromobenzene were then removed at 10 and $10^{-3}$ Torr, respectively. The crude product was recrystallised from

$CH_2Cl_2$/*n*-hexane (1:1) to give 1,1,3,3,-tetrabromo-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**16**) (326 mg, 0.45 mmol, 51%) as a colourless solid with m.p. 62-66°C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ ( (ppm) 0.31 (s, $^1J(^1H–^{13}C)$ = 120 Hz, $^2J(^1H–^{29}Si)$ = 7 Hz, 12H; $CH_3$), 1.36 (s, $^2J(^1H–^{117/119}Sn)$ = 110/115 Hz, 4H; $SiCH_2Sn$), 2.06 (s, $^1J(^1H–^{13}C)$ = 149 Hz, $^2J(^1H–^{117/119}Sn)$ = 73/76 Hz, 2H; $SnCH_2Sn$). **$^{13}$C{$^1$H} NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 2.92 (s, $^1J(^{13}C–^{29}Si)$ = 61 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 21 Hz; $CH_3$), 15.05 (s, $^1J(^{13}C–^{117/119}Sn)$ = 303/315 Hz, $^1J(^{13}C–^{29}Si)$ = 62 Hz; $SiCH_2Sn$), 17.74 (s, $^1J(^{13}C–^{117/119}Sn)$ = 323/338 Hz; $SnCH_2Sn$). **$^{29}$Si{$^1$H} NMR** ($CH_2Cl_2$, 59.63 MHz): $\delta$ (ppm) 14.2 (s, $^2J(^{29}Si–^{117/119}Sn)$ = 57 Hz). **$^{119}$Sn{$^1$H} NMR** ($CH_2Cl_2$, 111.92 MHz): $\delta$ (ppm) 29.4 (s, $^2J(^{119}Sn–^{117}Sn)$ = 305 Hz). Anal. Calc. for $C_7H_{18}Br_4OSn_2Si_2$ (731.43): C, 11.5; H, 2.5. Found: C, 28.5; H, 5.1%.

### 1,1,3,3,-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclo-octane-bis-(dimethylsulfoxide) (17)

To a solution of 1,1,3,3,-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**9**) (101 mg, 0.182 mmol) in dichloromethane (3 mL) was added at room temperature in one portion dimethylsulfoxide (29 mg, 0.365 mmol). The resulting solution was stirred at room temperature for 30 min and left to give 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-bis(dimethylsulfoxide) (**17**) (88 mg, 0.124 mmol, 68%) as a colourless solid with m.p. 123-126 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 0.28 (s, $^1J(^1H–^{13}C)$ = 119 Hz, $^2J(^1H–^{29}Si)$ = 8 Hz, 12H; $CH_3$), 1.07 (s, $^2J(^1H–^{117/119}Sn)$ = 126/131 Hz, 4H; $SiCH_2Sn$), 1.83 (s, $^2J(^1H–^{117/119}Sn)$ = 84/88 Hz, 2H; $SnCH_2Sn$), 2.69 (s, 12H; $(CH_3)_2SO$). **$^{13}$C{$^1$H} NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 2.82 (s, $^1J(^{13}C–^{29}Si)$ = 60 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 28 Hz; $CH_3$), 17.51 (s, $^1J(^{13}C–^{117/119}Sn)$ = 404/423 Hz, $^1J(^{13}C–^{29}Si)$ = 54 Hz; $SiCH_2Sn$), 24.07 (s, $^1J(^{13}C–^{117/119}Sn)$ = 478/500 Hz; $SnCH_2Sn$), 39.99 (s; $(CH_3)_2SO$). **$^{29}$Si{$^1$H} NMR** ($CDCl_3$, 79.49 MHz): $\delta$ (ppm) 11.4 (s, $^2J(^{29}Si–^{117/119}Sn)$ = 53 Hz). **$^{119}$Sn{$^1$H} NMR**

($CDCl_3$, 149.21 MHz): δ (ppm) 16.6 (s, $\nu^1/_2$ = 81 Hz). Anal. Calc. for $C_{11}H_{30}Cl_4O_3S_2Sn_2Si_2$ (709.88): C, 18.6; H, 4.3. Found: C, 24.5; H, 5.5%.

### 1,1,3,3,-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-dimethylsulfoxide (18)

Two crystals of 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-bis-(dimethylsulfoxide) (**17**) were dissolved at room temperature in dichloromethane (10 mL). To the resulting solution was added the same volume of *n*-hexane and the solution left to give 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-dimethylsulfoxide (**18**) as a colourless solid.

### 1,1,3,3,-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-bis(dimethylformamide) (19)

To a solution of 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**9**) (300 mg, 0.542 mmol) in dichloromethane (5 mL) was added at room temperature in one portion dimethylformamide (79 mg, 1.081 mmol). The resulting solution was stirred at room temperature for 20 min and then left to give 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-bis-(dimethylformamide) (**19**) (212 mg, 0.303 mmol, 56%) as a colourless solid with m.p. 78-83 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): δ (ppm) 0.28 (s, $^1J(^1H–^{13}C)$ = 119 Hz, $^2J(^1H–^{29}Si)$ = 8 Hz, 12H; $CH_3$), 1.12 (s, $^2J(^1H–^{117/119}Sn)$ = 127/133 Hz, 4H; $SiCH_2Sn$), 1.77 (s, $^2J(^1H–^{117/119}Sn)$ = 88/91 Hz, 2H; $SnCH_2Sn$), 2.89 (s, $^1J(^1H–^{13}C)$ = 139 Hz, 6H; $CH_3N$), 3.00 (s, $^1J(^1H–^{13}C)$ = 138 Hz, 6H; $CH_3N$), 8.00 (s, 2H; HCO). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100.63 MHz): δ (ppm) 2.79 (s, $^3J(^{13}C–^{117/119}Sn)$ = 26 Hz; $CH_3$), 17.04 (s, $\nu^1/_2$ = 2 Hz; $SiCH_2Sn$), 24.15 (s, $\nu^1/_2$ = 1 Hz; $SnCH_2Sn$), 32.23 (s; $CH_3N$), 37.33 (s; $CH_3N$), 163.35 (s; HCO). **$^{29}Si\{^1H\}$ NMR** ($CH_2Cl_2$, 59.63 MHz): δ (ppm) 11.2 (s, $^2J(^{29}Si–^{117/119}Sn)$ = 56 Hz). **$^{119}Sn\{^1H\}$ NMR** ($CH_2Cl_2$, 111.92 MHz): δ (ppm) –30.5

(s, $^{2}J(^{119}Sn–^{117}Sn)$ = 864 Hz). Anal. Calc. for $C_{14}H_{34}Cl_6O_3N_2Sn_2Si_2$ (784.73, **19** · $CH_2Cl_2$): C, 21.4; H, 4.4; N, 3.6. Found: C, 20.4; H, 4.3; N, 2.9%.

### 1,1,3,3,-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-1,3-dimethyl-imidazolidin-2-one (20)

1,3-Dimethylimidazolidin-2-one (61 mg, 0.531 mmol) was added at room temperature in one portion to a solution of 1,1,3,3,-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**9**) (147 mg, 0.266 mmol) in dichloromethane (5 mL). The resulting solution was stirred at room temperature for 30 min and then left to give 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclo-octane-1,3-dimethyl-imidazolidin-2-one (**20**) (103 mg, 0.154 mmol, 58%) as a colourless solid with m.p. 126-131 °C.

**$^{1}$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 0.31 (s, $^{1}J(^{1}H–^{13}C)$ = 120 Hz, $^{2}J(^{1}H–^{29}Si)$ = 7 Hz, 12H; $CH_3$), 1.23 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 118/123 Hz, 4H; $SiCH_2Sn$), 1.77 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 79/82 Hz, 2H; $SnCH_2Sn$), 2.78 (s, 6H; $CH_3N$), 3.28 (s, 4H; $NCH_2CH_2N$), 8.00 (s, 2H; HCO). **$^{13}$C{$^{1}$H} NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 2.77 (s, $^{1}J(^{13}C–^{29}Si)$ = 60 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 27 Hz; $CH_3$), 17.22 (s, $^{1}J(^{13}C–^{117/119}Sn)$ = 398/416 Hz, $^{1}J(^{13}C–^{29}Si)$ = 56 Hz; $SiCH_2Sn$), 24.84 (s, $^{1}J(^{13}C–^{117/119}Sn)$ = 468/489 Hz; $SnCH_2Sn$), 32.04 (s; $CH_3N$), 45.15 (s; $NCH_2CH_2N$), 161.84 (s; CO). **$^{29}$Si{$^{1}$H} NMR** ($CDCl_3$, 79.49 MHz): $\delta$ (ppm) 12.0 (s, $^{2}J(^{29}Si–^{117/119}Sn)$ = 56 Hz). **$^{119}$Sn{$^{1}$H} NMR** ($CDCl_3$, 149.21 MHz): $\delta$ (ppm) 20.3 (s, $\nu^{1}/_{2}$ = 52 Hz). Anal. Calc. for $C_{12}H_{28}Cl_4O_2N_2Sn_2Si_2$ (667.77): C, 21.6; H, 4.2; N, 4.2. Found: C, 21.7; H, 4.1; N, 4.2%.

### Bis(triiodostannyl)methane (21)

Iodine (10.00 g, 39.4 mmol) was added in small portions within 48h and in darkness to a solution of bis(triphenylstannyl)methane (**1**) (4.00 g, 5.6 mmol) in dichloromethane (60 mL) at 0 °C. The resulting solution was stirred in darkness at room temperature for 120 h, the solvent and the iodobenzene were then removed at 10 and $10^{-3}$ Torr, respectively, leaving a yellow-brown solid. The solid was then recrystallised from $CH_2Cl_2$/*n*-hexane (1:1) to give bis(triiodostannyl)methane (**21**) (5.44 g, 5.4 mmol, 96%) as a yellow solid with m.p. 82-84 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 3.56 (s, $^1J(^1H–^{13}C)$ = 139 Hz, $^2J(^1H–^{117/119}Sn)$ = 67 Hz, 2H; $SnCH_2Sn$). **$^{13}$C{$^1$H} NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 14.71 (s, $^1J(^{13}C–^{117/119}Sn)$ = 317 Hz; $SnCH_2Sn$). **$^{119}$Sn{$^1$H} NMR** ($CH_2Cl_2$, 111.92 MHz): $\delta$ (ppm) -835.2 (s, $^2J(^{119}Sn–^{117}Sn)$ = 474 Hz). Anal. Calc. for $CH_2I_6Sn_2$ (1012.85): C, 1.2; H, 0.2. Found: C, 1.2; H, 0.2%.

### Bis(triiodostannyl)propane (23)

To a solution of bis(triphenylstannyl)propane (**22**) (3.50 g, 4.7 mmol) in dichloromethane (60 mL) was added iodine (8.21 g, 32.4 mmol) in small portions within 48 h at 0 °C and in darkness. The resulting solution was stirred at room temperature for 72 h, dichoromethane as well as iodobenzene were then removed at 10 and $10^{-3}$ Torr, respectively, leaving a crude product as brown solid. The solid was recrystallised from $CH_2Cl_2$/Hexane (1:1) to give bis(triiodostannyl)propane (**23**) (4.68 g, 4.5 mmol, 95%) as a yellow solid with m.p. 80-85 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 1.98 (m, $^3J(^1H–^{117/119}Sn)$ = 119/124 Hz, 2H; $SnCH_2\mathit{CH_2}CH_2Sn$), 2.67 (t, $^2J$ $(^1H–^{117/119}Sn)$ = 58.1 Hz, 4H; $Sn\mathit{CH_2}CH_2\mathit{CH_2}Sn$). **$^{13}$C{$^1$H} NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 26.15 (s, $^2J(^{13}C–^{117/119}Sn)$ = 35 Hz; $SnCH_2\mathit{CH_2}CH_2Sn$), 30.20 (s, $^1J(^{13}C–^{117/119}Sn)$ = 134/140 Hz; $Sn\mathit{CH_2}CH_2\mathit{CH_2}Sn$). **$^{119}$Sn{$^1$H} NMR** ($CH_2Cl_2$, 111.92 MHz): $\delta$ (ppm) –622.4 (s, $^4J(^{119}Sn–^{117}Sn)$ = 432 Hz). Anal. Calc. for $C_3H_6I_6Sn_2$ (1040.90): C, 3.5; H, 0.6. Found: C, 3.6; H, 0.5%.

### Bis(triiodostannyl)methane-bis(dimethylsulfoxide) (24)

*Method A*: Dimethylsulfoxide (31 mg, 0.395 mmol) was added at room temperature in one portion to a solution of (triiodostannyl)methane (**21**) (200 mg, 0.197 mmol) in dichloromethane (15 mL). The resulting solution was then stirred at room temperature for 30 min and then left to give bis(triiodostannyl)methane-bis(dimethylsulfoxide) (**24**) (210 mg, 0.180 mmol, 91%) as a yellow solid with m.p. 150-156 °C.

*Method B*: Dimethylsulfoxide (19 mg, 0.238 mmol) was added in one portion to a solution of bis(triiodostannyl)methane (**21**) (241 mg, 0.238 mmol) in dichloromethane (20 mL) at room temperature. The resulting solution was then stirred at room temperature for 30 min and then left to give bis(triiodostannyl)methane-bis(dimethylsulfoxide) (**24**) (108 mg, 0.092 mmol, 78%) as a yellow solid with m.p. 150-156 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 2.71 (s, $^1J(^1H–^{13}C)$ = 139 Hz, 12H; $(CH_3)_2SO$), 3.51 (s, $^2J(^1H–^{117/119}Sn)$ = 67/69 Hz, 2H; $SnCH_2Sn$). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 18.00 (s, $\nu^1/_2$ = 6 Hz; $SnCH_2Sn$), 38.10 (s; $(CH_3)_2SO$). **$^{119}Sn\{^1H\}$ NMR** ($CDCl_3$, 149.21 MHz): $\delta$ (ppm) –878.3 ($\nu^1/_2$ = 127 Hz). Anal. Calc. for $C_5H_{14}I_6O_2S_2Sn_2$ (1169.11): C, 5.1; H, 1.2. Found: C, 5.2; H, 1.2%.

### Bis(triiodostannyl)methane-dimethylformamide (25)

*Method A*: To a solution of bis(triiodostannyl)methane (**21**) (300 mg, 0,296 mmol) in dichloromethane (20 mL) was added in one portion dimethylformamide (43 mg, 0.588 mmol) at room temperature. The resulting solution was stirred at room temperature for 20 min and then left to give bis(triiodostannyl)methane-dimethylformamide (**25**) (266 mg, 0.245 mmol, 83%) as a yellow solid with m.p. 123-128 °C.

*Method B*: To a solution of bis(triiodostannyl)methane (**21**) (300 mg, 0,296 mmol) in dichloromethane (20 mL) was added in one portion dimethylformamide (22 mg, 0.296 mmol) at room temperature. The resulting solution was stirred at room temperature for 20 min and then left to give bis(triiodostannyl)methane-dimethylformamide (**25**) (294 mg, 0.271 mmol, 92%) as a yellow solid with m.p. 123-128 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): δ (ppm) 2.88 (s, $^1J(^1H–^{13}C)$ = 138 Hz, 3H; $NCH_3$), 2.95 (s, $^1J(^1H–^{13}C)$ = 138 Hz, 3H; $NCH_3$), 3.56 (s, $^2J(^1H–^{117/119}Sn)$ = 68 Hz, $^1J(^1H–^{13}C)$ = 138 Hz, 2H; $SnCH_2Sn$), 7.98 (s, 1H; HCO). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100.63 MHz): δ (ppm) 18.31 (s, $^1J(^{13}C–^{117/119}Sn)$ = 351/369 Hz; $SnCH_2Sn$), 32.62 (s; $NCH_3$), 37.26 (s; $NCH_3$), 163.21 (complex pattern, HCO). **$^{119}Sn\{^1H\}$ NMR** ($CDCl_3$, 149.21 MHz): δ (ppm) –876.7 ($\nu^1/_2$ = 86 Hz). Anal. Calc. for $C_4H_9I_6ONSn_2$ (1085.94): C, 4.4; H, 0.8; N, 1.3. Found: C, 4.5; H, 0.9; N, 1,2%.

### 4-Dimethylaminopyridinium $[\{\{[Sn(Cl)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}$-$\{\{[Sn(OH)CH_2Si(Me_2)OSi$-$(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\cdot H_2O\cdot Cl]^-$ (28)

To a solution of $\{\{[Sn(Cl)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\{\{[Sn(OH)CH_2$-$Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}$ (**28**) (50 mg, 0.043 mmol) in dichloromethane (15 mL) was added in one portion 4-dimethylaminopyridine (21 mg, 0.172 mmol) at room temperature. The solution was stirred at room temperature for 20 min and then left to crystallise to give 4-dimethylaminopyridinium $[\{\{[Sn(Cl)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\{\{[Sn(OH)CH_2Si(Me_2)OSi(Me_2)$-$CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\cdot H_2O\cdot Cl]^-$ (**28**) as a crystalline colourless solid with m.p. >250 °C.

Unfortunately we did not obtain enough material to perform elemental analysis as well as any other analyses.

## 1.6 References

(1) Biallas, M. J.; Shriver, D. F. *J. Am. Chem. Soc.* **1966**, *88*, 375.

(2) Shriver, D. F.; Biallas, M. J. *J. Am. Chem. Soc.* **1967**, 1078.

(3) Antonisse, M. M. G.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1998**, 443.

(4) Beer, P. D.; Smith, D. K. in: *Progress in Inorganic Chemistry*, **1997**; *Vol. 46*.

(5) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.

(6) Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931.

(7) Tamao, K.; Hayashi, T.; Ito, Y. *J. Organomet. Chem.* **1996**, *506*, 85.

(8) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1997**, *16*, 5716.

(9) Chistyakov, A. L.; Stankevich, I. V.; Gambaryan, N. P.; Struchkov, Y. T.; Yanovsky, A. I.; Tikhonova, I. A.; Shur, V. B. *J. Organomet. Chem.* **1997**, *536*, 413.

(10) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153.

(11) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1987**, *109*, 4714.

(12) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1986**, *108*, 73.

(13) Vaugeois, J.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1215.

(14) Simard, M.; Vaugeois, J.; Wuest, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 370.

(15) Vaugeois, J.; Simard, M.; Wuest, J. D. *Coord. Chem. Rev.* **1995**, *145*, 55.

(16) Saied, O.; Simard, M.; Wuest, J. D. *Organometallics* **1996**, *15*, 2345.

(17) Bachaud, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015.

(18) Schier, A.; Riede, J.; Mehltretter, G.; Gabbaï, F. P. *Organometallics* **1998**, *17*, 2921.

(19) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267.

(20) Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297.

(21) Aoyagi, S.; Tanaka, K.; Takeuchi, Y. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1549.

(22) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294.

(23) Blanda, M. T.; Newcomb, M. *Tetrahedron Lett.* **1989**, *30*, 3501.

(24) Jurkschat, K.; Kuivila, H. G.; Liu, S.; Zubieta, J. A. *Organometallics* **1989**, *8*, 2755.

(25) Jurkschat, K.; Rühlemann, A.; Tzschach, A. *J. Organomet. Chem.* **1990**, *381*, C53.

(26) Horner, J. H.; Squatritto, P. J.; McGuire, N.; Riebenspies, J. P.; Newcomb, M. *Organometallics* **1991**, *10*, 1741.

(27) Swami, K.; Hutchinson, J.P.; Kuivila, H.G.; Zubieta, J. A. *Organometallics* **1984**, *3*, 1687.

(28) Gabbaï, F. P.; Schier, A.; Riede, J.; Schichl, D. *Organometallics* **1996**, *15*, 4119.

(29) Tschinkl, M.; Schier, A.; Riede, J.; Schmidt, E.; Gabbaï, F. P. *Organometallics* **1997**, *16*, 4759.

(30) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Inorg. Chem.* **1997**, *36*, 5706.

(31) Gabbaï, F. P.; Schier, A.; Riede, J. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 622.

(32) Austin, M.; Gebreyes, K.; Kuivila, H. G.; Swami, K.; Zubieta, J. A. *Organometallics* **1987**, *6*, 834.

(33) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106.

(34) Hyde, J. R.; Karol, T. J.; Hutchinson, J. P.; Kuivila, H. G.; Zubieta, J. *Organometallics* **1982**, *1*, 404.

(35) Gielen, M.; Jurkschat, K.; Meunier-Piret, J.; Meerssche, M. V. *Bull. Soc. Chim. Belg.* **1984**, *93*, 379.

(36) Dakternieks, D.; Jurkschat, K.; Zhu, H.; Tiekink, E. R. T. *Organometallics* **1995**, *14*, 2512.

(37) Jurkschat, K.; Hesselbarth, F.; Dargatz, M.; Lehmann, J.; Kleinpeter, E.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1990**, *388*, 259.

(38) Chaniotakis, N. A.; Jurkschat, K.; Rühlemann, A. *Anal. Chim. Acta* **1993**, *282*, 345.

(39) Tsagatakis, J. K.; Chaniotakis, N. A.; Jurkschat, K. *Helv. Chim. Acta* **1994**, *77*, 2191.

(40) Meunier-Piret, J.; Meerssche, M. v.; Jurkschat, K.; Gielen, M. *J. Organomet. Chem.* **1985**, *288*, 139.

(41) Kuivila, H. G.; Karol, T. J.; Swami, K. *Organometallics* **1983**, *2*, 909.

(42) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027.

(43) Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640.

(44) Eisch, J. J.; Kotowicz, B. W. *Eur. J. Inorg. Chem.* **1998**, 761.

(45) Jäkle, F.; Lough, A. J.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1999**, 453.

(46) Atwood, D. A.; Gabbaï, F. P.; Lu, J.; Remington, M. P.; Rutherford, D.; Sibi, M. P. *Organometallics* **1996**, *15*, 2308.

(47) Kaul, F. A. R.; Tschinkl, M.; Gabbaï, F. P. *J. Organomet. Chem.* **1997**, *539*, 187.

(48) Tschinkl, M.; Bachman, R. E.; Gabbaï, F. P. *J. Chem. Soc., Chem. Commun.* **1999**, 1367.

(49) Eisch, J. J.; Mackenzie, K.; Windisch, H.; Krüger, C. *Eur. J. Inorg. Chem.* **1999**, 153.

(50) Gabbaï, F. P.; Schier, A.; Riede, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1121.

(51) Gabbaï, F. P.; Schier, A.; Riede, J.; Hynes, M. J. *J. Chem. Soc., Chem. Commun.* **1998**, 897.

(52) Brondani, D.; Carrè, F. H.; Corriu, R. J. P.; Moreau, J. J. E.; Man, M. W. C. *Angew. Chem.* **1996**, *108*, 349.

(53) Tamao, K.; Hayashi, T.; Ito, Y. *J. Am. Chem. Soc.* **1990**, *112*, 2422.

(54) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099.

(55) Newcomb, M.; Blanda, M. T. *Tetrahedron Lett.* **1988**, *29*, 4261.

(56) Gielen, M.; Jurkschat, K. *J. Organomet. Chem.* **1984**, *273*, 303.

(57) Tsagatakis, J. K.; Chaniotakis, N. A.; Jurkschat, K. *Química Analítica* **1997**, *16*, 105.

(58) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 5858.

(59) Wuest, J. D. *Acc. Chem. Res.* **1999**, *32*, 81.

(60) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 380.

(61) Wuest, J. D.; Zacharie, B. *Organometallics* **1985**, *4*, 410.

(62) Tschinkl, M.; Bachman, R. E.; Gabbaï, F. P. *J. Organomet. Chem.* **1999**, *582*, 40.

(63) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Organometallics* **1999**, *18*, 1747.

(64) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Organometallics* **1999**, *18*, 2040.

(65) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Angew. Chem.* **1999**, *111*, 3769.

(66) Ooi, T.; Takahashi, M.; Maruoka, K. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 835.

(67) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 256.

(68) Gabriele, M.; Kuivila, H. G.; Kochran, J. C. *Main Group Metal Chem.* **1998**, *21*, 207.

(69) Ooi, T.; Asao, N.; Maruoka, K. *J. Synth. Org. Chem. Jpn.* **1998**, *56*, 377.

(70) Ooi, T.; Miura, T.; Maruoka, K. *Angew. Chem.* **1998**, *110*, 2524.

(71) Inukai, T.; Kojima, T. *J. Organomet. Chem.* **1966**, *32*, 872.

(72) Angus, P. M.; Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1993**, *32*, 450.

(73) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1985**, *107*, 6121.

(74) Williams, V. C.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Collins, S.; Marder, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 3244.

(75) Chen, Y. X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451.

(76) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem.* **2000**, *112*, 1368.

(77) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 1312.

(78) Kim, Y.; Eom, S. H.; Wang, J.; Lee, D. S.; Suh, S. W.; Steitz, T. A. *Nature* **1995**, *376*, 612.

(79) Hurst, P.; Takasaki, B. K.; Chin, J. *J. Am. Chem. Soc.* **1996**, *118*, 9982.

(80) Tsubonchi, A.; Bruice, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 7399.

(81) Gielen, M.; Jurkschat, K. *Bull. Soc. Chim. Belg.* **1984**, *93*, 153.

(82) Gielen, M.; Jurkschat, K. *J. Organomet. Chem.* **1982**, *236*, 69.

(83) Meunier-Piret, J.; Meerssche, M. v.; Gielen, M.; Jurkschat, K. *J. Organomet. Chem.* **1983**, *252*, 289.

(84) Gielen, M.; Jurkschat, K. *Bull. Soc. Chim. Belg.* **1982**, *91*, 803.

(85) Hermann, W. A. *Advanced Organomet. Chem.* **1982**, *20*, 159.

(86) Glidewell, C.; Liles, D. C. *J. Organomet. Chem.* **1982**, *15*, 234.

(87) Schulte, M.; Schürmann, M.; Jurkschat, K. *Chem. Eur. J.* **2001**, *7*, 347.

(88) Schulte, M.; Gabriele, G.; Schürmann, M.; Jurkschat, K.; Duthie, A.; Dakternieks, D. *Organometallics* **2003**, *22*, 328.

(89) Preut, H.; Bleckmann, P.; Mitchell, T.; Fabisch, B. *Acta Crystallogr., Sect. C* **1984**, *40*, 370.

(90) Willem, R.; Gielen, M.; Meunier-Piret, J.; Meerssche, M. v.; Jurkschat, K.; Tzschach, A. *J. Organomet. Chem.* **1984**, *277*, 335.

(91) Schulte, M. *Dissertation*, Dortmund University **2000**.

(92) Hummeltenberg, R. *Dissertation*, Dortmund University **1997**.

(93) MacGillivray, L. R.; Atwood, J. L. *Angew. Chem.* **1999**, *111*, 1080.

(94) Altmann, R. *Dissertation*, Dortmund University **1998**.

(95) Dakternieks, D.; Jurkschat, K.; Zobel, B.; Tiekink, E. R. T. *Z. Krystallogr.* **1996**, *211*, 757.

(96) Holecek, J.; Nadvornik, M.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* **1983**, *241*, 177.

(97) Klassen, R. *Dissertation*, Dortmund University **2000**.

(98) Kühn, S. *Dissertation*, Dortmund University **1997**.

(99) Schmidbaur, H.; Waldmann, S. *Chem. Ber.* **1964**, *97*, 3381.

(100) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120.

(101) Wrackmeyer, B. *Annual Reports on NMR Spectroscopy*, **1985**, *16*, 73.

(102) Hadjikakou, S.; Jurkschat, K.; Schürmann, M., unpublished result.

(103) Dakternieks, D.; Altmann, R.; Jurkschat, K.; Tiekink, E. R. T. *Z. Kristallogr.* **1998**, *213*, 525.

(104) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry - Principles of Structure and Reactivity*; 4th Edition, HarperCollins College Publishers, New York **1993**.

(105) Kolb, U.; Dräger, M.; Jousseaume, B. *Organometallics* **1991**, *10*, 2737.

(106) Dräger, M. *J. Organomet. Chem.* **1983**, *251*, 209.

(107) Kolb, U.; Beuter, M.; Dräger, M. *Inorg. Chem.* **1994**, *33*, 4522.

(108) Ferguson, G.; Low, J. N.; Ross, J.-N.; Storey, E. J.; Wardell, J. L. *Main Group Metal Chem.* **1999**, *22*, 453.

(109) Willem, R.; Delmotte, A.; Borger, I. D.; Biesemans, M.; Gielen, M.; Kayser, F.; Tiekink, E. R. T. *J. Organomet. Chem.* **1994**, *480*, 255.

(110) Jurkschat, K.; Schilling, J.; Mügge, C.; Tzschach, A.; Meunier-Piret, J.; Meerssche, M. v.; Gielen, M.; Willem, R. *Organometallics* **1988**, *7*, 38.

(111) Dräger, M.; Engler, R. *Z. Anorg. Allg. Chem.* **1975**, *413*, 229.

(112) Barrow, M. J.; Ebsworth, E. A. V.; Harding, A. A. *Acta Crystallogr., Sect. B* **1979**, *35*, 2093.

(113) Tomlins, P. E.; Lydon, J. E.; Akrigg, D.; Sheldrick, B. *Acta Crystallogr., Sect. C* **1985**, *41*, 292.

(114) Karle, I. L. ; Karle, J. M. ; Nielesen, C. J. *Acta Crystallogr., Sect. C* **1986**, *42*, 64.

(115) Zimmer, H.; Mosle, H. G. *Chem. Ber.* **1954**, *87*, 1255.

(116) Kerk, G. J. M. v.; Noltes, J. G. *J. Appl. Chem.* **1957**, *7*, 366.

(117) Zobel, B.; Duthie, A.; Dakternieks, D.; Tiekink, E. R. T. *Organometallics* **2001**, *20*, 2820.

(118) Zobel, B.; Duthie, A.; Dakternieks, D.; Tiekink, E. R. T. *Organometallics* **2001**, *20*, 3347.

(119) Dakternieks, D.; Zobel, B.; Tiekink, E. R. T. *Main Group Met. Chem.* **2000**, *23*, 253.

(120) Gielen, M.; Jurkschat, K.; Mikawa, Y.; Sasaki, Y. *Bull. Chem. Soc. Belg.* **1984**, *93*, 379.

(121) Dakternieks, D.; Zobel, B.; Tiekink, E. R. T. *Main Group Met. Chem.* **2000**, *23*, 321.

(122) Jousseaume, B.; Riague, H. ; Toupance, T. ; Lahcini, M. ; Mountford, P. ; Tyrrell, B. R. *Organometallics* **2002**, *21*, 4590.

(123) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, Pergamon Press, New York **1988**.

(124) Aslanov, L. A.; Ionov, V. M.; Attiya, V. M.; Permin, A. B.; Petrosyan, V. S. *Russ. J. Struct. Chem.* **1978**, *19*, 109.

(125) Ng, S. W. ; Kumar Das, V. G. *Acta Crystallogr., Sect. C* **1993**, *49*, 754.

(126) Clarke, B.; Cunningham, D.; Gallagher, J. F.; Higgins, T.; McArdle, P.; McGinley, J.; Cholchuin, N. M.; Sheerin, D. *J. Chem. Soc., Dalton Trans.* **1994**, 2473.

(127) Reuter, H.; Puff, H. *J. Organomet. Chem.* **1992**, *424*, 23.

(128) Altmann, R.; Gausset, O.; Horn, D.; Jurkschat, K.; Schürmann, M.; Fontani, M.; Zanello, P. *Organometallics* **2000**, *19*, 430.

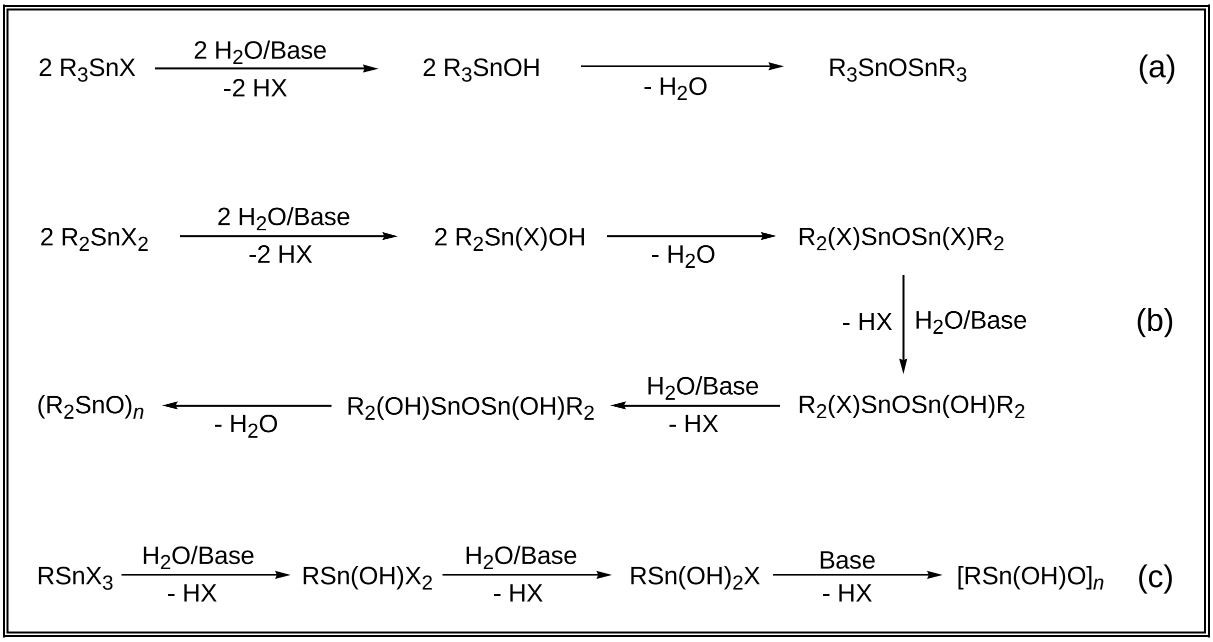
# *Chapter 2*

# 2 Novel methylene-bridged tetraorganodistannoxanes: solvent-controlled crystal structures

## 2.1 Introduction

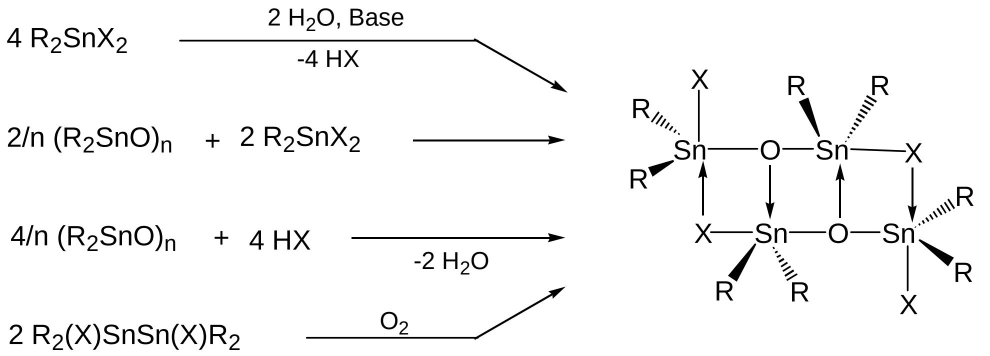
In recent years there has been considerable interest in organotin compounds because of their applications[1-10] as well as their structural diversity.[11] The attention of a number of researchers has been principally attracted by organotin assemblies containing Sn-O bonds. One of the simplest ways to prepare organotin compounds containing Sn-O bonds is by the hydrolysis of the corresponding halides.

The complete basic hydrolysis of organotin $R_nSnX_{4-n}$ species (R, R' = alkyl, aryl; X = halide, OC(O)R', OR', NR'$_2$; n = 1-3) affords organotin oxides with different structures, depending on the number of the organic groups (Scheme 1).[12,13]



**Scheme 1** Basic hydrolysis of organotin $R_nSnX_{4-n}$ compounds (R, R' = alkyl, aryl; X = halide, OC(O)R', OR', NR'$_2$; n = 1-3).

Tetraorganodistannoxanes are a well established class of compounds with a great variety of applications. They can be prepared by controlled basic hydrolysis of diorganotin dihalides, by reaction of diorganotin oxides $(RSnO)_n$ with diorganotin dihalides $R_2SnX_2$ or acids HX, as well as by oxidation of tetraorganoditin compounds $R_2(X)SnSn(X)R_2$ (Scheme 2).[13,16]



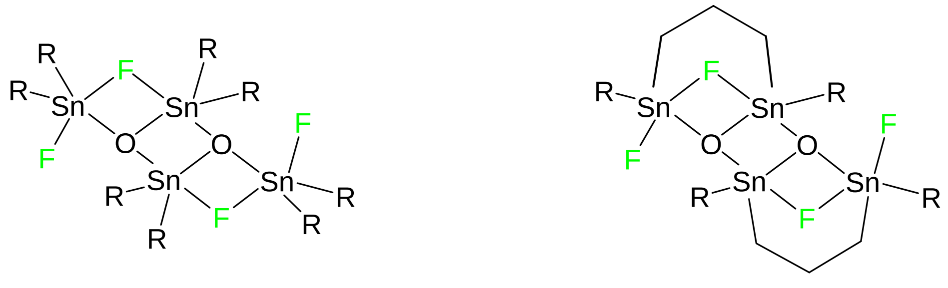
X = halide, OH, OR', OC(O)R', OSiR'$_3$, NR'$_2$, NCO, NCS
R, R' = alkyle, aryle

**Scheme 2** Synthetic methodologies to provide tetraorganodistannoxanes.

In 1914 Pfeiffer and Brack suggested the first structural proposal for the monomeric unit $R_2(X)SnOSn(X)R_2$.[17] While the dimeric structure of tetraorganodistannoxanes was first clarified in the sixties by molecular weights measurements[18-25] and then by the first molecular structure determination.[26]

Within the last thirty years a large number of tetraorganodistannoxanes was completely characterized by molecular structure determination.

In 1981 Puff reported the first tetraorganodistannoxane with X = OH,[31] while in 1998 Jurkschat reported the first two fluoro-bridged ladders (Figure 1).[36,37]



a

b

R = *t*-Bu

R = $CH(SiMe_3)_2$

**Figure 1** Dimeric structures of the first two fluoro-bridged ladders.

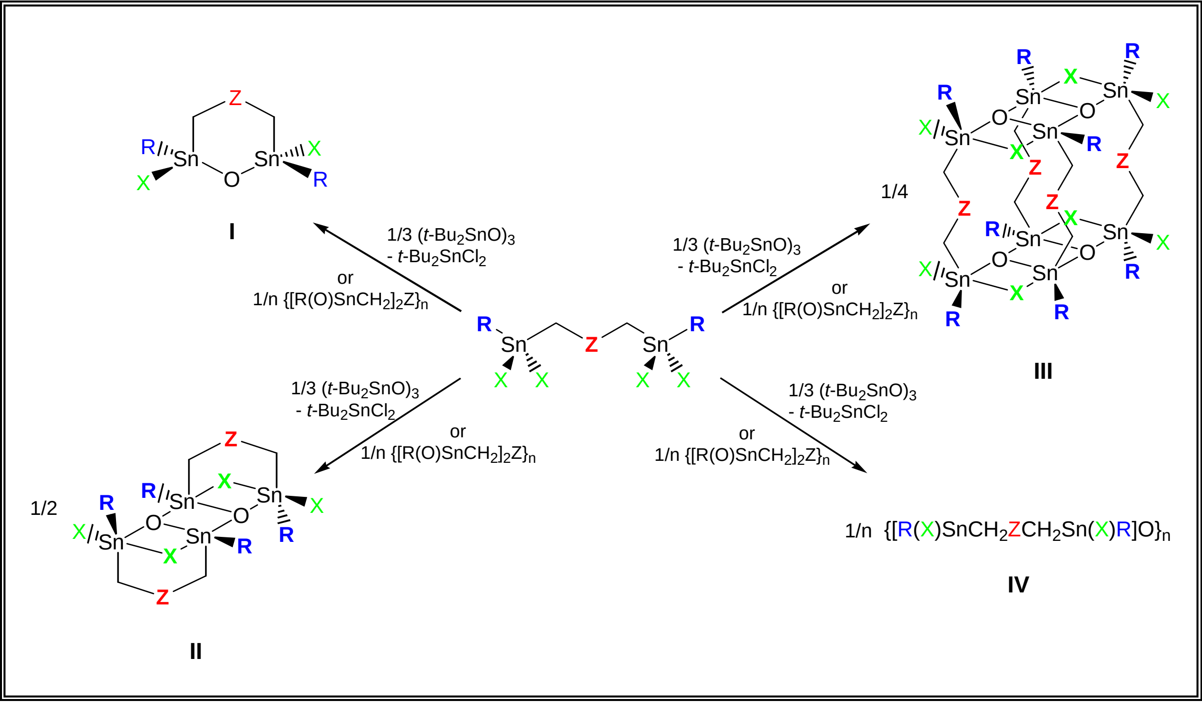
The ladder with R = $CH(SiMe_3)_2$ (Figure 1b) contains two alkylene bridges that connect alternate tin atoms in a *trans* geometry. Recently Schulte reported the synthesis of a dihydroxy bridged ladder containing the alkylene bridges in a *cis* geometry by reaction of the acetylene bridged ditin derivative $[Me_3SiCH_2(Cl_2)SnCH_2(Me_2)Si]_2C_2$.[38]

Dimeric tetraorganodistannoxanes possess a typical “ladder” structure characterized by an almost planar $Sn_4X_4O_2$ layer and a central centrosymmetric four-membered $Sn_2O_2$ ring. These compounds are normally high melting, crystalline solids well soluble in unpolar solvents and retain the dimeric structure also in solution. In the last years high-resolution multinuclear NMR-spectroscopy revealed their formation mechanisms and the substituents influence on their structures.[27-30]

Ladder compounds have demonstrated to be effective homogeneous catalysts in different organic reactions, such as the synthesis of urethanes from alcohols and isocyanates,[42-47] of acetales from alcohols and aldeydes or ketones,[48,49] the formation of carbonic acids esters from alcohols and carbonic acids, the transesterification between carbonic acid esters and alcohols,[6,7,50-56] the transesterification of cyclic carbonic acid esters,[57] the acylation of amines[58] as well as the synthesis of dialkylcarbonates.[59] However, until now it is not completely clear whether the catalytical active species are the dimeric tetraorganodistannoxanes or the monomeric derivatives.[39-41,60]

Furthermore, the antitumor activity of some tetraorganodistannoxanes with carboxy substituents was also investigated.[32-35,61-64]

When α,ω-bis(dihaloorganostannyl)alkanes are reacted with [*t*-$Bu_2SnO]_3$ or with the corresponding oxides, spacer-bridged tetraorganodistannoxanes with different structures are obtained (Scheme 3). The structure of these compounds seems to be influenced by the bridging group Z, the organic group R, as well as, the substituent X.



**Scheme 3** Possible spacer-bridged tetraorganodistannoxane structures.

Until now the monomeric structure **I** was reported only for the sterically demanding organic group R = $CH(SiMe_3)_2$ and Z = $CH_2$.[37]

For Z = $SiMe_2$, $Me_2SiCCSiMe_2$, $Me_2SiOSiMe_2$ and X = Cl, OH only dimeric structures of the type **II** are obtained.[38,54,65]

For Z = $(CH_2)_n$ and X = halide, OH, OAc tetrameric double ladder structures of the type **III** are obtained.[54,65-67]

For Z = $(CH_2)_n$ (n = 2-6, 8, 10) and Z = $CH_2$ and X = OAc the double ladder compounds exist in solution in equilibrium with the dimeric forms.[9,54,65,68,69]

For Z = $(CH_2)_3$ and R = $CH_2SiMe_3$ oligomers and polymers of the type **IV** are obtained.[37,70]

In 1997 Jurkschat et al. reported the synthesis of the first hexamer triple ladder containing alkylene bridges, as well the attempts to prepare quadruple ladder species.[67]

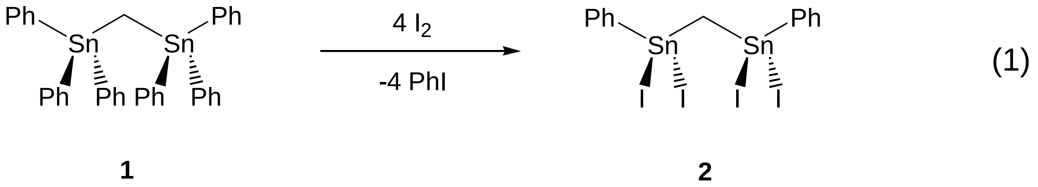
In 2002 Dakternieks et al. reported the new spacer-bridged double ladders $\{[R(Cl)Sn(CH_2)_nSn(Cl)R]O\}_4$ (R = $CH_2SiMe_3$; n = 5-8, 10, 12).[69]
Interestingly, no double ladder was known for methylene-bridged ditin compounds.

Presently, well accepted models used in chemical education exist which help to understand the way atoms assemble to form molecules of different size and shape and to explain chemical transformations. However the factors that control the way molecules assemble in the solid state are much less known and research in the direction of crystal design and engineering is growing.[73]
Weak intermolecular forces such as donor-acceptor bonds[74-77] or hydrogen bonds[78-83] are known to influence the crystallization process and the reversibility in the formation of hydrogen bonds leads to a better control over the latter. As a result of cooperative effects[84] the resulting hydrogen-bonded networks are normally very stable.
In the last years different discrete organotin oxo clusters have been reported [14,15,67,85,86] and the interest to connect tin-containing clusters together is growing.[87]
In this chapter a simple approach to assemble *via* hydrogen-bonding the novel organotin oxo cluster $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ into one- and two-dimensional polymers will be presented.[88] The aptitude of the solvent to form hydrogen bonds is the factor that determines the structure and controls in the solid state the association of the organotin oxo cluster.

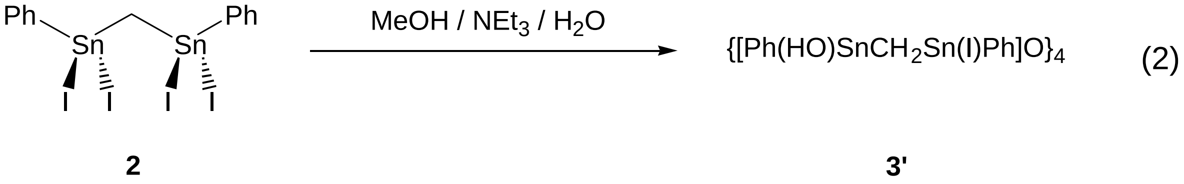
## 2.2 Results

### 2.2.1 Synthesis of the organotin oxo clusters

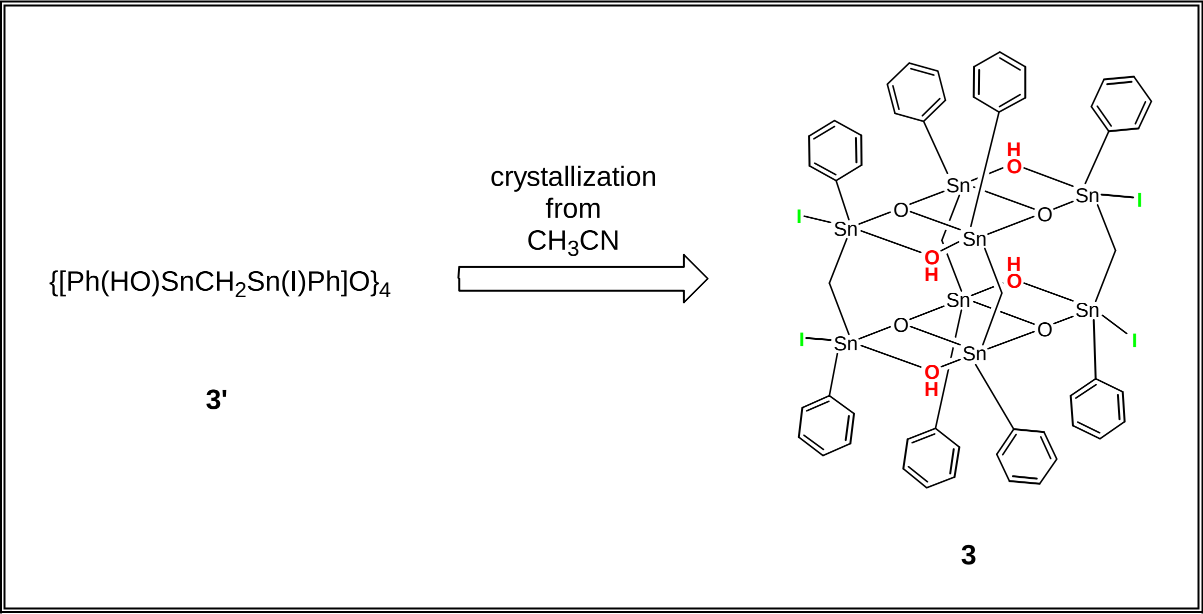
Reaction of bis(triphenylstannyl)methane[89,90] (**1**) with four molar equivalents of iodine provided the organotin specie **2** in 90% yield as a light-yellow oil (equation 1). The $^{119}$Sn-NMR of **2** ($CDCl_3$) shows a single resonance at $\delta$ -241.0 ($^2J(^{119}Sn-^{117}Sn)$ = 274 Hz, $^1J(^{119}Sn-^{13}C)$ = 660 Hz) ppm. The signal at $\delta$ -241.0 ppm in the $^{119}$Sn-NMR spectrum is typical for substances with $C_2SnI_2$ substitution pattern.[91]



Hydrolysis of $[PhSn(I_2)]_2CH_2$ (**2**) in a $MeOH/H_2O/NEt_3$ mixture afforded the organotin oxo cluster $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ (**3'**) as a waxy-type solid (equation 2).



Subsequent crystallisation of derivative **3'** from different solvents afforded building blocks as solvent-adducts. On the other hand crystallisation of the waxy-type solid from $CH_3CN$ provided the solvent-free double ladder **3** as a colourless crystalline solid (Scheme 4).



**Scheme 4** Crystallisation of the novel organotin oxo cluster **3**.

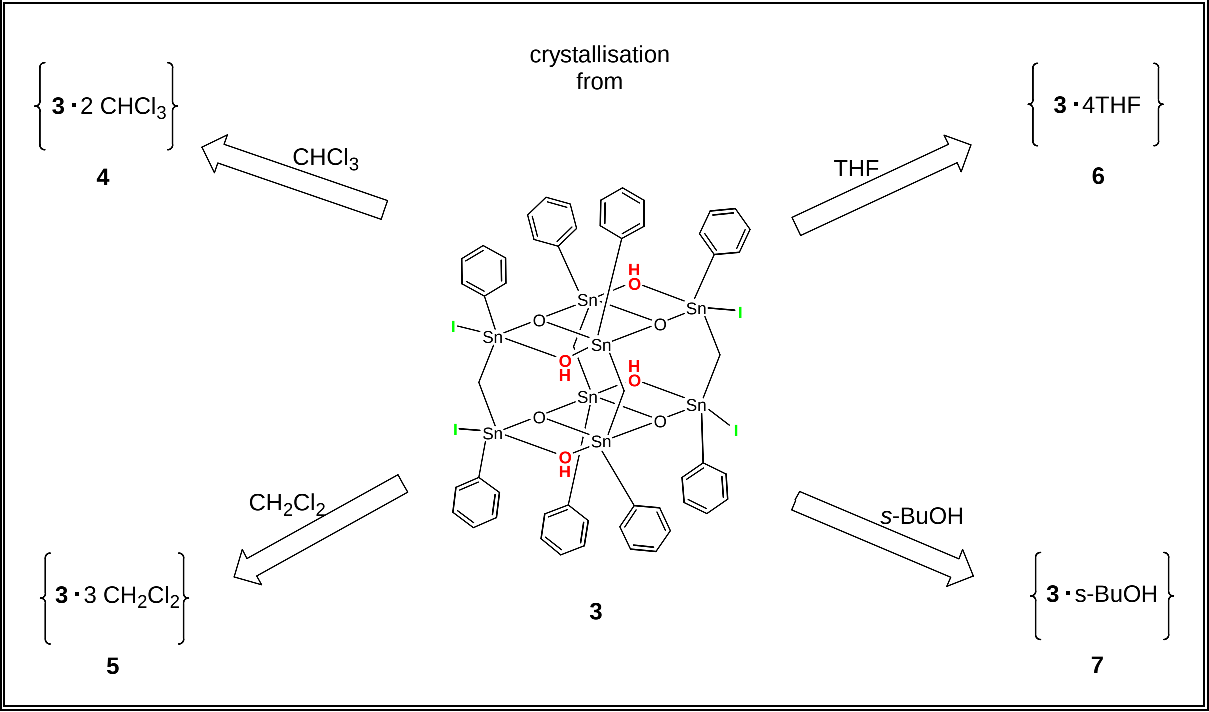
Similar to previously described double ladder structures,[66,72] compound **3** consists of two at first approximation planar $Sn_4I_2O_4$ layers linked together by four methylene spacers.

The $^{119}$Sn-NMR of the cluster **3** in $CDCl_3$ shows two resonances at $\delta$ –222.0 ($^2J(^{119}Sn-^{117/119}Sn)$ = 140 Hz) and –244.0 ($^2J(^{119}Sn-^{117/119}Sn)$ = 140 Hz) ppm, in agreement with the presence of four exocyclic as well as four endocyclic tin atoms.

The crystal structure of the solvent-free double ladder **3** will be discussed in paragraph 2.2.2.

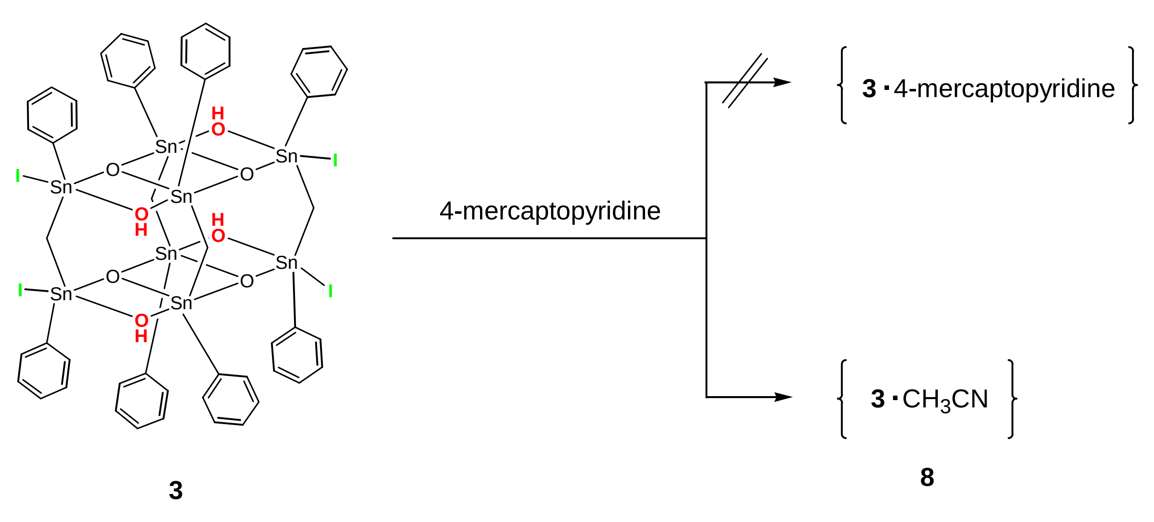
As already mentioned, crystallisation of derivative **3’** from different solvents give the corresponding solvent-adduct (Scheme 5). When the waxy-like residue **3’** is crystallised from $CHCl_3$, the 1:2 adduct **4** is formed, while from $CH_2Cl_2$ the 1:3 complex **5** is obtained. Crystallisation of **3’** from THF as well as *s*-BuOH afforded, respectively, the 1:4 adduct **6** and the 1:1 adduct **7**.

In the latter case ($\underline{+}$) *s*-BuOH was used as crystallisation solvent, however the crystallisation from enantiopure chiral solvents might lead to enantiopure compounds.



**Scheme 5** Solvent-controlled different solid state structures of **3**.

Somewhat surprisingly, when the residue **3’** is dissolved in $CH_3CN$ and treated with 4-mercaptopyridine, the 1:1 $CH_3CN$-adduct **8** is obtained and not, as expected, the corresponding pyridine complex (Scheme 6).



**Scheme 6** Unexpected formation of the **3** · $CH_3CN$ adduct **8**.

All of the organotin oxo clusters presented here are high-melting colourless crystalline solids. The molecular as well as the crystal structures of all the novel methylene-bridged tetraorganodistannoxanes will be discussed in paragraph 2.2.2.

### 2.2.2 Molecular and crystal structures of $\{[Ph(HO)SnCH_2Sn(I)\text{-}Ph]O\}_4$ (3), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 2CHCl_3$ (4), $\{[Ph(HO)SnCH_2Sn(I)Ph]\text{-}O\}_4 \cdot 3CH_2Cl_2$ (5), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 4THF$ (6), $\{[Ph(HO)Sn\text{-}CH_2Sn(I)Ph]O\}_4 \cdot$*s*-BuOH (7) and $\{[Ph(HO)SnCH_2Sn(I)\text{-}Ph]O\}_4 \cdot CH_3CN$ (8)

Suitable crystals for the molecular and crystal structure determination of compounds **3**, **4**, **5**, **6**, **7** and **8** are obtained by slow evaporation of acetonitrile for derivatives **3** and **8** at room temperature, and by slow evaporation of the corresponding crystallization solvent for **4**, **5**, **6** and **7** at room temperature. Compound **3** crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Adduct **4** crystallises in the triclinic space group $P$-1 with two molecules in the unit cell. Derivative **5** crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Compound **6** crystallises in the monoclinic space group $C2/c$ with four molecules in the unit cell. Adduct **7** crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Compound **8** crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The molecular structures of compounds **3**, **4**, **5**, **6**, **7** and **8** are illustrated in Figures 2, 5, 7, 9, 11 and 14, while their crystal structures are illustrated in Figures 3, 4, 6, 8, 10, 13, 15 and 16, in Figure 12 are illustrated the two enantiomers of *s*-BuOH found in the crystal lattice of **7**. Selected bond lengths and angles for **3**, **4**, **5**, **6**, **7** and **8** are listed in Tables 1, 2, 3, 4, 5 and 6, twist angles of the $Sn_4I_2O_4$ layers for the six compounds are listed in Table 7.

As already mentioned in paragraph 2.2.1, compound **3** consists of two at first approximation planar $Sn_4I_2O_4$ layers, with a mean deviation of 0.1167 Å and a twist of 29.15(3)°, which are bound by four methylene-bridged groups (Figure 2).[88] The molecular structure of **3** is characterized by four exocyclic tin atoms, Sn(1) and Sn(4) in one layer and Sn(5) and Sn(8) in the other layer, as well as four endocyclic tin atoms, Sn(2), Sn(3), Sn(6) and Sn(7). All the exo- and endocyclic tin centers are pentacoordinated and exhibit a distorted trigonal bipyramidal configuration with C(1), C(11), O(1) for Sn(1), C(4, C(41), O(2) for Sn(4), C(1), C(51), O(5) for Sn(5), C(4, C(81),O(6) for Sn(8) and C(2), C(21), O(1) for Sn(2), C(3), C(31), O(2) for Sn(3), C(2), C(61), O(6) for Sn(6), C(3), C(71), O(5) for Sn(7) in the equatorial positions. The axial positions are occupied by I(1), O(3) for Sn(1), I(2), O(4) for Sn(4), I(3), O(7) for Sn(5), I(4), O(8) for Sn(8) and O(2), O(3) for Sn(2), O(1), O(4) for Sn(3), O(5), O(8) for Sn(6), O(6), O(7) for Sn(7).

The Sn-C(Ph) bonds have lengths within the range 2.103(11)-2.139(12) Å, the Sn-C($\mathrm{CH_2}$) bonds have distances within the range 2.105(11)-2.135(10) Å. The bonds of the tin to the iodine atoms have lengths within the range 2.8829(12)-2.9026(11) Å and those to the oxygen atoms within the range 2.025(6)-2.197(7) Å. The Sn(1)-O(3)-Sn(2), Sn(3)-O(4)-Sn(4), Sn(5)-O(7)-Sn(7) and Sn(6)-O(8)-Sn(8) bridges are only slightly asymmetrical by 0.015, 0.017, 0.005 and 0.014 Å, respectively,.

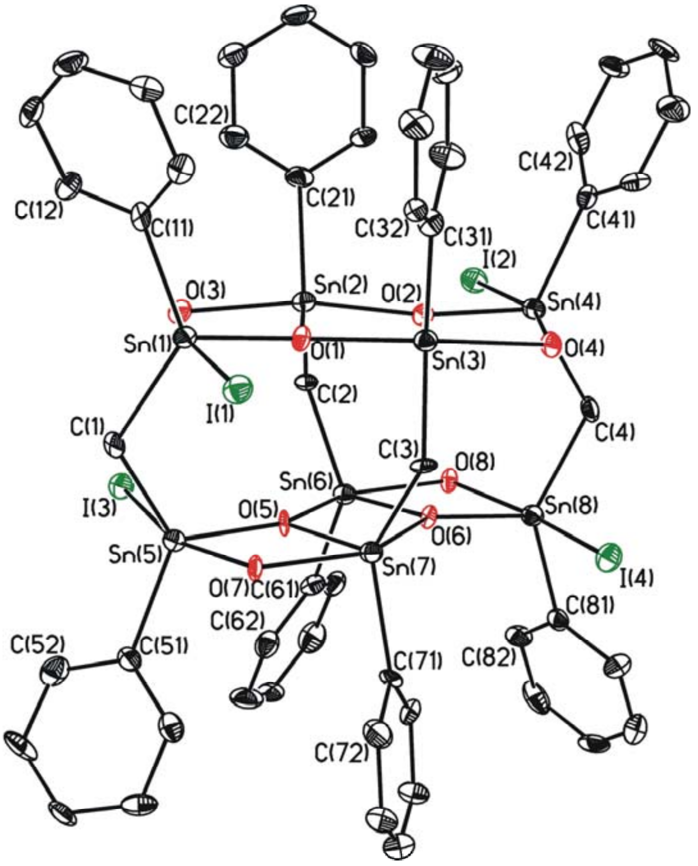


**Figure 2** Molecular structure (SHELXL-97) of **3** showing 30% probability displacement ellipsoids and the atom numbering scheme.

The O(3)-Sn(1)-I(1), O(4)-Sn(4)-I(2), O(7)-Sn(5)-I(3) and O(8)-Sn(8)-I(4) angles relative to the exocyclic tin atoms amounting to 164.62(19)°, 164.59(17)°, 160.86(18)° and 160.16(19)° are deviated from the ideal value of 180°. The angles relative to the endocyclic tin atoms O(2)-Sn(2)-O(3), O(1)-Sn(3)-O(4), O(5)-Sn(6)-O(8) and O(6)-Sn(7)-O(7) amounting to 148.9(3)°, 147.9(3)°, 146.8(2)° and 146.5(2)° also present large deviations from the ideal value of 180°. The deviation from the ideal value can be explained as result of internal tensions as well as steric effects, with the deviation being greater for the endocyclic tin atoms.

The crystal structure of the solvent-free cluster **3** (Figure 3 and 4) is characterized by a two-dimensional network which is realized by a combination of two intermolecular Sn-O-H···I-Sn hydrogen bonds with O···I distance of 3.514(7) Å and three weak intermolecular Sn-I···I-Sn interactions ranging from 4.1296(11) to 4.2017(16) Å, the latter being close to the sum of the van der Waals radii of two iodine atoms (3.90-4.24 Å).[92] They are probably the result of crystal packing and contribute only little to the crystal energy.[93] Moreover, compound **3** lacks any symmetry and exhibits chirality with both enantiomers being present in the crystal lattice.

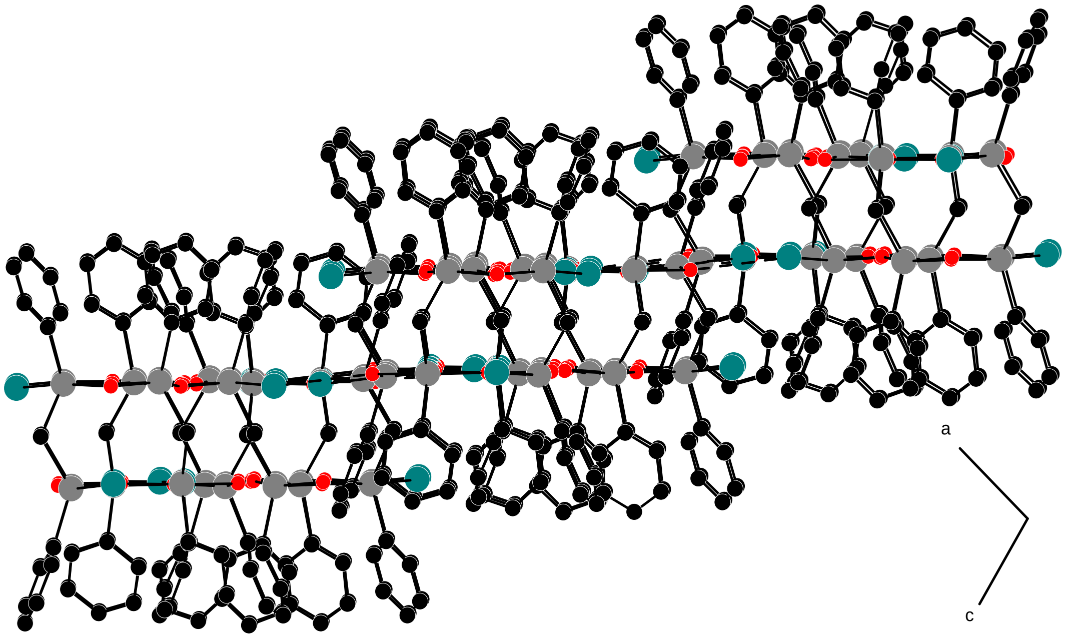


**Figure 3** Crystal structure of **3** showing the planarity of the $Sn_4I_2O_4$ layers and the different planes in the two-dimensional network.

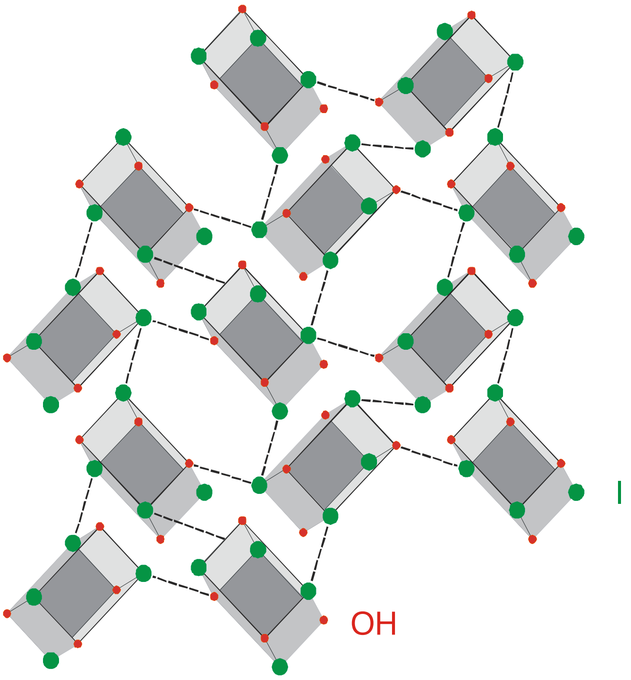


**Figure 4** Schematic representation of the two-dimensional network of **3**.

**Table 1** Selected bond lengths [Å] and bond angles [°] of **3**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.122(11) | Sn(6)-C(61) | 2.136(13) |
| Sn(1)-C(11) | 2.126(12) | Sn(6)-O(5) | 2.131(7) |
| Sn(1)-I(1) | 2.8861(11) | Sn(6)-O(6) | 2.036(7) |
| Sn(1)-O(1) | 2.028(7) | Sn(6)-O(8) | 2.148(7) |
| Sn(1)-O(3) | 2.181(7) | Sn(7)-C(3) | 2.106(10) |
| Sn(2)-C(2) | 2.105(11) | Sn(7)-C(71) | 2.103(11) |
| Sn(2)-C(21) | 2.139(12) | Sn(7)-O(5) | 2.075(6) |
| Sn(2)-O(1) | 2.043(7) | Sn(7)-O(6) | 2.147(7) |
| Sn(2)-O(2) | 2.135(6) | Sn(7)-O(7) | 2.160(7) |
| Sn(2)-O(3) | 2.196(7) | Sn(8)-C(4) | 2.116(10) |
| Sn(3)-C(3) | 2.135(10) | Sn(8)-C(81) | 2.133(13) |
| Sn(3)-C(31) | 2.128(12) | Sn(8)-I(4) | 2.9026(11) |

**Table 1** continued.

| | | | |
|---|---|---|---|
| Sn(3)-O(1) | 2.147(6) | Sn(8)-O(6) | 2.030(6) |
| Sn(3)-O(2) | 2.067(7) | Sn(8)-O(8) | 2.162(6) |
| Sn(3)-O(4) | 2.180(7) | I(1)-O(8A) | 3.514(7) |
| Sn(4)-C(4) | 2.121(12) | I(1)-I(3B) | 4.1296(11) |
| Sn(4)-C(41) | 2.132(12) | I(4)-I(4C) | 4.2017(16) |
| Sn(4)-I(2) | 2.8829(12) | C(11)-C(12) | 1.379(14) |
| Sn(4)-O(2) | 2.058(7) | C(21)-C(22) | 1.374(16) |
| Sn(4)-O(4) | 2.197(7) | C(31)-C(32) | 1.366(15) |
| Sn(5)-C(1) | 2.116(11) | C(41)-C(42) | 1.383(15) |
| Sn(5)-C(51) | 2.124(12) | C(51)-C(52) | 1.380(15) |
| Sn(5)-I(3) | 2.8951(12) | C(61)-C(62) | 1.409(15) |
| Sn(5)-O(5) | 2.025(6) | C(71)-C(72) | 1.395(15) |
| Sn(5)-O(7) | 2.155(6) | C(81)-C(82) | 1.389(15) |
| Sn(6)-C(2) | 2.124(10) | | |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(11) | 126.8(4) | C(1)-Sn(5)-O(5) | 119.5(3) |
| C(1)-Sn(1)-I(1) | 92.3(3) | C(1)-Sn(5)-O(7) | 93.5(4) |
| C(1)-Sn(1)-O(1) | 118.5(4) | C(51)-Sn(5)-I(3) | 95.9(3) |
| C(1)-Sn(1)-O(3) | 91.1(4) | C(51)-Sn(5)-O(5) | 115.5(4) |
| C(11)-Sn(1)-I(1) | 94.7(3) | C(51)-Sn(5)-O(7) | 95.9(4) |
| C(11)-Sn(1)-O(1) | 114.2(4) | I(3)-Sn(5)-O(5) | 87.30(18) |
| C(11)-Sn(1)-O(3) | 95.2(4) | I(3)-Sn(5)-O(7) | 160.86(18) |
| I(1)-Sn(1)-O(1) | 90.06(19) | O(5)-Sn(5)-O(7) | 74.0(2) |
| I(1)-Sn(1)-O(3) | 164.62(19) | C(2)-Sn(6)-C(61) | 123.1(4) |
| O(1)-Sn(1)-O(3) | 75.2(3) | C(2)-Sn(6)-O(5) | 100.3(3) |
| C(2)-Sn(2)-C(21) | 130.0(4) | C(2)-Sn(6)-O(6) | 120.6(3) |
| C(2)-Sn(2)-O(1) | 120.2(3) | C(2)-Sn(6)-O(8) | 96.6(3) |
| C(2)-Sn(2)-O(2) | 96.5(3) | C(61)-Sn(6)-O(5) | 100.4(4) |
| C(2)-Sn(2)-O(3) | 97.9(4) | C(61)-Sn(6)-O(6) | 115.9(4) |
| C(21)-Sn(2)-O(1) | 109.7(4) | C(61)-Sn(6)-O(8) | 93.8(4) |
| C(21)-Sn(2)-O(2) | 98.5(4) | O(5)-Sn(6)-O(6) | 74.7(2) |
| C(21)-Sn(2)-O(3) | 93.0(4) | O(5)-Sn(6)-O(8) | 146.8(2) |

**Table 1** continued.

| | | | |
|---|---|---|---|
| O(1)-Sn(2)-O(2) | 74.4(3) | O(6)-Sn(6)-O(8) | 72.1(3) |
| O(1)-Sn(2)-O(3) | 74.5(3) | C(3)-Sn(7)-C(71) | 128.0(4) |
| O(2)-Sn(2)-O(3) | 148.9(3) | C(3)-Sn(7)-O(5) | 123.3(3) |
| C(3)-Sn(3)-C(31) | 130.2(4) | C(3)-Sn(7)-O(6) | 99.4(3) |
| C(3)-Sn(3)-O(1) | 95.4(3) | C(3)-Sn(7)-O(7) | 97.5(4) |
| C(3)-Sn(3)-O(2) | 122.7(4) | C(71)-Sn(7)-O(5) | 108.5(4) |
| C(3)-Sn(3)-O(4) | 95.0(4) | C(71)-Sn(7)-O(6) | 99.4(4) |
| C(31)-Sn(3)-O(1) | 98.8(4) | C(71)-Sn(7)-O(7) | 92.5(3) |
| C(31)-Sn(3)-O(2) | 107.1(4) | O(5)-Sn(7)-O(6) | 73.6(2) |
| C(31)-Sn(3)-O(4) | 97.4(4) | O(5)-Sn(7)-O(7) | 72.9(2) |
| O(1)-Sn(3)-O(2) | 73.7(3) | O(6)-Sn(7)-O(7) | 146.5(2) |
| O(1)-Sn(3)-O(4) | 147.9(3) | C(4)-Sn(8)-C(81) | 129.3(4) |
| O(2)-Sn(3)-O(4) | 75.2(3) | C(4)-Sn(8)-I(4) | 92.1(3) |
| C(4)-Sn(4)-C(41) | 125.8(4) | C(4)-Sn(8)-O(6) | 117.1(4) |
| C(4)-Sn(4)-I(2) | 92.5(3) | C(4)-Sn(8)-O(8) | 93.0(4) |
| C(4)-Sn(4)-O(2) | 120.8(3) | C(81)-Sn(8)-I(4) | 95.8(3) |
| C(4)-Sn(4)-O(4) | 90.8(4) | C(81)-Sn(8)-O(6) | 113.1(3) |
| C(41)-Sn(4)-I(2) | 98.5(3) | C(81)-Sn(8)-O(8) | 95.8(4) |
| C(41)-Sn(4)-O(2) | 112.1(4) | I(4)-Sn(8)-O(6) | 88.7(2) |
| C(41)-Sn(4)-O(4) | 91.8(4) | I(4)-Sn(8)-O(8) | 160.16(19) |
| I(2)-Sn(4)-O(2) | 90.49(18) | O(6)-Sn(8)-O(8) | 71.9(3) |
| I(2)-Sn(4)-O(4) | 164.59(17) | Sn(5)-O(5)-Sn(6) | 144.1(3) |
| O(2)-Sn(4)-O(4) | 74.9(2) | Sn(5)-O(5)-Sn(7) | 110.4(3) |
| Sn(1)-O(1)-Sn(2) | 110.1(3) | Sn(5)-O(7)-Sn(7) | 102.5(3) |
| Sn(1)-O(3)-Sn(2) | 99.4(3) | Sn(5)-C(51)-C(52) | 120.6(9) |
| Sn(1)-O(1)-Sn(3) | 142.3(4) | Sn(6)-O(5)-Sn(7) | 105.4(3) |
| Sn(1)-C(11)-C(12) | 121.0(9) | Sn(6)-O(6)-Sn(7) | 106.2(3) |
| Sn(2)-O(1)-Sn(3) | 105.9(3) | Sn(6)-O(6)-Sn(8) | 112.3(3) |
| Sn(2)-O(2)-Sn(3) | 105.5(3) | Sn(6)-O(8)-Sn(8) | 103.2(3) |
| Sn(2)-O(2)-Sn(4) | 145.3(3) | Sn(6)-C(61)-C(62) | 121.5(10) |
| Sn(2)-C(21)-C(22) | 119.7(9) | Sn(7)-O(6)-Sn(8) | 140.7(3) |
| Sn(3)-O(2)-Sn(4) | 109.2(3) | Sn(7)-C(71)-C(72) | 121.7(10) |
| Sn(3)-O(4)-Sn(4) | 100.4(3) | Sn(8)-C(81)-C(82) | 118.9(9) |

**Table 1** continued.

| | | | |
|---|---|---|---|
| Sn(3)-C(31)-C(32) | 124.2(9) | Sn(1)-C(1)-Sn(5) | 116.2(5) |
| Sn(4)-C(41)-C(42) | 122.3(9) | Sn(2)-C(2)-Sn(6) | 118.3(5) |
| C(1)-Sn(5)-C(51) | 124.7(4) | Sn(3)-C(3)-Sn(7) | 117.7(5) |
| C(1)-Sn(5)-I(3) | 92.0(3) | Sn(4)-C(4)-Sn(8) | 117.7(5) |

All the solvent-adducts **4**, **5**, **6**, **7** and **8** have almost the same molecular structure as **3**, being different for instance in the deviation from the planarity of the $Sn_4I_2O_4$ layers, their twist as well as the presence of interactions to the corresponding crystallisation solvent which leads to different one- and two-dimensional networks.

Compound **4** consists of the typical double ladder structure of **3** being additionally coordinated to two $CHCl_3$ molecules *via* two Sn-I···Cl interactions and presents a twist of the two $Sn_4I_2O_4$ layers of 27.77(1)° (Figure 5). Furthermore, the crystal structure of compound **4** is characterized by a two-dimensional network (Figure 6). The two-dimensional polymer is realised by a combination of six intermolecular Sn-I···H-O-Sn hydrogen bonds with O···I distances ranging from 3.494(3) to 3.770(3) Å and three Sn-I···Cl distances within the range 4.0232(17)-4.159(3) Å. The latter distances are at the borderline or slightly longer than the sum of the van der Waals radii of iodine and chlorine (3.65-4.02 Å).[92]

The tin oxo cluster **4** as already observed for **3** has no symmetry and exhibits chirality with both enantiomers in the crystal lattice.

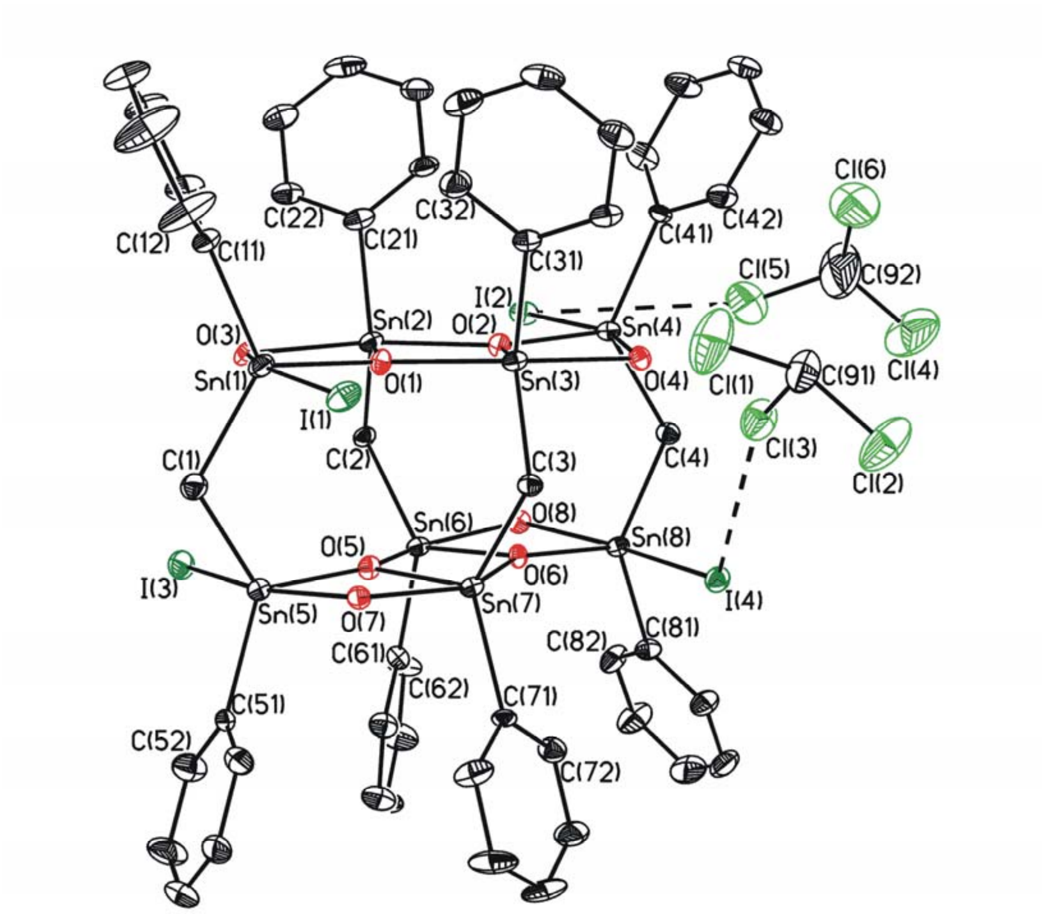


**Figure 5** Molecular structure (SHELXL-97) of **4** showing 30% probability displacement ellipsoids and the atom numbering scheme.

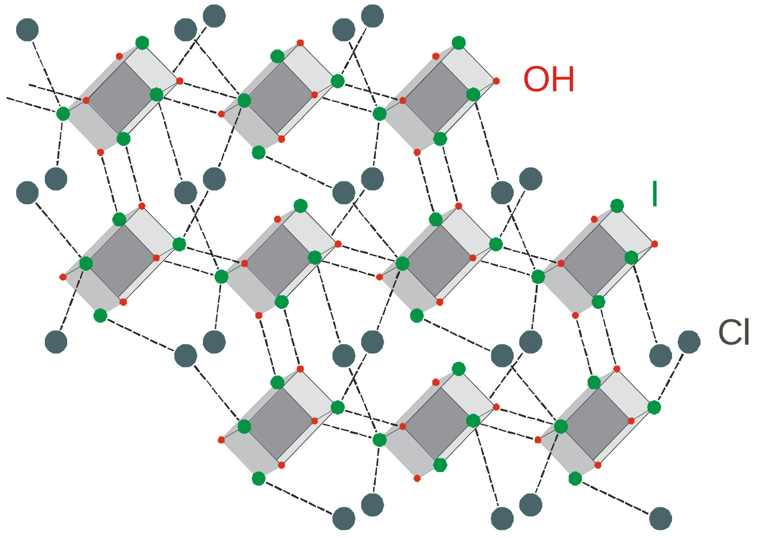


**Figure 6** Schematic representation of the two-dimensional network of **4**.

**Table 2** Selected bond lengths [Å] and bond angles [°] of **4**.

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.140(5) | Sn(6)-O(6) | 2.066(3) |
| Sn(1)-C(11) | 2.136(5) | Sn(6)-O(8) | 2.159(3) |
| Sn(1)-I(1) | 2.8797(5) | Sn(7)-C(3) | 2.114(5) |
| Sn(1)-O(1) | 2.039(3) | Sn(7)-C(71) | 2.127(5) |
| Sn(1)-O(3) | 2.181(7) | Sn(7)-O(5) | 2.072(3) |
| Sn(2)-C(2) | 2.122(5) | Sn(7)-O(6) | 2.132(3) |
| Sn(2)-C(21) | 2.126(5) | Sn(7)-O(7) | 2.158(3) |
| Sn(2)-O(1) | 2.059(3) | Sn(8)-C(4) | 2.127(5) |
| Sn(2)-O(2) | 2.131(3) | Sn(8)-C(81) | 2.144(5) |
| Sn(2)-O(3) | 2.163(3) | Sn(8)-I(4) | 2.8747(5) |
| Sn(3)-C(3) | 2.126(4) | Sn(8)-O(6) | 2.033(3) |
| Sn(3)-C(31) | 2.123(5) | Sn(8)-O(8) | 2.169(3) |
| Sn(3)-O(1) | 2.136(3) | I(1)-Cl(4B) | 4.159(3) |
| Sn(3)-O(2) | 2.054(3) | I(2)-Cl(2D) | 4.111(2) |
| Sn(3)-O(4) | 2.164(3) | I(2)-Cl(5) | 4.053(4) |
| Sn(4)-C(4) | 2.129(5) | I(4)-Cl(3) | 4.0232(17) |
| Sn(4)-C(41) | 2.134(5) | I(1)-O(7A) | 3.566(3) |
| Sn(4)-I(2) | 2.8758(5) | I(2)-O(8C) | 3.494(3) |
| Sn(4)-O(2) | 2.039(3) | I(3)-O(3E) | 3.770(3) |
| Sn(4)-O(4) | 2.187(3) | C(11)-C(12) | 1.379(14) |
| Sn(5)-C(1) | 2.129(5) | C(21)-C(22) | 1.374(16) |
| Sn(5)-C(51) | 2.130(5) | C(31)-C(32) | 1.366(15) |
| Sn(5)-I(3) | 2.8667(5) | C(41)-C(42) | 1.383(15) |
| Sn(5)-O(5) | 2.023(3) | C(51)-C(52) | 1.380(15) |
| Sn(5)-O(7) | 2.184(3) | C(61)-C(62) | 1.409(15) |
| Sn(6)-C(2) | 2.112(4) | C(71)-C(72) | 1.395(15) |
| Sn(6)-C(61) | 2.122(5) | C(81)-C(82) | 1.389(15) |
| Sn(6)-O(5) | 2.120(3) | | |

| Bond angles [°] | | | |
|---|---|---|---|
| C(1)-Sn(1)-C(11) | 126.1(2) | C(1)-Sn(5)-O(5) | 119.51(16) |
| C(1)-Sn(1)-I(1) | 92.15(14) | C(1)-Sn(5)-O(7) | 92.11(17) |

**Table 2** continued.

| | | | |
|---|---|---|---|
| C(1)-Sn(1)-O(1) | 119.07(16) | C(51)-Sn(5)-I(3) | 98.14(15) |
| C(1)-Sn(1)-O(3) | 93.26(17) | C(51)-Sn(5)-O(5) | 116.09(16) |
| C(11)-Sn(1)-I(1) | 96.38(15) | C(51)-Sn(5)-O(7) | 91.30(17) |
| C(11)-Sn(1)-O(1) | 114.37(17) | I(3)-Sn(5)-O(5) | 88.03(9) |
| C(11)-Sn(1)-O(3) | 94.82(17) | I(3)-Sn(5)-O(7) | 162.07(8) |
| I(1)-Sn(1)-O(1) | 87.87(9) | O(5)-Sn(5)-O(7) | 74.10(12) |
| I(1)-Sn(1)-O(3) | 161.33(9) | C(2)-Sn(6)-C(61) | 129.96(18) |
| O(1)-Sn(1)-O(3) | 73.90(12) | C(2)-Sn(6)-O(5) | 98.69(16) |
| C(2)-Sn(2)-C(21) | 123.63(18) | C(2)-Sn(6)-O(6) | 121.52(16) |
| C(2)-Sn(2)-O(1) | 121.98(15) | C(2)-Sn(6)-O(8) | 93.90(16) |
| C(2)-Sn(2)-O(2) | 99.61(16) | C(61)-Sn(6)-O(5) | 100.09(16) |
| C(2)-Sn(2)-O(3) | 96.05(17) | C(61)-Sn(6)-O(6) | 108.18(16) |
| C(21)-Sn(2)-O(1) | 114.17(16) | C(61)-Sn(6)-O(8) | 94.13(16) |
| C(21)-Sn(2)-O(2) | 99.70(18) | O(5)-Sn(6)-O(6) | 74.09(12) |
| C(21)-Sn(2)-O(3) | 94.73(18) | O(5)-Sn(6)-O(8) | 147.78(12) |
| O(1)-Sn(2)-O(2) | 74.05(12) | O(6)-Sn(6)-O(8) | 74.03(12) |
| O(1)-Sn(2)-O(3) | 73.70(12) | C(3)-Sn(7)-C(71) | 127.43(18) |
| O(2)-Sn(2)-O(3) | 147.71(12) | C(3)-Sn(7)-O(5) | 121.72(15) |
| C(3)-Sn(3)-C(31) | 125.11(18) | C(3)-Sn(7)-O(6) | 98.03(15) |
| C(3)-Sn(3)-O(1) | 99.62(16) | C(3)-Sn(7)-O(7) | 94.99(16) |
| C(3)-Sn(3)-O(2) | 122.38(15) | C(71)-Sn(7)-O(5) | 110.70(16) |
| C(3)-Sn(3)-O(4) | 94.48(16) | C(71)-Sn(7)-O(6) | 99.79(16) |
| C(31)-Sn(3)-O(1) | 99.75(17) | C(71)-Sn(7)-O(7) | 95.90(16) |
| C(31)-Sn(3)-O(2) | 112.24(15) | O(5)-Sn(7)-O(6) | 73.71(12) |
| C(31)-Sn(3)-O(4) | 94.99(17) | O(5)-Sn(7)-O(7) | 73.74(12) |
| O(1)-Sn(3)-O(2) | 74.05(12) | O(6)-Sn(7)-O(7) | 147.11(11) |
| O(1)-Sn(3)-O(4) | 148.27(11) | C(4)-Sn(8)-C(81) | 124.40(19) |
| O(2)-Sn(3)-O(4) | 74.38(12) | C(4)-Sn(8)-I(4) | 94.34(14) |
| C(4)-Sn(4)-C(41) | 124.54(19) | C(4)-Sn(8)-O(6) | 119.10(16) |
| C(4)-Sn(4)-I(2) | 92.76(14) | C(4)-Sn(8)-O(8) | 92.27(16) |
| C(4)-Sn(4)-O(2) | 118.58(16) | C(81)-Sn(8)-I(4) | 97.62(14) |
| C(4)-Sn(4)-O(4) | 92.63(16) | C(81)-Sn(8)-O(6) | 115.55(17) |
| C(41)-Sn(4)-I(2) | 98.29(14) | C(81)-Sn(8)-O(8) | 92.78(16) |

**Table 2** continued.

| | | | |
|---|---|---|---|
| C(41)-Sn(4)-O(2) | 115.96(16) | I(4)-Sn(8)-O(6) | 87.29(8) |
| C(41)-Sn(4)-O(4) | 92.75(16) | I(4)-Sn(8)-O(8) | 161.56(8) |
| I(2)-Sn(4)-O(2) | 88.16(9) | O(6)-Sn(8)-O(8) | 74.47(12) |
| I(2)-Sn(4)-O(4) | 161.99(9) | Sn(5)-O(5)-Sn(6) | 143.28(16) |
| O(2)-Sn(4)-O(4) | 74.19(12) | Sn(5)-O(5)-Sn(7) | 110.13(13) |
| Sn(1)-O(1)-Sn(2) | 110.37(14) | Sn(5)-O(7)-Sn(7) | 101.29(13) |
| Sn(1)-O(3)-Sn(2) | 101.77(14) | Sn(5)-C(51)-C(52) | 123.9(4) |
| Sn(1)-O(1)-Sn(3) | 143.61(16) | Sn(6)-O(5)-Sn(7) | 106.08(14) |
| Sn(1)-C(11)-C(12) | 121.3(4) | Sn(6)-O(6)-Sn(7) | 105.85(13) |
| Sn(2)-O(1)-Sn(3) | 105.73(14) | Sn(6)-O(6)-Sn(8) | 109.48(14) |
| Sn(2)-O(2)-Sn(3) | 106.10(13) | Sn(6)-O(8)-Sn(8) | 101.30(12) |
| Sn(2)-O(2)-Sn(4) | 143.56(16) | Sn(6)-C(61)-C(62) | 121.3(4) |
| Sn(2)-C(21)-C(22) | 119.6(4) | Sn(7)-O(6)-Sn(8) | 144.18(16) |
| Sn(3)-O(2)-Sn(4) | 110.09(15) | Sn(7)-C(71)-C(72) | 120.1(4) |
| Sn(3)-O(4)-Sn(4) | 100.88(13) | Sn(8)-C(81)-C(82) | 118.5(4) |
| Sn(3)-C(31)-C(32) | 121.1(4) | Sn(1)-C(1)-Sn(5) | 116.5(2) |
| Sn(4)-C(41)-C(42) | 119.0(4) | Sn(2)-C(2)-Sn(6) | 118.0(2) |
| C(1)-Sn(5)-C(51) | 122.98(19) | Sn(3)-C(3)-Sn(7) | 117.9(2) |
| C(1)-Sn(5)-I(3) | 95.43(15) | Sn(4)-C(4)-Sn(8) | 117.4(2) |

In the molecular structure of adduct **5** the organotin oxo cluster $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ is coordinated to three $CH_2Cl_2$ molecules by two Sn-I···Cl and one Cl···Cl contacts and presents a twist of the two $Sn_4I_2O_4$ layers of 29.00(2)° (Figure 7).

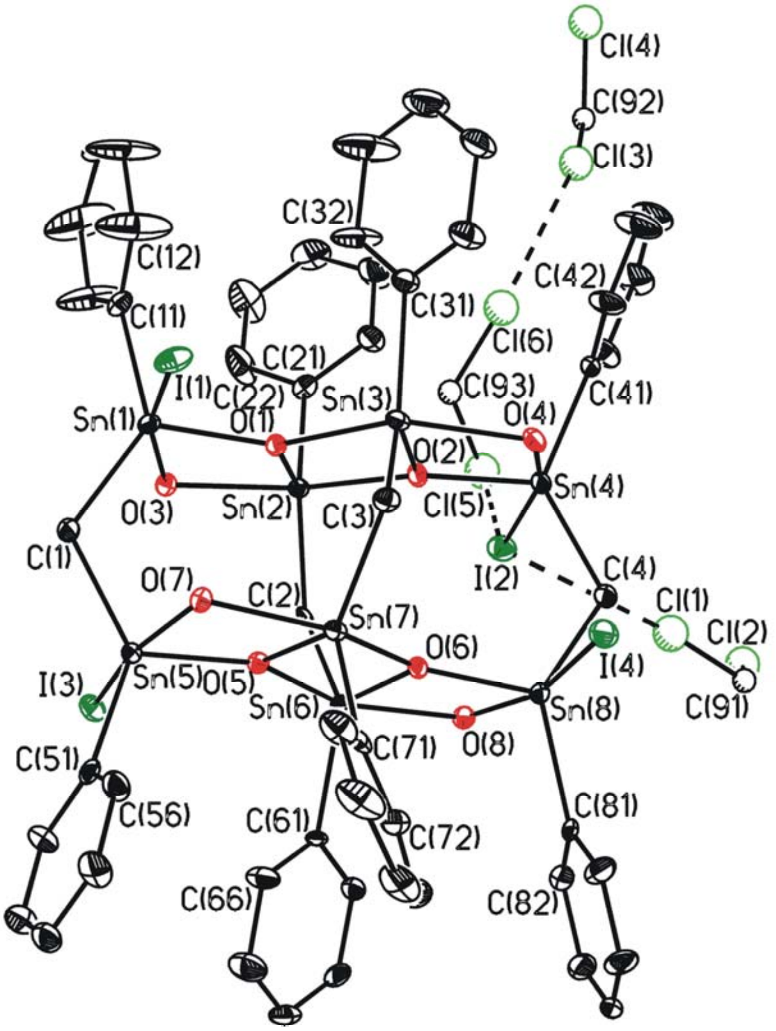


**Figure 7** Molecular structure (SHELXL-97) of **5** showing 30% probability displacement ellipsoids and the atom numbering scheme.

In the crystal structure of **5** the double ladders are linked together by intermolecular hydrogen bonds of the type Sn-O-H···I-Sn with O···I distance of 3.759(5) Å to give a one-dimensional polymer (Figure 8). Noteworthy, only one out of four iodines of each cluster are involved in the hydrogen-bonding. As already said, a second iodide of each cluster interacts with two $CH_2Cl_2$ molecules *via* Sn-I···Cl interactions of 3.824(2) and 3.926(3) Å, respectively, being close to the sum of the van der Waals radii of these atoms (3.65-4.02 Å).[92] The third $CH_2Cl_2$ molecule is related to one of the iodine-bonded $CH_2Cl_2$ molecules by an intramolecular Cl···Cl distance of 3.584(4) Å being close to the sum of the van der Waals radii of two chlorine atoms (3.40-3.80 Å).[92]

Remarkably, the crystal structure of the organotin oxo cluster **5** contains a similar chain-type structural motif as observed for **3**. Moreover, compound **5**, as already observed for **3** and **4**, lacks any symmetry and exhibits chirality with both enantiomers being present in the crystal lattice.

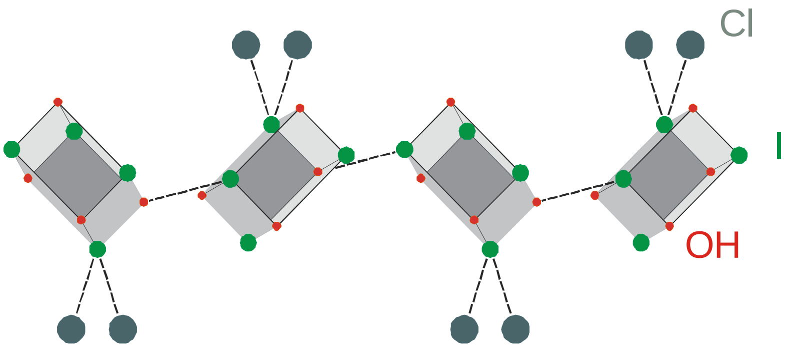


**Figure 8** Schematic representation of the one-dimensional network of **5** being the third $CH_2Cl_2$ molecule omitted.

**Table 3** Selected bond lengths [Å] and bond angles [°] of **5.**

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.138(6) | Sn(6)-C(61) | 2.124(6) |
| Sn(1)-C(11) | 2.110(7) | Sn(6)-O(5) | 2.122(4) |
| Sn(1)-I(1) | 2.8919(7) | Sn(6)-O(6) | 2.058(4) |
| Sn(1)-O(1) | 2.040(4) | Sn(6)-O(8) | 2.148(4) |
| Sn(1)-O(3) | 2.201(4) | Sn(7)-C(3) | 2.101(6) |
| Sn(2)-C(2) | 2.110(6) | Sn(7)-C(71) | 2.125(7) |
| Sn(2)-C(21) | 2.113(7) | Sn(7)-O(5) | 2.064(4) |
| Sn(2)-O(1) | 2.064(4) | Sn(7)-O(6) | 2.122(4) |
| Sn(2)-O(2) | 2.132(5) | Sn(7)-O(7) | 2.165(4) |
| Sn(2)-O(3) | 2.167(4) | Sn(8)-C(4) | 2.123(6) |
| Sn(3)-C(3) | 2.111(6) | Sn(8)-C(81) | 2.144(7) |
| Sn(3)-C(31) | 2.127(7) | Sn(8)-I(4) | 2.8738(8) |

**Table 3** continued.

| | | | |
|---|---|---|---|
| Sn(3)-O(1) | 2.121(4) | Sn(8)-O(6) | 2.028(4) |
| Sn(3)-O(2) | 2.064(4) | Sn(8)-O(8) | 2.203(5) |
| Sn(3)-O(4) | 2.167(5) | I(2)-Cl(1) | 3.824(2) |
| Sn(4)-C(4) | 2.120(7) | I(2)-Cl(5) | 3.926(3) |
| Sn(4)-C(41) | 2.146(6) | I(3)-O(4A) | 3.759(5) |
| Sn(4)-I(2) | 2.8824(8) | Cl(3)-Cl(6) | 3.584(4) |
| Sn(4)-O(2) | 2.045(4) | C(11)-C(12) | 1.332(11) |
| Sn(4)-O(4) | 2.197(7) | C(21)-C(22) | 1.376(11) |
| Sn(5)-C(1) | 2.162(5) | C(31)-C(32) | 1.368(11) |
| Sn(5)-C(51) | 2.134(7) | C(41)-C(42) | 1.387(10) |
| Sn(5)-I(3) | 2.8984(7) | C(51)-C(52) | 1.382(9) |
| Sn(5)-O(5) | 2.027(4) | C(61)-C(62) | 1.374(9) |
| Sn(5)-O(7) | 2.180(4) | C(71)-C(72) | 1.370(10) |
| Sn(6)-C(2) | 2.118(7) | C(81)-C(82) | 1.382(10) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(11) | 131.2(3) | C(1)-Sn(5)-O(5) | 119.0(2) |
| C(1)-Sn(1)-I(1) | 92.2(2) | C(1)-Sn(5)-O(7) | 91.6(2) |
| C(1)-Sn(1)-O(1) | 118.7(2) | C(51)-Sn(5)-I(3) | 98.4(2) |
| C(1)-Sn(1)-O(3) | 90.4(2) | C(51)-Sn(5)-O(5) | 109.6(2) |
| C(11)-Sn(1)-I(1) | 97.5(2) | C(51)-Sn(5)-O(7) | 92.1(2) |
| C(11)-Sn(1)-O(1) | 109.0(2) | I(3)-Sn(5)-O(5) | 89.11(12) |
| C(11)-Sn(1)-O(3) | 92.8(2) | I(3)-Sn(5)-O(7) | 163.18(11) |
| I(1)-Sn(1)-O(1) | 90.14(12) | O(5)-Sn(5)-O(7) | 74.96(17) |
| I(1)-Sn(1)-O(3) | 163.81(12) | C(2)-Sn(6)-C(61) | 128.0(2) |
| O(1)-Sn(1)-O(3) | 74.63(17) | C(2)-Sn(6)-O(5) | 98.6(2) |
| C(2)-Sn(2)-C(21) | 129.3(3) | C(2)-Sn(6)-O(6) | 121.4(2) |
| C(2)-Sn(2)-O(1) | 120.9(2) | C(2)-Sn(6)-O(8) | 94.7(2) |
| C(2)-Sn(2)-O(2) | 97.9(2) | C(61)-Sn(6)-O(5) | 99.1(2) |
| C(2)-Sn(2)-O(3) | 95.3(2) | C(61)-Sn(6)-O(6) | 110.4(2) |
| C(21)-Sn(2)-O(1) | 109.7(2) | C(61)-Sn(6)-O(8) | 94.7(2) |
| C(21)-Sn(2)-O(2) | 98.6(2) | O(5)-Sn(6)-O(6) | 73.53(17) |
| C(21)-Sn(2)-O(3) | 94.7(2) | O(5)-Sn(6)-O(8) | 148.59(17) |

**Table 3** continued.

| | | | |
|---|---|---|---|
| O(1)-Sn(2)-O(2) | 74.04(17) | O(6)-Sn(6)-O(8) | 75.24(17) |
| O(1)-Sn(2)-O(3) | 74.89(17) | C(3)-Sn(7)-C(71) | 121.6(3) |
| O(2)-Sn(2)-O(3) | 148.76(17) | C(3)-Sn(7)-O(5) | 123.3(2) |
| C(3)-Sn(3)-C(31) | 127.5(3) | C(3)-Sn(7)-O(6) | 97.4(2) |
| C(3)-Sn(3)-O(1) | 97.6(2) | C(3)-Sn(7)-O(7) | 96.3(2) |
| C(3)-Sn(3)-O(2) | 121.4(2) | C(71)-Sn(7)-O(5) | 115.0(2) |
| C(3)-Sn(3)-O(4) | 93.8(2) | C(71)-Sn(7)-O(6) | 100.5(2) |
| C(31)-Sn(3)-O(1) | 102.0(2) | C(71)-Sn(7)-O(7) | 96.9(2) |
| C(31)-Sn(3)-O(2) | 110.7(2) | O(5)-Sn(7)-O(6) | 73.43(17) |
| C(31)-Sn(3)-O(4) | 94.6(2) | O(5)-Sn(7)-O(7) | 74.58(16) |
| O(1)-Sn(3)-O(2) | 74.27(17) | O(6)-Sn(7)-O(7) | 147.68(17) |
| O(1)-Sn(3)-O(4) | 147.71(17) | C(4)-Sn(8)-C(81) | 128.5(3) |
| O(2)-Sn(3)-O(4) | 73.98(18) | C(4)-Sn(8)-I(4) | 93.1(2) |
| C(4)-Sn(4)-C(41) | 128.4(3) | C(4)-Sn(8)-O(6) | 118.1(2) |
| C(4)-Sn(4)-I(2) | 91.5(2) | C(4)-Sn(8)-O(8) | 90.4(2) |
| C(4)-Sn(4)-O(2) | 118.2(2) | C(81)-Sn(8)-I(4) | 98.5(2) |
| C(4)-Sn(4)-O(4) | 92.0(3) | C(81)-Sn(8)-O(6) | 111.9(2) |
| C(41)-Sn(4)-I(2) | 96.7(2) | C(81)-Sn(8)-O(8) | 91.2(2) |
| C(41)-Sn(4)-O(2) | 112.8(2) | I(4)-Sn(8)-O(6) | 90.31(13) |
| C(41)-Sn(4)-O(4) | 94.0(2) | I(4)-Sn(8)-O(8) | 164.35(11) |
| I(2)-Sn(4)-O(2) | 89.36(13) | O(6)-Sn(8)-O(8) | 74.61(17) |
| I(2)-Sn(4)-O(4) | 163.13(12) | Sn(5)-O(5)-Sn(6) | 143.9(2) |
| O(2)-Sn(4)-O(4) | 74.45(18) | Sn(5)-O(5)-Sn(7) | 109.34(19) |
| Sn(1)-O(1)-Sn(2) | 109.5(2) | Sn(5)-O(7)-Sn(7) | 100.35(17) |
| Sn(1)-O(3)-Sn(2) | 100.25(18) | Sn(5)-C(51)-C(52) | 122.7(6) |
| Sn(1)-O(1)-Sn(3) | 143.6(2) | Sn(6)-O(5)-Sn(7) | 106.33(19) |
| Sn(1)-C(11)-C(12) | 122.9(7) | Sn(6)-O(6)-Sn(7) | 106.56(19) |
| Sn(2)-O(1)-Sn(3) | 105.84(18) | Sn(6)-O(6)-Sn(8) | 109.29(19) |
| Sn(2)-O(2)-Sn(3) | 105.43(19) | Sn(6)-O(8)-Sn(8) | 99.99(18) |
| Sn(2)-O(2)-Sn(4) | 144.8(2) | Sn(6)-C(61)-C(62) | 119.4(5) |
| Sn(2)-C(21)-C(22) | 121.7(6) | Sn(7)-O(6)-Sn(8) | 143.4(2) |
| Sn(3)-O(2)-Sn(4) | 109.4(2) | Sn(7)-C(71)-C(72) | 122.2(6) |
| Sn(3)-O(4)-Sn(4) | 101.5(2) | Sn(8)-C(81)-C(82) | 117.6(6) |

**Table 3** continued.

| | | | |
|---|---|---|---|
| Sn(3)-C(31)-C(32) | 121.0(6) | Sn(1)-C(1)-Sn(5) | 116.0(3) |
| Sn(4)-C(41)-C(42) | 116.8(5) | Sn(2)-C(2)-Sn(6) | 117.7(3) |
| C(1)-Sn(5)-C(51) | 130.5(2) | Sn(3)-C(3)-Sn(7) | 117.8(3) |
| C(1)-Sn(5)-I(3) | 91.5(2) | Sn(4)-C(4)-Sn(8) | 117.6(3) |

Compound **6** consists of the organotin oxo cluster {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$ connected to four THF molecules by four Sn-O-H···O hydrogen bonds and is characterized by a twist of the Sn$_4$I$_2$O$_4$ layers of 28.02(4)° (Figure 9).

Noteworthy derivative **6**, contrary to all the organotin oxo clusters presented in this work, exhibits a centre of symmetry.

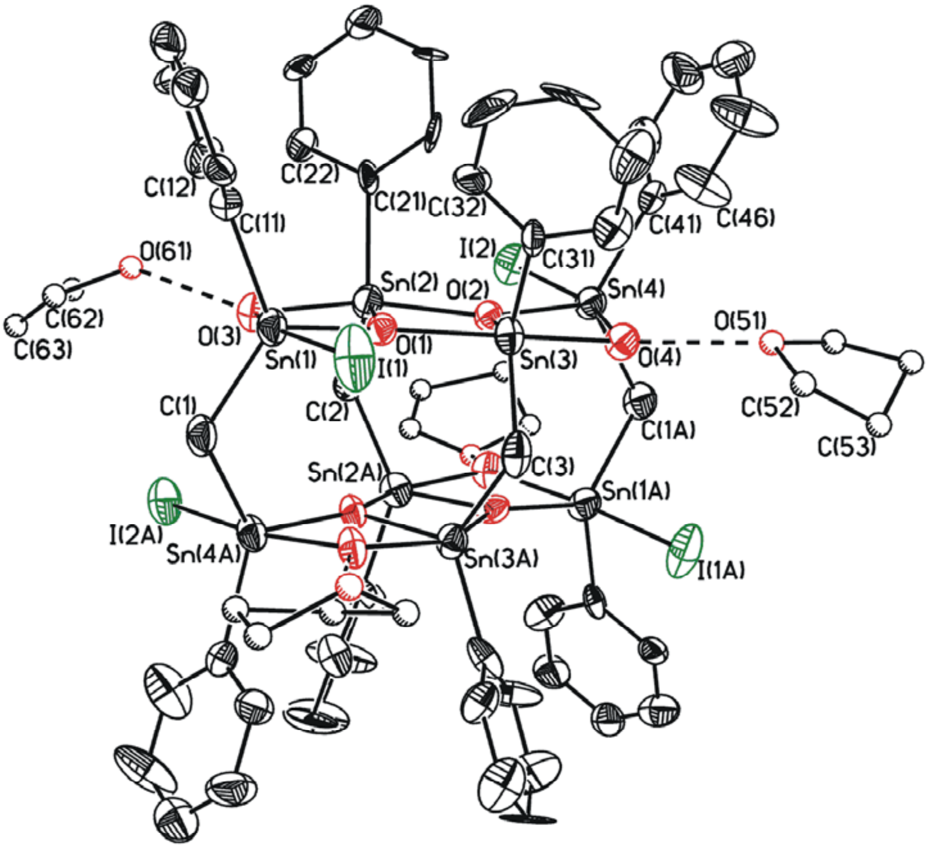


**Figure 9** Molecular structure (SHELXL-97) of **6** showing 30% probability displacement ellipsoids and the atom numbering scheme.

The THF molecules forming Sn-O-H···O hydrogen bonds, with distances in the range between 2.617(9)-2.698(13) Å, prevent in this way formation of a polymeric hydrogen-bonded network (Figure 10).

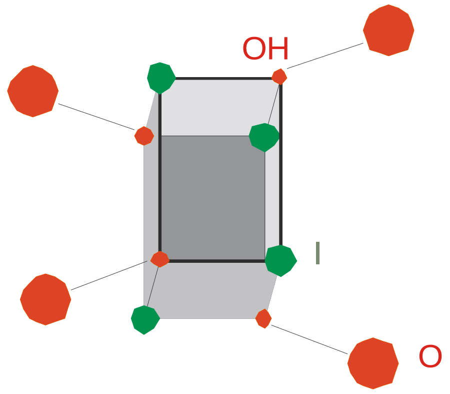


**Figure 10** Schematic representation of the monomeric structure of **6**.

**Table 4** Selected bond lengths [Å] and bond angles [°] of **6.**

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.133(14) | Sn(3)-O(2) | 2.077(8) |
| Sn(1)-C(11) | 2.203(10) | Sn(3)-O(4) | 2.120(8) |
| Sn(1)-I(1) | 2.8881(16) | Sn(4)-C(1A) | 2.140(13) |
| Sn(1)-O(1) | 2.015(7) | Sn(4)-C(41) | 2.184(13) |
| Sn(1)-O(3) | 2.155(9) | Sn(4)-I(2) | 2.8588(14) |
| Sn(2)-C(2) | 2.119(9) | Sn(4)-O(2) | 2.030(7) |
| Sn(2)-C(21) | 2.202(13) | Sn(4)-O(4) | 2.196(8) |
| Sn(2)-O(1) | 2.072(8) | Sn(2A)-C(2) | 2.119(9) |
| Sn(2)-O(2) | 2.114(7) | Sn(3A)-C(3) | 2.118(9) |
| Sn(2)-O(3) | 2.113(9) | Sn(4A)-C(1) | 2.140(13) |
| Sn(3)-C(3) | 2.118(8) | O(3)-O(61) | 2.698(13) |

**Table 4** continued.

| | | | |
|---|---|---|---|
| Sn(3)-C(31) | 2.051(15) | O(4)-O(51) | 2.617(19) |
| Sn(3)-O(1) | 2.134(7) | | |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(11) | 126.4(5) | O(1)-Sn(3)-O(4) | 148.5(3) |
| C(1)-Sn(1)-I(1) | 94.1(4) | O(2)-Sn(3)-O(4) | 74.7(3) |
| C(1)-Sn(1)-O(1) | 119.2(4) | C(1A)-Sn(4)-C(41) | 124.9(6) |
| C(1)-Sn(1)-O(3) | 93.0(5) | C(1A)-Sn(4)-I(2) | 95.2(4) |
| C(11)-Sn(1)-I(1) | 99.2(4) | C(1A)-Sn(4)-O(2) | 117.1(4) |
| C(11)-Sn(1)-O(1) | 112.8(4) | C(1A)-Sn(4)-O(4) | 90.9(4) |
| C(11)-Sn(1)-O(3) | 89.9(4) | C(41)-Sn(4)-I(2) | 100.2(4) |
| I(1)-Sn(1)-O(1) | 88.6(2) | C(41)-Sn(4)-O(2) | 115.5(5) |
| I(1)-Sn(1)-O(3) | 161.9(2) | C(41)-Sn(4)-O(4) | 88.4(5) |
| O(1)-Sn(1)-O(3) | 73.4(3) | I(2)-Sn(4)-O(2) | 90.0(2) |
| C(2)-Sn(2)-C(21) | 127.9(7) | I(2)-Sn(4)-O(4) | 163.9(2) |
| C(2)-Sn(2)-O(1) | 123.0(4) | O(2)-Sn(4)-O(4) | 74.0(3) |
| C(2)-Sn(2)-O(2) | 99.1(3) | Sn(1)-O(1)-Sn(2) | 109.6(4) |
| C(2)-Sn(2)-O(3) | 94.2(3) | Sn(1)-O(3)-Sn(2) | 103.0(4) |
| C(21)-Sn(2)-O(1) | 109.0(6) | Sn(1)-O(1)-Sn(3) | 144.7(4) |
| C(21)-Sn(2)-O(2) | 97.3(4) | Sn(1)-C(11)-C(12) | 120.5(7) |
| C(21)-Sn(2)-O(3) | 97.6(5) | Sn(2)-O(1)-Sn(3) | 105.2(3) |
| O(1)-Sn(2)-O(2) | 74.7(3) | Sn(2)-O(2)-Sn(3) | 105.7(3) |
| O(1)-Sn(2)-O(3) | 73.2(3) | Sn(2)-O(2)-Sn(4) | 144.6(4) |
| O(2)-Sn(2)-O(3) | 147.5(3) | Sn(2)-C(21)-C(22) | 117.5(8) |
| C(3)-Sn(3)-C(31) | 119.7(7) | Sn(3)-O(2)-Sn(4) | 108.7(3) |
| C(3)-Sn(3)-O(1) | 98.2(3) | Sn(3)-O(4)-Sn(4) | 101.3(4) |
| C(3)-Sn(3)-O(2) | 121.6(4) | Sn(3)-C(31)-C(32) | 120.5(11) |
| C(3)-Sn(3)-O(4) | 94.0(2) | Sn(4)-C(41)-C(42) | 118.1(9) |
| C(31)-Sn(3)-O(1) | 101.7(5) | Sn(1)-C(1)-Sn(4A) | 116.5(5) |
| C(31)-Sn(3)-O(2) | 118.5(7) | Sn(2)-C(2)-Sn(2A) | 115.2(8) |
| C(31)-Sn(3)-O(4) | 97.2(6) | Sn(3)-C(3)-Sn(3A) | 117.1(7) |
| O(1)-Sn(3)-O(2) | 74.1(3) | Sn(4)-C(1A)-Sn(1A) | 116.5(5) |

In the molecular structure of adduct **7** the organotin oxo cluster {[Ph(HO)SnCH$_2$-Sn(I)Ph]O}$_4$ is coordinated to one *s*-BuOH molecule by one Sn-I···H-O(*s*-BuOH) and one O···H-O hydrogen bonds; furthermore the twist of the $Sn_4I_2O_4$ layers amount to 29.68(2)° (Figure 11). The crystal lattice contains both enantiomers because racemic *s*-BuOH was used for the crystallisation (Figure 12).

The crystal structure of **7** does not consist of a polymeric hydrogen-bonding network but of dimers (Figure 13) in which the two oxo clusters are linked by a combination of two intermolecular hydrogen bonds of the type Sn-O-H···I-Sn with O···I distance of 3.567(5) Å. A second iodine atom and one hydroxy group of each cluster interact with a *s*-BuOH molecule, respectively, *via* Sn-I···H-O(*s*-BuOH) contacts with O···I distance of 3.358(17) and 3.78(2) Å and O···H-O contacts with O···O distance of 2.709(17) and 2.70(2) Å.

Attempts to obtain single crystals of **7** with enantiomerically pure *s*-BuOH failed. In principle, it should be possible in this way to obtain a chiral crystal lattice.

Furthermore, as already observed for compounds **3**, **4** and **5**, derivative **7** lacks any symmetry. The compound is chiral with both enantiomers present in the crystal lattice.

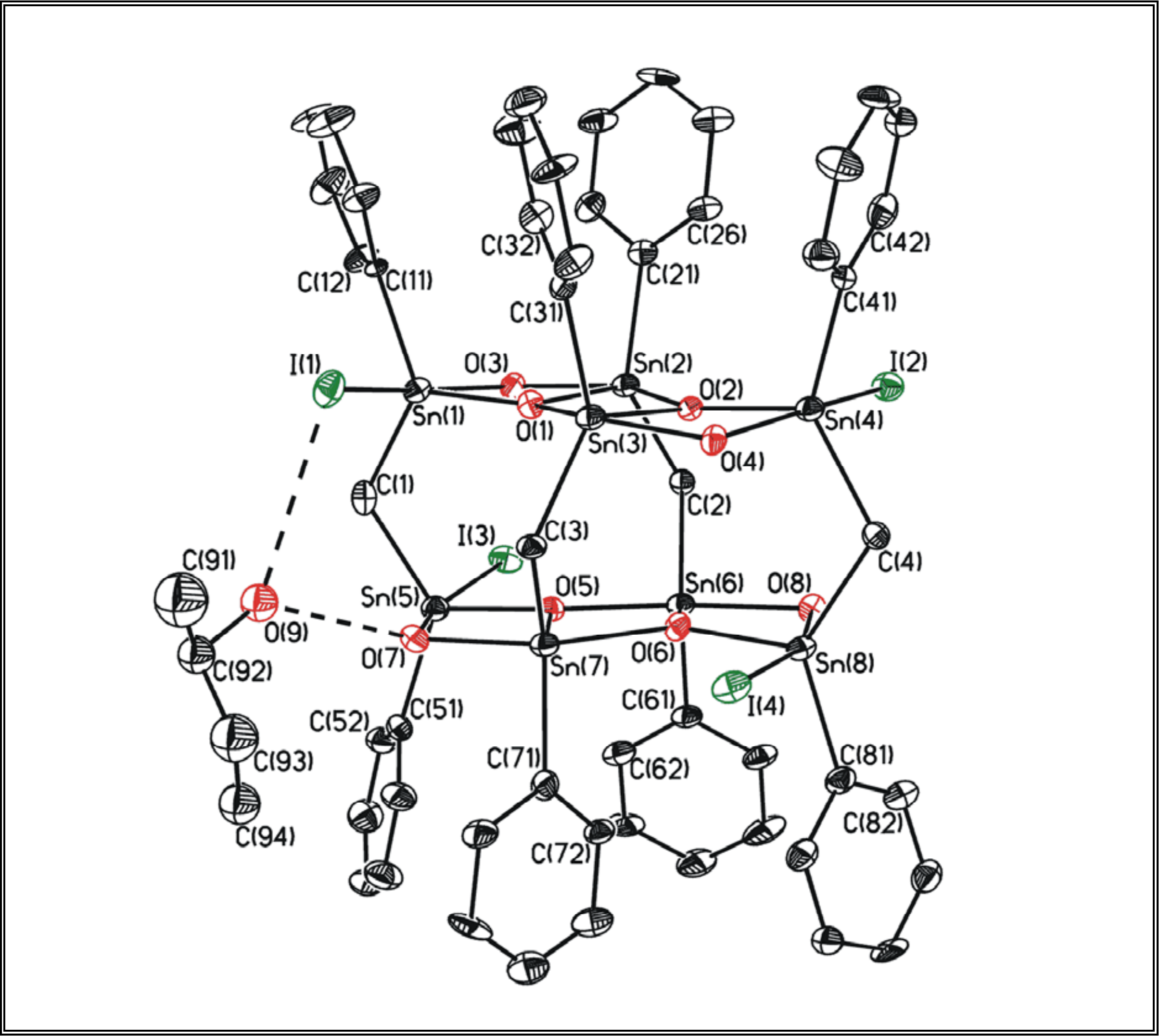


**Figure 11** Molecular structure (SHELXL-97) of **7** showing 30% probability displacement ellipsoids and the atom numbering scheme.

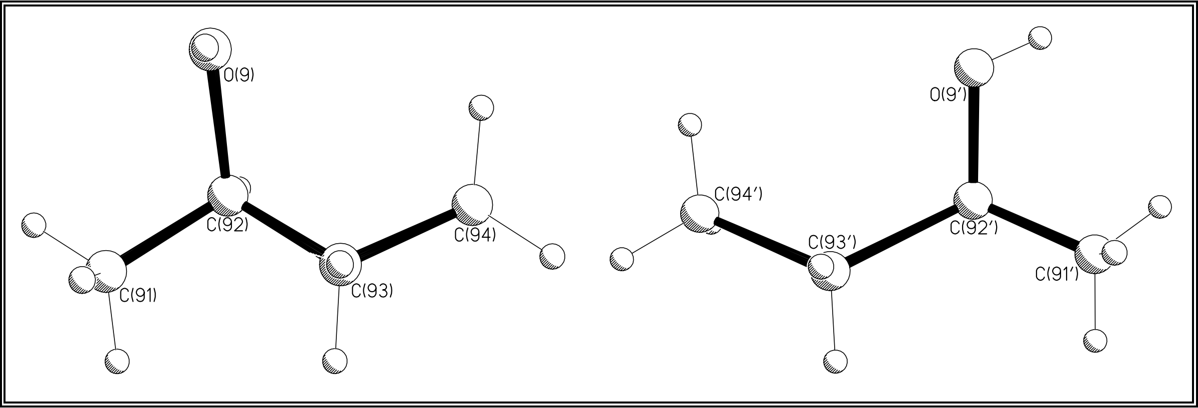


**Figure 12** Enantiomers (SHELXTL-PLUS) of *s*-BuOH in the crystal lattice of **7**.

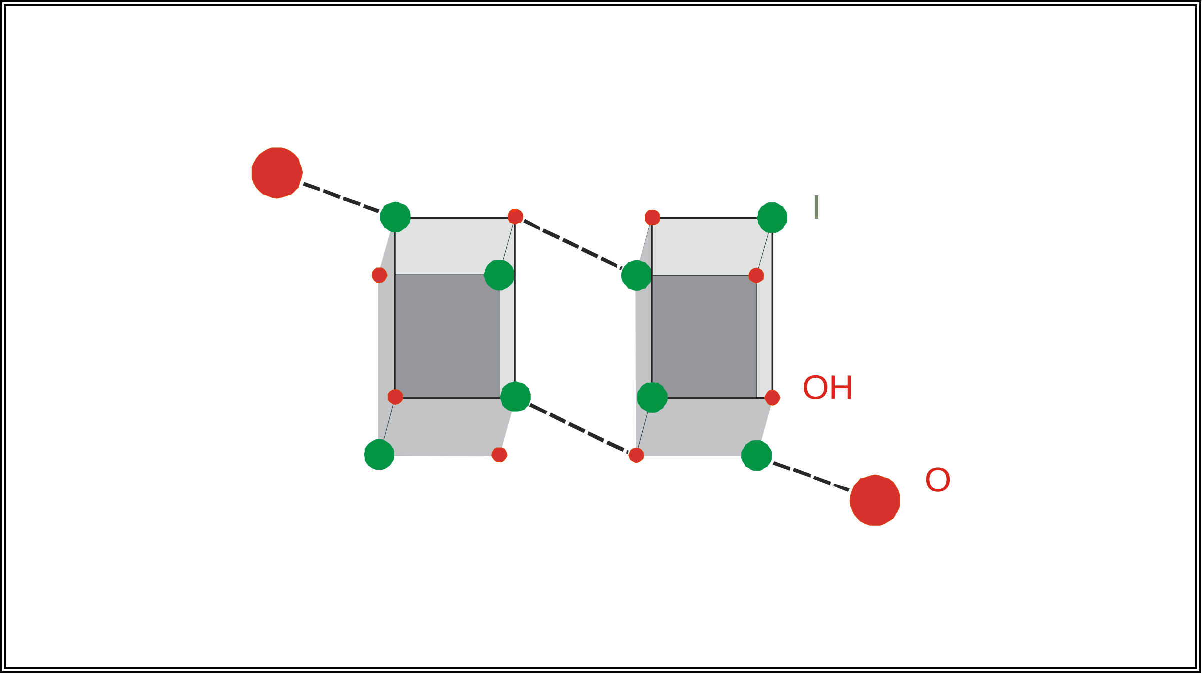


**Figure 13** Schematic representation of the dimeric structure of **7**.

**Table 5** Selected bond lengths [Å] and bond angles [°] of **7.**

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.115(10) | Sn(6)-O(5) | 2.137(5) |
| Sn(1)-C(11) | 2.131(9) | Sn(6)-O(6) | 2.066(5) |
| Sn(1)-I(1) | 2.8690(9) | Sn(6)-O(8) | 2.191(5) |
| Sn(1)-O(1) | 2.043(5) | Sn(7)-C(3) | 2.104(9) |
| Sn(1)-O(3) | 2.189(5) | Sn(7)-C(71) | 2.118(10) |
| Sn(2)-C(2) | 2.097(9) | Sn(7)-O(5) | 2.065(5) |
| Sn(2)-C(21) | 2.131(10) | Sn(7)-O(6) | 2.115(5) |
| Sn(2)-O(1) | 2.060(5) | Sn(7)-O(7) | 2.139(5) |
| Sn(2)-O(2) | 2.168(5) | Sn(8)-C(4) | 2.121(9) |
| Sn(2)-O(3) | 2.159(5) | Sn(8)-C(81) | 2.114(10) |
| Sn(3)-C(3) | 2.135(8) | Sn(8)-I(4) | 2.9331(9) |
| Sn(3)-C(31) | 2.108(10) | Sn(8)-O(6) | 2.034(5) |
| Sn(3)-O(1) | 2.107(5) | Sn(8)-O(8) | 2.205(5) |
| Sn(3)-O(2) | 2.057(5) | I(1)-O(9) | 3.358(17) |
| Sn(3)-O(4) | 2.169(5) | I(1)-O(9A) | 3.78(2) |
| Sn(4)-C(4) | 2.137(9) | I(2)-O(3A) | 3.567(5) |

**Table 5** continued.

| | | | |
|---|---|---|---|
| Sn(4)-C(41) | 2.139(10) | O(7)-O(9) | 2.709(17) |
| Sn(4)-I(2) | 2.8702(9) | O(7)-O(9A) | 2.70(2) |
| Sn(4)-O(2) | 2.037(5) | O(9)-C(92) | 1.50(3) |
| Sn(4)-O(4) | 2.196(5) | C(11)-C(12) | 1.376(11) |
| Sn(5)-C(1) | 2.122(10) | C(21)-C(22) | 1.378(11) |
| Sn(5)-C(51) | 2.135(10) | C(31)-C(32) | 1.395(12) |
| Sn(5)-I(3) | 2.9094(9) | C(41)-C(42) | 1.384(12) |
| Sn(5)-O(5) | 2.052(5) | C(51)-C(52) | 1.381(12) |
| Sn(5)-O(7) | 2.145(5) | C(61)-C(62) | 1.385(12) |
| Sn(6)-C(2) | 2.114(8) | C(71)-C(72) | 1.366(12) |
| Sn(6)-C(61) | 2.114(10) | C(81)-C(82) | 1.387(12) |
| Bond angles [°] | | | |
| C(1)-Sn(1)-C(11) | 120.1(3) | C(1)-Sn(5)-O(5) | 117.9(3) |
| C(1)-Sn(1)-I(1) | 100.8(2) | C(1)-Sn(5)-O(7) | 91.7(3) |
| C(1)-Sn(1)-O(1) | 118.2(3) | C(51)-Sn(5)-I(3) | 95.6(3) |
| C(1)-Sn(1)-O(3) | 91.5(3) | C(51)-Sn(5)-O(5) | 112.2(3) |
| C(11)-Sn(1)-I(1) | 95.4(2) | C(51)-Sn(5)-O(7) | 94.1(3) |
| C(11)-Sn(1)-O(1) | 119.8(3) | I(3)-Sn(5)-O(5) | 89.00(14) |
| C(11)-Sn(1)-O(3) | 90.2(3) | I(3)-Sn(5)-O(7) | 163.08(14) |
| I(1)-Sn(1)-O(1) | 87.86(14) | O(5)-Sn(5)-O(7) | 74.5(2) |
| I(1)-Sn(1)-O(3) | 161.44(14) | C(2)-Sn(6)-C(61) | 129.6(3) |
| O(1)-Sn(1)-O(3) | 74.04(19) | C(2)-Sn(6)-O(5) | 97.5(3) |
| C(2)-Sn(2)-C(21) | 130.7(3) | C(2)-Sn(6)-O(6) | 119.2(3) |
| C(2)-Sn(2)-O(1) | 123.4(3) | C(2)-Sn(6)-O(8) | 96.5(3) |
| C(2)-Sn(2)-O(2) | 96.0(3) | C(61)-Sn(6)-O(5) | 98.6(3) |
| C(2)-Sn(2)-O(3) | 97.2(3) | C(61)-Sn(6)-O(6) | 111.2(3) |
| C(21)-Sn(2)-O(1) | 106.0(3) | C(61)-Sn(6)-O(8) | 94.5(3) |
| C(21)-Sn(2)-O(2) | 98.9(3) | O(5)-Sn(6)-O(6) | 73.46(19) |
| C(21)-Sn(2)-O(3) | 94.9(3) | O(5)-Sn(6)-O(8) | 147.94(19) |
| O(1)-Sn(2)-O(2) | 73.31(19) | O(6)-Sn(6)-O(8) | 74.53(19) |
| O(1)-Sn(2)-O(3) | 74.36(19) | C(3)-Sn(7)-C(71) | 128.7(3) |
| O(2)-Sn(2)-O(3) | 147.23(18) | C(3)-Sn(7)-O(5) | 121.4(3) |

**Table 5** continued.

| | | | |
|---|---|---|---|
| C(3)-Sn(3)-C(31) | 129.4(3) | C(3)-Sn(7)-O(6) | 98.3(3) |
| C(3)-Sn(3)-O(1) | 96.0(3) | C(3)-Sn(7)-O(7) | 96.9(3) |
| C(3)-Sn(3)-O(2) | 121.0(3) | C(71)-Sn(7)-O(5) | 109.8(3) |
| C(3)-Sn(3)-O(4) | 95.0(3) | C(71)-Sn(7)-O(6) | 98.1(3) |
| C(31)-Sn(3)-O(1) | 99.7(3) | C(71)-Sn(7)-O(7) | 93.9(3) |
| C(31)-Sn(3)-O(2) | 109.5(3) | O(5)-Sn(7)-O(6) | 73.93(19) |
| C(31)-Sn(3)-O(4) | 94.9(3) | O(5)-Sn(7)-O(7) | 74.4(2) |
| O(1)-Sn(3)-O(2) | 74.65(19) | O(6)-Sn(7)-O(7) | 148.3(2) |
| O(1)-Sn(3)-O(4) | 149.75(19) | C(4)-Sn(8)-C(81) | 130.5(3) |
| O(2)-Sn(3)-O(4) | 75.53(19) | C(4)-Sn(8)-I(4) | 91.5(2) |
| C(4)-Sn(4)-C(41) | 128.3(3) | C(4)-Sn(8)-O(6) | 117.9(3) |
| C(4)-Sn(4)-I(2) | 91.7(2) | C(4)-Sn(8)-O(8) | 92.6(3) |
| C(4)-Sn(4)-O(2) | 118.8(3) | C(81)-Sn(8)-I(4) | 95.4(3) |
| C(4)-Sn(4)-O(4) | 90.8(3) | C(81)-Sn(8)-O(6) | 111.1(3) |
| C(41)-Sn(4)-I(2) | 98.1(3) | C(81)-Sn(8)-O(8) | 93.6(3) |
| C(41)-Sn(4)-O(2) | 111.8(3) | I(4)-Sn(8)-O(6) | 89.63(14) |
| C(41)-Sn(4)-O(4) | 92.2(3) | I(4)-Sn(8)-O(8) | 164.07(14) |
| I(2)-Sn(4)-O(2) | 90.31(14) | O(6)-Sn(8)-O(8) | 74.85(19) |
| I(2)-Sn(4)-O(4) | 164.75(14) | Sn(5)-O(5)-Sn(6) | 145.1(3) |
| O(2)-Sn(4)-O(4) | 75.34(19) | Sn(5)-O(5)-Sn(7) | 108.5(2) |
| Sn(1)-O(1)-Sn(2) | 109.7(2) | Sn(5)-O(7)-Sn(7) | 102.5(2) |
| Sn(1)-O(3)-Sn(2) | 101.0(2) | Sn(5)-C(51)-C(52) | 122.7(8) |
| Sn(1)-O(1)-Sn(3) | 142.8(3) | Sn(6)-O(5)-Sn(7) | 105.6(2) |
| Sn(1)-C(11)-C(12) | 117.5(8) | Sn(6)-O(6)-Sn(7) | 106.4(2) |
| Sn(2)-O(1)-Sn(3) | 106.9(2) | Sn(6)-O(6)-Sn(8) | 110.1(2) |
| Sn(2)-O(2)-Sn(3) | 104.8(2) | Sn(6)-O(8)-Sn(8) | 99.7(2) |
| Sn(2)-O(2)-Sn(4) | 145.6(3) | Sn(6)-C(61)-C(62) | 122.5(8) |
| Sn(2)-C(21)-C(22) | 120.5(8) | Sn(7)-O(6)-Sn(8) | 141.9(3) |
| Sn(3)-O(2)-Sn(4) | 108.8(2) | Sn(7)-C(71)-C(72) | 120.5(7) |
| Sn(3)-O(4)-Sn(4) | 99.4(2) | Sn(8)-C(81)-C(82) | 120.5(7) |
| Sn(3)-C(31)-C(32) | 120.9(8) | Sn(1)-C(1)-Sn(5) | 117.7(4) |
| Sn(4)-C(41)-C(42) | 122.6(8) | Sn(2)-C(2)-Sn(6) | 118.1(3) |

**Table 5** continued.

| | | | |
|---|---|---|---|
| C(1)-Sn(5)-C(51) | 129.2(3) | Sn(3)-C(3)-Sn(7) | 117.5(4) |
| C(1)-Sn(5)-I(3) | 92.9(2) | Sn(4)-C(4)-Sn(8) | 115.4(3) |

Compound **8** crystallises with one $CH_3CN$ molecule and its molecular structure consists of the organotin oxo cluster $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ connected to one $CH_3CN$ molecule by one Sn-O-H···N hydrogen bond (Figure 14). Furthermore, the twist between the two $Sn_4I_2O_4$ layers amount to 27.74(4)°.

The crystal structure of adduct **8**, in contrast to that of **3**, is characterized by a one-dimensional network in which the double ladders are arranged in different planes, as already observed for the solvent-free compound **3**, but just in one direction (Figure 15). The one-dimensional polymeric structure of **8** is realized by a combination of one intermolecular Sn-I···H-O-Sn hydrogen bond with O···I distance of 3.596(4) Å, one Sn-O-H···N hydrogen bond with O···N distance of 2.888(12) Å and one Sn-I···N contact (Figure 16). Noteworthily only one out of four iodines and two out of four hydroxy groups of each cluster are involved in the hydrogen-bonding, while a second iodine atom interacts with an additional $CH_3CN$ molecule *via* one Sn-I···N contact with I···N distance of 3.970(11) Å, being slightly longer than the sum of the van der Waals radii of iodine and nitrogen (3.50-3.65 Å).[92]

Remarkably, the crystal structure of the cluster **8** contains a similar chain-type structural motif as observed for **3** and **5**. Also in this case compound **8**, as already observed for **3**, **4**, **5** and **7**, has no symmetry and exhibits chirality with both enantiomers present in the crystal lattice.

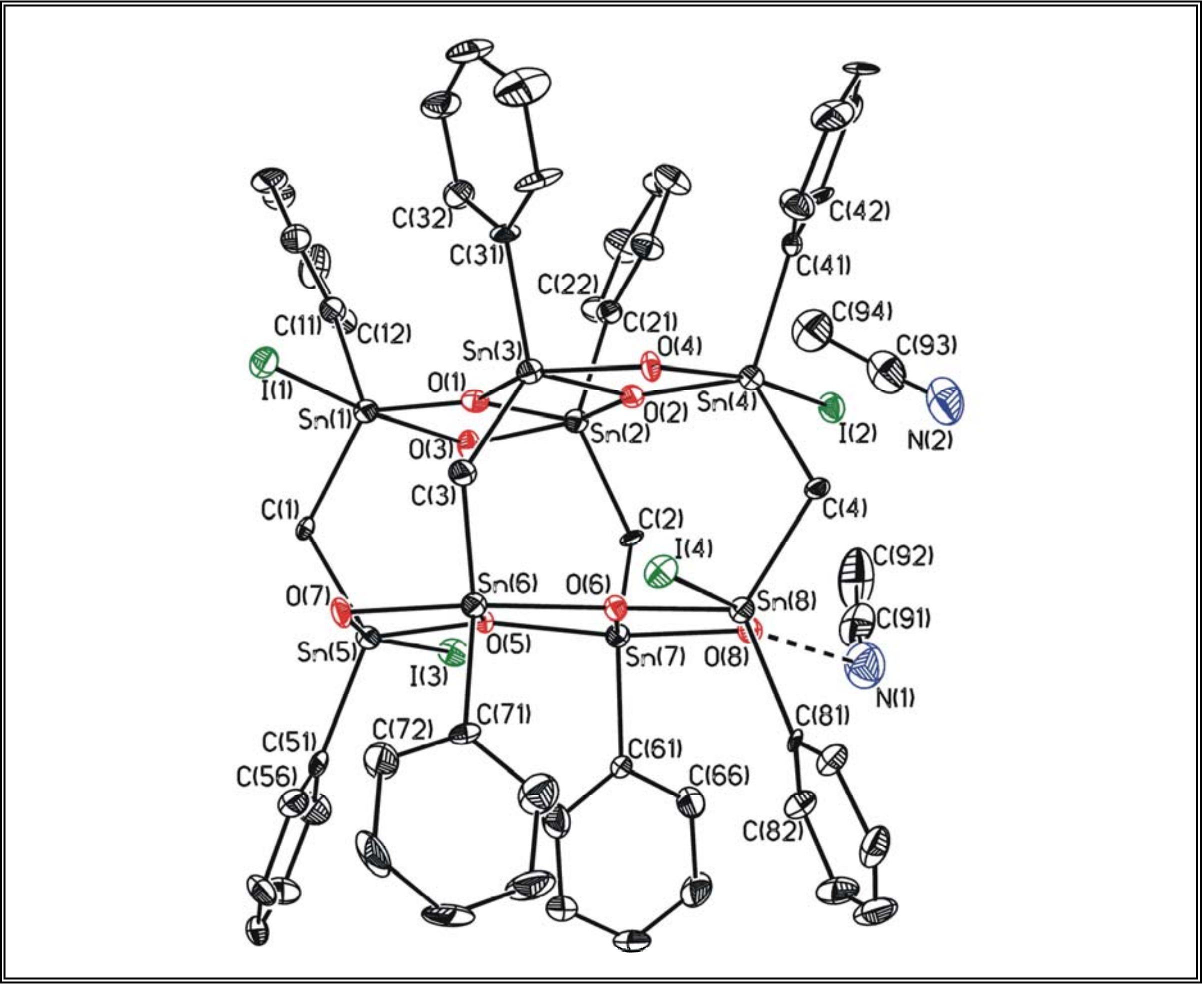


**Figure 14** Molecular structure (SHELXL-97) of **8** showing 30% probability displacement ellipsoids and the atom numbering scheme.

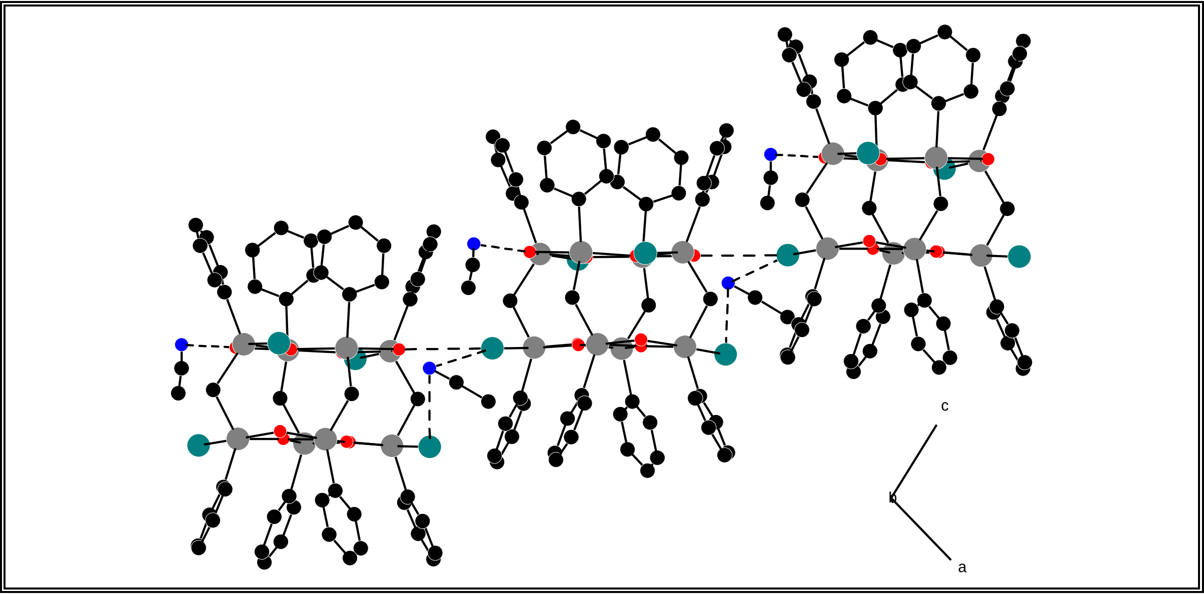


**Figure 15** Crystal structure of **8** showing the planarity of the $Sn_4I_2O_4$ layers and the different planes in the mono-dimensional network.

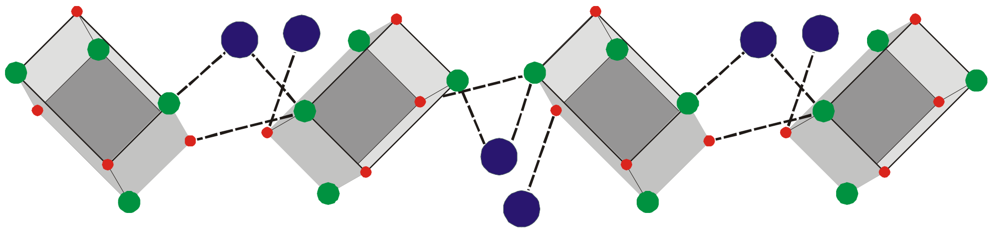


**Figure 16** Schematic representation of the one-dimensional polymer of **8**.

**Table 6** Selected bond lengths [Å] and bond angles [°] of **8.**

| Bond lengths [Å] | | | |
|---|---|---|---|
| Sn(1)-C(1) | 2.138(8) | Sn(6)-C(71) | 2.150(9) |
| Sn(1)-C(11) | 2.156(9) | Sn(6)-O(5) | 2.050(5) |
| Sn(1)-I(1) | 2.8563(9) | Sn(6)-O(6) | 2.157(4) |
| Sn(1)-O(1) | 2.045(5) | Sn(6)-O(7) | 2.141(5) |
| Sn(1)-O(3) | 2.219(5) | Sn(7)-C(2) | 2.112(8) |
| Sn(2)-C(2) | 2.131(8) | Sn(7)-C(61) | 2.124(8) |
| Sn(2)-C(21) | 2.133(9) | Sn(7)-O(5) | 2.134(4) |
| Sn(2)-O(1) | 2.062(5) | Sn(7)-O(6) | 2.073(5) |
| Sn(2)-O(2) | 2.137(6) | Sn(7)-O(8) | 2.161(5) |
| Sn(2)-O(3) | 2.157(5) | Sn(8)-C(4) | 2.126(7) |
| Sn(3)-C(3) | 2.111(8) | Sn(8)-C(81) | 2.141(9) |
| Sn(3)-C(31) | 2.113(9) | Sn(8)-I(4) | 2.9389(9) |
| Sn(3)-O(1) | 2.123(5) | Sn(8)-O(6) | 2.007(5) |
| Sn(3)-O(2) | 2.030(5) | Sn(8)-O(8) | 2.106(5) |
| Sn(3)-O(4) | 2.176(5) | I(2)-O(7) | 3.596(4) |
| Sn(4)-C(4) | 2.125(8) | N(1)-O(8) | 2.888(12) |
| Sn(4)-C(41) | 2.116(9) | N(2)-I(2) | 3.970(11) |
| Sn(4)-I(2) | 2.8678(9) | C(11)-C(12) | 1.383(12) |
| Sn(4)-O(2) | 2.053(5) | C(21)-C(22) | 1.352(12) |

**Table 6** continued.

| | | | |
|---|---|---|---|
| Sn(4)-O(4) | 2.184(5) | C(31)-C(32) | 1.378(12) |
| Sn(5)-C(1) | 2.128(8) | C(41)-C(42) | 1.377(11) |
| Sn(5)-C(51) | 2.151(9) | C(51)-C(52) | 1.376(12) |
| Sn(5)-I(3) | 2.9026(9) | C(61)-C(62) | 1.388(11) |
| Sn(5)-O(5) | 2.035(5) | C(71)-C(72) | 1.366(11) |
| Sn(5)-O(7) | 2.168(6) | C(81)-C(82) | 1.35963(11) |
| Sn(6)-C(3) | 2.104(8) | | |

| Bond angles [°] | | | |
|---|---|---|---|
| C(1)-Sn(1)-C(11) | 120.9(3) | C(1)-Sn(5)-O(5) | 117.3(2) |
| C(1)-Sn(1)-I(1) | 94.2(2) | C(1)-Sn(5)-O(7) | 94.1(3) |
| C(1)-Sn(1)-O(1) | 120.0(3) | C(51)-Sn(5)-I(3) | 96.1(3) |
| C(1)-Sn(1)-O(3) | 93.2(3) | C(51)-Sn(5)-O(5) | 114.9(3) |
| C(11)-Sn(1)-I(1) | 97.7(3) | C(51)-Sn(5)-O(7) | 94.7(3) |
| C(11)-Sn(1)-O(1) | 118.0(3) | I(3)-Sn(5)-O(5) | 88.83(14) |
| C(11)-Sn(1)-O(3) | 91.5(3) | I(3)-Sn(5)-O(7) | 161.09(12) |
| I(1)-Sn(1)-O(1) | 88.60(14) | O(5)-Sn(5)-O(7) | 72.52(19) |
| I(1)-Sn(1)-O(3) | 163.14(13) | C(3)-Sn(6)-C(71) | 128.6(3) |
| O(1)-Sn(1)-O(3) | 74.57(19) | C(3)-Sn(6)-O(5) | 119.0(3) |
| C(2)-Sn(2)-C(21) | 125.4(3) | C(3)-Sn(6)-O(6) | 99.6(2) |
| C(2)-Sn(2)-O(1) | 123.3(3) | C(3)-Sn(6)-O(7) | 96.3(3) |
| C(2)-Sn(2)-O(2) | 97.2(3) | C(71)-Sn(6)-O(5) | 112.3(3) |
| C(2)-Sn(2)-O(3) | 95.7(3) | C(71)-Sn(6)-O(6) | 97.7(3) |
| C(21)-Sn(2)-O(1) | 111.3(3) | C(71)-Sn(6)-O(7) | 94.5(3) |
| C(21)-Sn(2)-O(2) | 99.7(3) | O(5)-Sn(6)-O(6) | 74.39(18) |
| C(21)-Sn(2)-O(3) | 96.0(3) | O(5)-Sn(6)-O(7) | 72.79(19) |
| O(1)-Sn(2)-O(2) | 73.22(19) | O(6)-Sn(6)-O(7) | 147.2(2) |
| O(1)-Sn(2)-O(3) | 75.57(19) | C(2)-Sn(7)-C(61) | 129.1(3) |
| O(2)-Sn(2)-O(3) | 148.41(18) | C(2)-Sn(7)-O(5) | 100.5(2) |
| C(3)-Sn(3)-C(31) | 126.4(3) | C(2)-Sn(7)-O(6) | 119.5(3) |
| C(3)-Sn(3)-O(1) | 97.5(3) | C(2)-Sn(7)-O(8) | 95.2(2) |
| C(3)-Sn(3)-O(2) | 123.1(3) | C(61)-Sn(7)-O(5) | 99.4(2) |
| C(3)-Sn(3)-O(4) | 94.8(3) | C(61)-Sn(7)-O(6) | 110.9(3) |

**Table 6** continued.

| | | | |
|---|---|---|---|
| C(31)-Sn(3)-O(1) | 100.7(3) | C(61)-Sn(7)-O(8) | 93.9(3) |
| C(31)-Sn(3)-O(2) | 110.3(3) | O(5)-Sn(7)-O(6) | 74.45(19) |
| C(31)-Sn(3)-O(4) | 94.6(3) | O(5)-Sn(7)-O(8) | 145.6(2) |
| O(1)-Sn(3)-O(2) | 74.2(2) | O(6)-Sn(7)-O(8) | 73.20(19) |
| O(1)-Sn(3)-O(4) | 148.92(19) | C(4)-Sn(8)-C(81) | 125.1(3) |
| O(2)-Sn(3)-O(4) | 75.21(19) | C(4)-Sn(8)-I(4) | 93.5(2) |
| C(4)-Sn(4)-C(41) | 123.9(3) | C(4)-Sn(8)-O(6) | 118.5(3) |
| C(4)-Sn(4)-I(2) | 93.0(2) | C(4)-Sn(8)-O(8) | 94.5(3) |
| C(4)-Sn(4)-O(2) | 119.1(3) | C(81)-Sn(8)-I(4) | 93.4(2) |
| C(4)-Sn(4)-O(4) | 92.4(3) | C(81)-Sn(8)-O(6) | 116.2(3) |
| C(41)-Sn(4)-I(2) | 97.6(2) | C(81)-Sn(8)-O(8) | 96.0(3) |
| C(41)-Sn(4)-O(2) | 115.8(3) | I(4)-Sn(8)-O(6) | 87.47(14) |
| C(41)-Sn(4)-O(4) | 91.8(3) | I(4)-Sn(8)-O(8) | 161.04(13) |
| I(2)-Sn(4)-O(2) | 89.64(15) | O(6)-Sn(8)-O(8) | 73.61(19) |
| I(2)-Sn(4)-O(4) | 163.98(13) | Sn(5)-O(5)-Sn(6) | 111.4(2) |
| O(2)-Sn(4)-O(4) | 74.56(19) | Sn(5)-O(5)-Sn(7) | 141.4(3) |
| Sn(1)-O(1)-Sn(2) | 109.4(2) | Sn(5)-O(7)-Sn(6) | 103.1(2) |
| Sn(1)-O(3)-Sn(2) | 100.0(2) | Sn(5)-C(51)-C(52) | 122.1(8) |
| Sn(1)-O(1)-Sn(3) | 144.6(3) | Sn(6)-O(5)-Sn(7) | 106.2(2) |
| Sn(1)-C(11)-C(12) | 118.1(8) | Sn(6)-O(6)-Sn(7) | 104.5(2) |
| Sn(2)-O(1)-Sn(3) | 106.0(2) | Sn(6)-O(6)-Sn(8) | 143.8(3) |
| Sn(2)-O(2)-Sn(3) | 106.6(2) | Sn(7)-O(6)-Sn(8) | 111.0(2) |
| Sn(2)-O(2)-Sn(4) | 143.6(3) | Sn(6)-C(71)-C(72) | 119.4(7) |
| Sn(2)-C(21)-C(22) | 119.4(7) | Sn(7)-O(8)-Sn(8) | 104.0(2) |
| Sn(3)-O(2)-Sn(4) | 109.5(3) | Sn(7)-C(61)-C(62) | 121.1(7) |
| Sn(3)-O(4)-Sn(4) | 99.8(2) | Sn(8)-C(81)-C(82) | 120.3(7) |
| Sn(3)-C(31)-C(32) | 121.0(7) | Sn(1)-C(1)-Sn(5) | 117.4(3) |
| Sn(4)-C(41)-C(42) | 122.9(7) | Sn(2)-C(2)-Sn(7) | 118.3(3) |
| C(1)-Sn(5)-C(51) | 127.3(3) | Sn(3)-C(3)-Sn(6) | 119.1(4) |
| C(1)-Sn(5)-I(3) | 91.7(2) | Sn(4)-C(4)-Sn(8) | 117.1(3) |

**Table 7** Twist angles [°] of the $Sn_4I_2O_4$ layers of **3**, **4**, **5**, **6**, **7** and **8**.

| Compounds | Twist angles [°] |
|---|---|
| $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ **3** | 29.15(3) |
| $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 2CHCl_3$ **4** | 27.77(1) |
| $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 3CH_2Cl_2$ **5** | 29.00(2) |
| $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 4THF$ **6** | 28.02(4) |
| $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot$ *s*-BuOH **7** | 29.68(2) |
| $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 2CH_3CN$ **8** | 27.74(2) |

## 2.3 Experimental section

### 2.3.1 General methods

The synthesis and working up of oxidation- and hydrolysis-sensitive compounds were carried out under an inert atmosphere of nitrogen. The latter was dried by a gas-cleaning equipment with molecular sieve 4 Å. The solvents were purified by distillation from appropriate drying agents under argon.[95]

### 2.3.2 Spectroscopic and analytical methods

The spectroscopic and analytical methods were already described in chapter 1, paragraph 1.4.2.

To obtain elemental analyses of compounds **4**, **5**, **6**, **7** and **8** proved to be difficult because of loss of solvent.

### 2.3.3 Synthesis of the new compounds

Bis(triphenylstannyl)methane[89,90] as well as all the other starting materials were synthesized according to literature methods. Iodine, sodium, triethylamine, 4-mercaptopyridine as well as all the other compounds mentioned in the experimental section were commercial products.

#### Bis(diiodophenylstannyl)methane (2)

To an ice-cooled magnetically stirred solution of bis(triphenylstannyl)methane (30.01 g, 42 mmol) in dichloromethane (300 mL) was added iodine (42.67 g, 168 mmol) in small portions within 8 h. The ice bath was then removed and the resulted solution was stirred at room temperature in darkness for 16 h, the solvent as well as the iodobenzene were then removed at 10 and $10^{-3}$ Torr, respectively, leaving bis(diiodophenylstannyl)methane (**2**) (34.56 g, 38 mmol, 90% yield) as a yellow oil.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 2.77 (s, $^2J(^1H–^{119}Sn)$ = 65 Hz, 2H; $CH_2$), 7.43–7.69 (complex pattern, 10H; $H_{aryl}$). **$^{13}$C NMR** ($CDCl_3$, 100.63 MHz): $\delta$ (ppm) 12.15 (s, $^1J(^{13}C–^{117/119}Sn)$ = 269/280 Hz; $CH_2$), 129.2 (s, $^3J(^{13}C–^{119/117}Sn)$ = 80/85 Hz; $C_m$), 131.4 (s, $^4J(^{13}C–^{119/117}Sn)$ = 17 Hz; $C_p$), 134.5 (s, $^2J(^{13}C–^{119}Sn)$ = 67 Hz; $C_o$), 135.5 (s; $C_i$). **$^{119}$Sn NMR** ($CDCl_3$, 149.21 MHz): $\delta$ (ppm) -241.0 ($^2J(^{119}Sn–^{117}Sn)$ = 274 Hz, $^1J(^{119}Sn-^{13}C_i)$ = 660 Hz). Anal. Calc. for $C_{13}H_{12}I_4Sn_2$ (913.22): C, 17.1; H, 1.3. Found: C, 17.3; H, 1.3%.

### {[Ph(HO)SnCH$_2$Sn(I)Ph]O}$_4$ (3)

To a solution of bis(diiodophenylstannyl)methane (1.95 g, 2.135 mmol) in methanol (4.7 mL) was added dropwise within 10 min under magnetical stirring a solution of triethylamine (0.94 mL) in water (28.1 mL) to give a suspension. The stirring was continued for 1 h and the resulting waxy-type precipitate was allowed to settle. The supernatant solution was decanted and the residue was washed with water and then recrystallised from acetonitrile to give the organotin oxo cluster $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ (**3**) as a colourless crystalline solid with m.p. > 250 °C.

**$^1$H NMR** ($CDCl_3$, 400.13 MHz): $\delta$ (ppm) 2.04 (s, $^2J(^1H–^{119}Sn)$ = 76 Hz, 4H; $CH_2$), 2.52 (s, $^2J(^1H–^{119}Sn)$ = 70 Hz, 4H; $CH_2$), 3.74 (s, 4H; OH), 6.80–7.26 (complex pattern, 24H; $H_{aryl}$), 7.30 (d, $^3J(^1H–^{119}Sn)$ = 87 Hz, 8H; $H_{ortho}$), 7.65 (d, $^3J(^1H–^{119}Sn)$ = 87 Hz, 8H; $H_{ortho}$). **$^{119}$Sn NMR** ($CDCl_3$, 149.21 MHz): $\delta$ (ppm) –222.0 ($^2J(^{119}Sn–^{117/119}Sn)$ = 140 Hz), –244.0 ($^2J(^{119}Sn–^{117/119}Sn)$ = 140 Hz). **IR** (KBr): $\nu$(OH) 3300–3550 $cm^{-1}$. Anal. Calc. for $C_{52}H_{52}I_4O_8Sn_8$ (2262.25): C, 27.6; H, 2.3. Found: C, 27.7; H, 2.3%.

### $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 2CHCl_3$ (4), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 3CH_2Cl_2$ (5), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 4THF$ (6), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot$ s-BuOH (7)

The waxy-type residue obtained as previously described was then recrystallised from trichloromethane, dichloromethane, tetrahydrofurane and racemic *s*-butanole to give, respectively, $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 2CHCl_3$ (**4**), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 3CH_2Cl_2$ (**5**), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 4THF$ (**6**) and $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot$ *s*-BuOH (**7**) as colourless crystalline solids with m.p. > 250 °C.

### $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot CH_3CN$ (8)

The waxy-type residue obtained as previously described was then dissolved in acetonitrile and to the resulted solution was added in one portion 4-mercaptopyridine. The solution was then left to give $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot CH_3CN$ (**8**) as a colourless crystalline solid with m.p. > 250 °C.

## 2.4 References

(1) Barnes, J. M.; Magos, L. *Organomet. Chem. Rev.* **1968**, *3*, 137.

(2) Gielen, M. *Coord. Chem. Rev.* **1996**, *151*, 41.

(3) Willem, R.; Dalil, H.; Broekaert, P.; Biesemans, M.; Ghys, L.; Nooter, K.; de Vos, D.; Ribot, F.; Gielen, M. *Main Group Metal Chem.* **1997**, *20*, 535.

(4) de Vos, D.; Willem, R. ; Gielen, M. ; Wingerden, K. E. v.; Nooter, K. *Met. Based Drugs* **1998**, *5*, 179.

(5) Kemmer, M.; Gielen, M. ; Biesemans, M.; de Vos, D.; Willem, R. *Met. Based Drugs* **1998**, *5*, 189.

(6) Orita, A.; Mitsutome, A.; Otera, J. *J. Org. Chem.* **1998**, *63*, 2420.

(7) Orita, A.; Sakamoto, K.; Hamada, Y.; Mitsutome, A.; Otera, J. *Tetrahedron* **1999**, *55*, 2899.

(8) Otera, J. *Chem. Rev.* **1993**, *93*, 1449.

(9) Durand, S.; Sakamoto, K.; Fukuyama, T.; Orita, A.; Otera, J.; Duthie, A.; Dakternieks, D.; Schulte, M.; Jurkschat, K. *Organometallics* **2000**, *19*, 3220.

(10) Orita, A.; Hamada, Y.; Nakano, T.; Toyoshima, S.; Otera, J. *Chem. Eur. J.* **2001**, *7*, 3321.

(11) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190.

(12) Bloodworth, A. J.; Davies, A. G. in: *Organotin Compounds*, Sawyer, A. K.(Ed.), Marcel Dekker, New York **1971**.

(13) Davies, A. G. *Organotin Chemistry*; VCH, Weinheim **1997**.

(14) Puff, H.; Reuter, H. *J. Organomet. Chem.* **1989**, *368*, 173.

(15) Baron, C. E.; Ribot, F.; Steunou, N.; Sanchez, C.; Fayon, F. ; Biesemans, M. ; Martins, J.C. ; Willem, R. *Organometallics* **2000**, *19*, 1940.

(16) Okawara, R.; Wada, M. in: *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R. (Eds.), Academic Press, New York **1967**, *Vol. 5*.

(17) Pfeiffer, P.; Brack, O. *Z. Anorg. Chem.* **1914**, *87*, 229.

(18) Alleston, D. L.; Davies, A. G.; Hancock, M.; White, R. F. M. *J. Chem. Soc.* **1963**, 5469.

(19) Okawara, R.; Wada, M. *J. Organomet. Chem.* **1963**, *1*, 81.

(20) Okawara, R.; White, D. G.; Fujitani, K.; Sato, H. *J. Am. Chem. Soc.* **1961**, *83*, 1342.

(21) Wada, M.; Nishino, M.; Okawara, R. *J. Organomet. Chem.* **1965**, *3*, 70.

(22) Considine, W. J.; Ventura, J. J. *J. Org. Chem.* **1963**, *28*, 221.

(23) Considine, W. J.; Ventura, J. J.; Gibbons, A. J.; Ross, A. *Can. J. Chem.* **1963**, *41*, 1239.

(24) Poller, R. C. *J. Chem. Soc.* **1963**, 706.

(25) Alleston, D. L.; Davies, A. G.; Hancock, M. *Proc. Chem. Soc.* **1961**, 457.

(26) Okawara, R. *Proc. Chem. Soc.* **1961**, 383.

(27) Gross, D. C. *Inorg. Chem.* **1989**, *28*, 2355.

(28) Ribot, F.; Sanchez, C.; Meddour, A.; Gielen, M.; Tiekink, E. R. T.; Biesemans, M.; Willem, R. *J. Organomet. Chem.* **1998**, *552*, 177.

(29) Primel, O.; Llauro, M.-F.; Pétiaud, R.; Michel, A. *J. Organomet. Chem.* **1998**, *558*, 19.

(30) Gimenez, J.; Michel, A.; Pétiaud, R.; Llauro, M.-F. *J. Organomet. Chem.* **1999**, *575*, 286.

(31) Puff, H.; Friedrichs, E.; Visel, F. *Z. Anorg. Allg. Chem.* **1981**, *477*, 50.

(32) Gielen, M.; Biesemans, M.; Khloufi, A. E.; Meunier-Piret, J.; Kayser, F.; Willem, R. *J. Fluorine Chem.* **1993**, *64*, 279.

(33) Gielen, M.; Meunier-Piret, J.; Biesemans, M.; Willem, R.; Khloufi, A. E. *Appl. Organometal. Chem.* **1992**, *6*, 59.

(34) Bouâlam, M.; Willem, R.; Biesemans, M.; Mahieu, B.; Meunier-Piret, J.; Gielen, M. *Main Group Metal Chem.* **1991**, *14*, 41.

(35) Gielen, M.; Tiekink, E. R. T.; Bouhdid, A.; de Vos, D.; Biesemans, M.; Verbruggen, I.; Willem, R. *Appl. Organometal. Chem.* **1995**, *9*, 639.

(36) Beckmann, J.; Biesemans, M.; Hassler, K.; Jurkschat, K.; Martins, J. C.; Schürmann, M.; Willem, R. *Inorg. Chem.* **1998**, *37*, 4891.

(37) Zobel, B.; Shürmann, M.; Jurkschat, K.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 4096.

(38) Schulte, M.; Schürmann, M.; Dakternieks, D.; Jurkschat, K. *J. Chem. Soc., Chem. Commun.* **1999**, 1291.

(39) Primel, O.; Llauro, M. F.; Pétiaud, A.; Michel, A. *J. Organomet. Chem.* **1998**, *558*, 191.

(40) Tierney, D. L.; Moehs, P. J.; Hasha, D. L. *J. Organomet. Chem.* **2001**, *620*, 211.

(41) Hasha, D. L. *J. Organomet. Chem.* **2001**, *620*, 296.

(42) Otera, J.; Yano, T.; Okawara, R. *Chem. Lett.* **1985**, 901.

(43) Houghton, R. P.; Mulvaney, A. W. *J. Organomet. Chem.* **1996**, *518*, 21.

(44) Houghton, R. P.; Mulvaney, A. W. *J. Organomet. Chem.* **1996**, *517*, 107.

(45) van der Weij, F. W. *J. Polym. Sci.* **1981**, *19*, 3063.

(46) Otera, J.; Yano, T.; Okawara, R. *Organometallics* **1986**, *5*, 1167.

(47) Otera, J.; Fujita, Y.; Sato, T. *Synlett* **1995**, 433.

(48) Otera, J.; Mizutani, T.; Nozaki, H. *Organometallics* **1989**, *8*, 2063.

(49) Otera, J.; Dan-oh, N.; Nozaki, H. *Tetrahedron* **1992**, *48*, 1449.

(50) Otera, J.; Dan-oh, N.; Nozaki, H. *J. Org. Chem.* **1991**, *56*, 5307.

(51) Otera, J. *Chem. Rev.* **1993**, *93*, 1449.

(52) Otera, J.; Dan-oh, N.; Nozaki, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1742.

(53) Otera, J.; Ioka, S.; Nozaki, H. *J. Org. Chem.* **1989**, *54*, 4013.

(54) Mehring, M.; Schürmann, M.; Paulus, I.; Horn, D.; Jurkschat, K.; Orita, A.; Otera, J.; Dakternieks, D.; Duthie, A. *J. Organomet. Chem.* **1999**, *574*, 176.

(55) Otera, J.; Dan-oh, N.; Nozaki, H. *Tetrahedron* **1993**, *49*, 3065.

(56) Otera, J.; Yano, T.; Kawabata, A.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 2383.

(57) Hori, Y.; Hagiwara, T. *Int. J. Bio. Macromolecules* **1999**, *25*, 237.

(58) Morcuende, A.; Ors, M.; Valverde, S.; Herradón, B. *J. Org. Chem.* **1996**, *61*, 5264.

(59) Suciu, E. N.; Kuhlmann, B.; Knudsen, G. A.; Michaelson, R. C. *J. Organomet. Chem.* **1998**, *556*, 41.

(60) Jousseaume, B.; Laporte, C.; Rascle, M. C. ; Toupance, T. *Chem. Com.* **2003**, 1428.

(61) Gielen, M. in: *Antitumor Active Organotin Compounds*, Cardarelli, N. F. (Ed.), CRC Press, **1986**.

(62) Gielen, M.; Khloufi, A. E.; Biesemans, M.; Willem, R.; Meunier-Piret, J. *Polyhedron* **1992**, *11*, 1861.

(63) Xueqing, S.; Zhiqiang, Y.; Qinglan, X.; Jinshan, L. *J. Organomet. Chem.* **1998**, *566*, 103.

(64) Gielen, M.; Dalil, H.; Biesemans, M.; Mahieu, B.; de Vos, D.; Willem, R. *Appl. Organometal. Chem.* **1999**, *13*, 515.

(65) Schulte, M.; Mehring, M.; Paulus, I.; Schürmann, M.; Jurkschat, K.; Dakternieks, D.; Duthie, A.; Orita, A.; Otera, J. *Phosphorus, Sulfur and Silicon* **1999**, *150-151*, 201.

(66) Dakternieks, D.; Jurkschat, K.; Schollmeyer, D.; Wu, H. *Organometallics* **1994**, *13*, 4121.

(67) Mehring, M.; Schürmann, M.; Reuter, H.; Dakternieks, D.; Jurkschat, K. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1112.

(68) Costisella, B.; Dakternieks, D.; Jurkschat, K.; Mehring, M.; Paulus, I.; Schürmann, M. *Chemistry of Heterocycles Compounds*, **2001**, *37*, 1405.

(69) Dakternieks, D.; Duthie, A.; Jurkschat, K.; Schürmann, M.; Tiekink, E. R. T. *Main Group Metal Chem.* **2002**, *25*, 73.

(70) Mehring, M. *Diploma Thesis*, Dortmund University **1995**.

(71) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1.

(72) Mehring, M.; Paulus, I.; Zobel, B.; Schürmann, M.; Jurkschat, K.; Duthie, A.; Dakternieks, D. *Eur. J. Inorg. Chem.* **2001**, 153.

(73) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.

(74) Cotton, T. F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759.

(75) Janiak, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1431.

(76) Shimizu, G. K. H.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A.; Wayner, D. D. M. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1407.

(77) Janiak, C.; Scharmann, T. G.; Brzezinka, K. W.; Reich, P. *Chem. Ber.* **1995**, *128*, 323.

(78) MacDonald, J. C.; Dorrestein, P. C.; Pilley, M. M.; Foote, M. M.; Lundberg, J. L.; Henning, R. W.; Schultz, J.; Manson, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 11692.

(79) Vaid, P.; Sydora, O. L.; Douthwaite, R. E. ; Wolczanski, P. T. ; Lobkovsky, E. B. *Chem. Commun.* **2001**, 1300.

(80) Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S.; Lorimer, K. R. *Chem. Commun.* **2000**, 935.

(81) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107.

(82) Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1815.

(83) Biradha, K.; Seward, C.; Zaworotko, M. J. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 492.

(84) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2382.

(85) Mahon, M. F.; Molloy, K. C. *Main Group Chem.* **1996**, *1*, 309.

(86) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190.

(87) Ribot, F.; Sanchez, C. *Comments Inorg. Chem.* **1999**, *20*, 327.

(88) Mehring, M. ; Gabriele, G. ; Hadjikakou, S.; Schürmann, M.; Dakternieks, D.; Jurkschat, K. *Chem. Commun.* **2002**, 834.

(89) Gielen, M.; Jurkschat, K. *Org. Mass Spectron* **1983**, *18*, 224.

(90) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106.

(91) Wrackmeyer, B. *Annual Reports on NMR Spectroscopy*, **1985**, *16*, 73.

(92) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(93) Pedireddi, V. R.; Reddy, D. S.; Goud, B. S.; Craig, D. C.; Rae, A. D.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2353.

(94) Barandika, M. G.; Hernández-Pino, M. L.; Urtiaga,. M. K.; Cortés, R.; Lezama, L. ; Arriortua, M. I.; Rojo, T. *J. Chem. Soc., Dalton Trans.* **2000**, 1469.

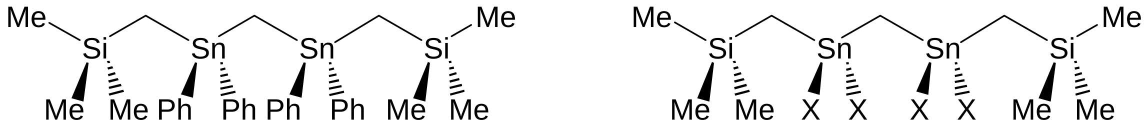
(95) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, Pergamon Press, New York **1988**.

# 3 Summary

## Chapter 1

Aim of the first part of this work was the synthesis of new tin-containing multicentric Lewis acids as well as the study of their complexation behaviour towards neutral donor molecules such as DMSO, DMF and 1,3-dimethyl-imidazolidin-2-one.

The ditin compound **6** was prepared and treatment of this compound with $I_2$ and $HgCl_2$ afforded the species **7** and **8** (Figure 1).



**6**

**7**, X = I
**8**, X = Cl

**Figure 1** Ditin derivatives **6**, **7** and **8**.

By reaction of *cyclo*-$CH_2[Sn(Ph_2)CH_2Si(Me_2)]_2O$ (**10**) with $I_2$, $Br_2$ as well as with *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**), the eight-membered rings **11**, **14**, **15** and **16** were obtained (Figure 2).

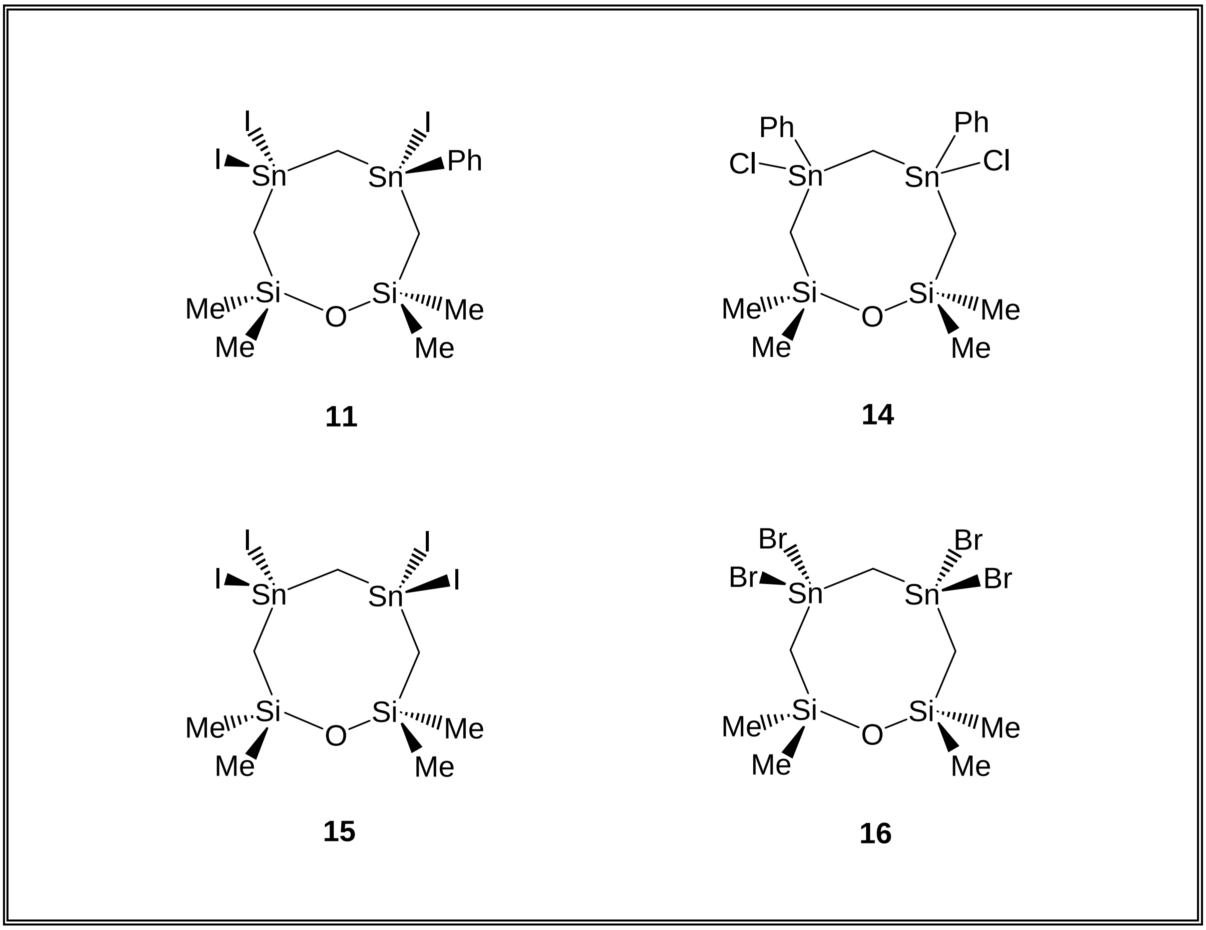


**Figure 2** Eight-membered rings **11**, **14**, **15** and **16**.

Treatment of *cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2O$ (**9**) with DMSO, DMF or 1,3-dimethylimidazolidin-2-one gave the 1:1 complexes **18** and **20** as well as the 1:2 complexes **17** and **19**, respectively (Figure 3).

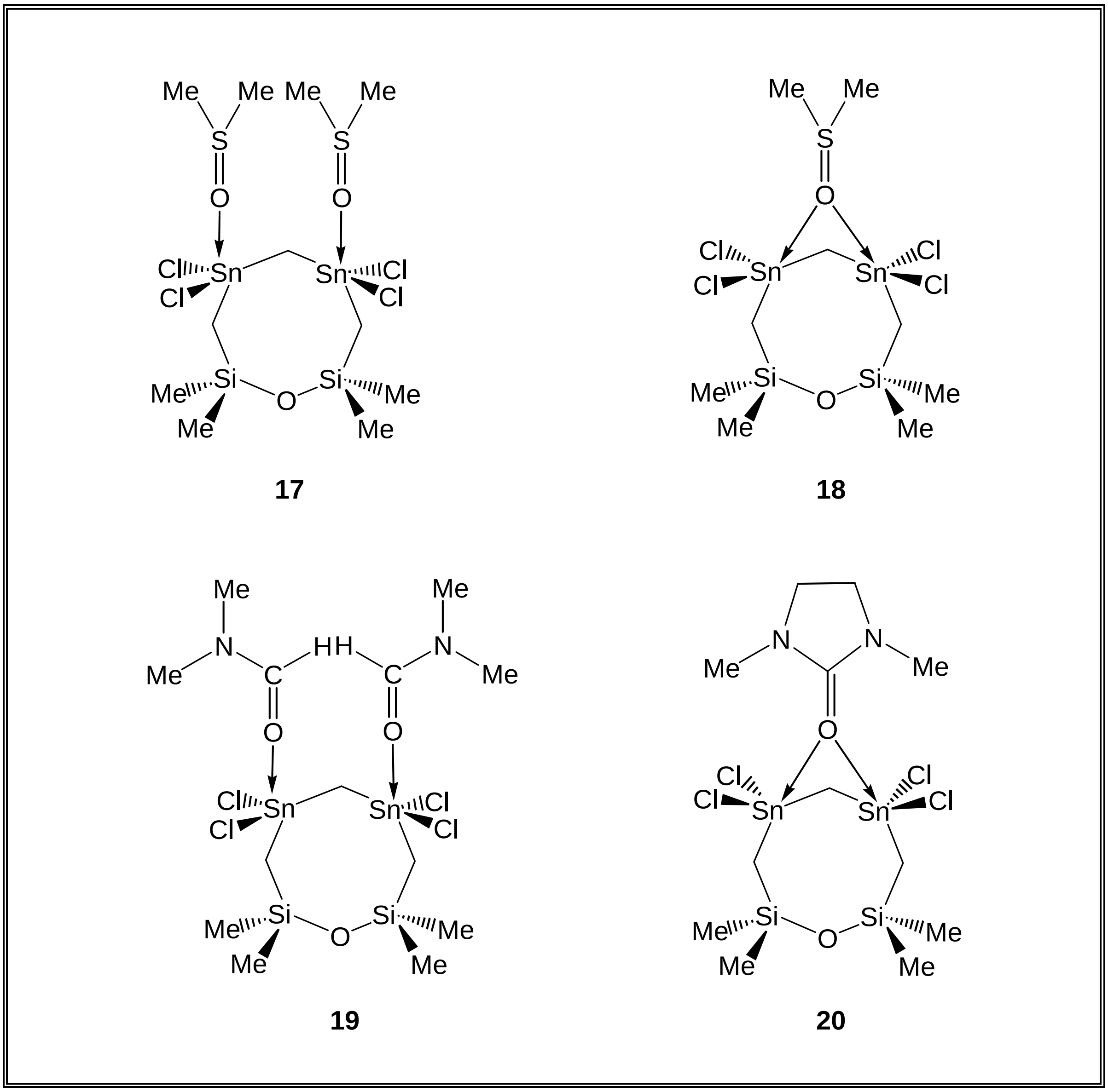


**Figure 3** DMSO, DMF as well as 1,3-dimethyl-imidazolidin-2-one complexes of *cyclo*-[$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] **17**, **18**, **19** and **20**.

Furthermore, the first bis(triiodostannyl)alkanes $I_3Sn(CH_2)_nSnI_3$ (n = 1, 3) **21** and **23** as well as their DMSO and DMF complexes **24** and **25** were synthesised (Figure 4).

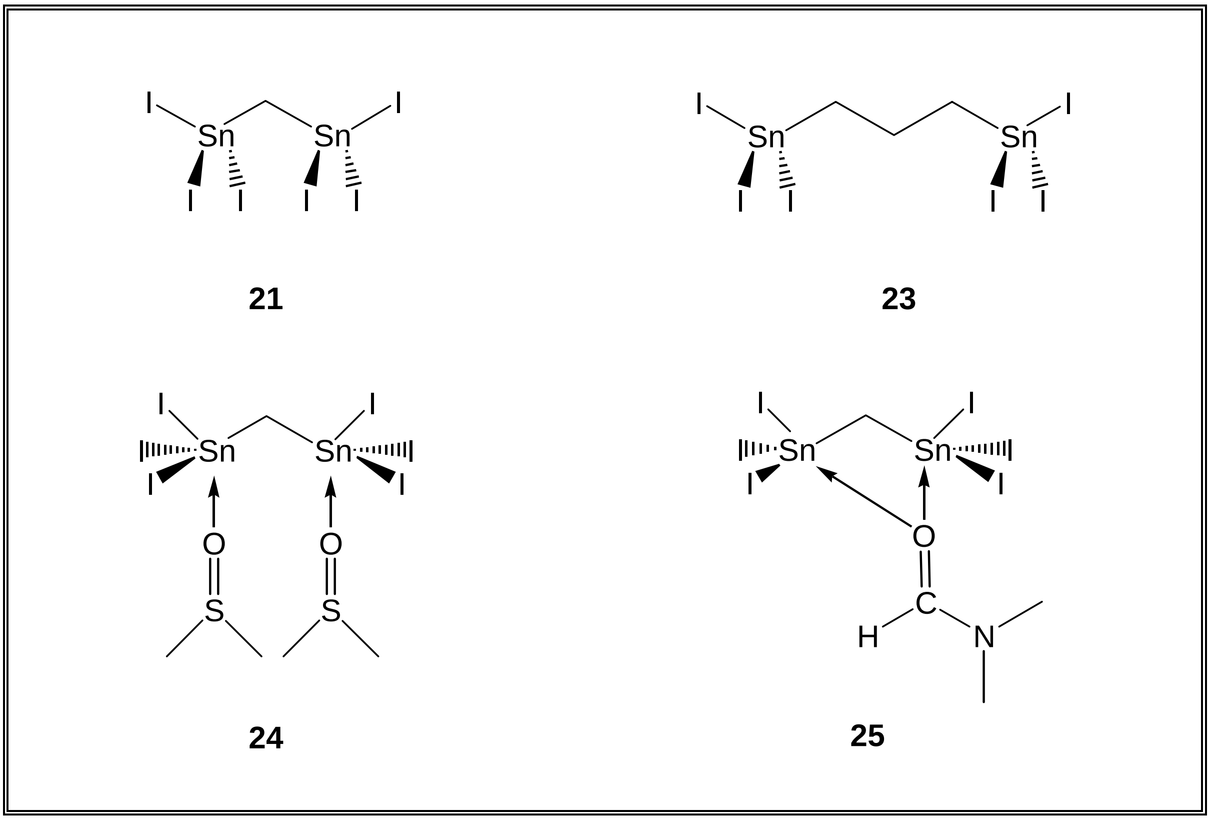
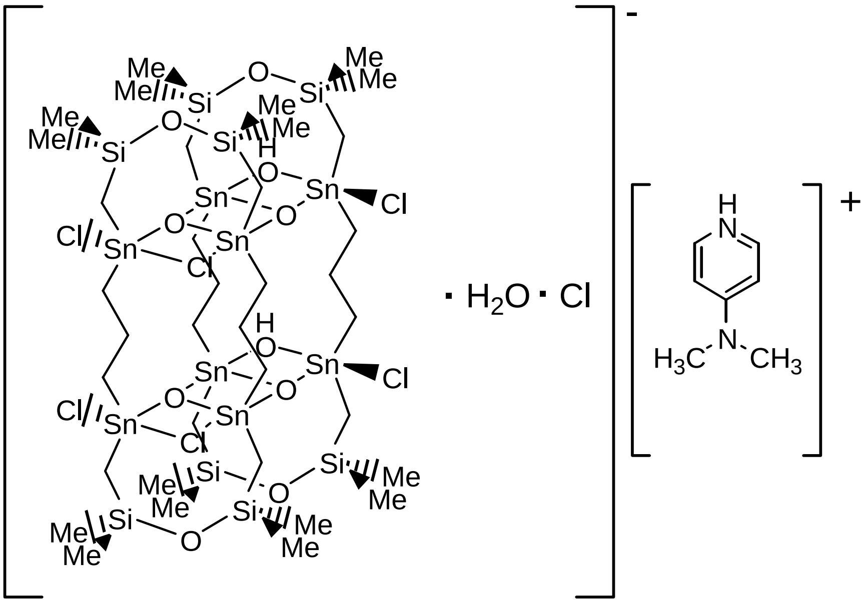


**Figure 4** First bis(triiodostannyl)alkanes **21** and **23** as well as their DMSO and DMF complexes **24** and **25**.

In order to confirm the identity of the 20-membered ring *cyclo*-$CH_2[CH_2Sn(Cl_2)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl_2)CH_2]_2CH_2$ (**26**), the latter was reacted with 4-dimethylaminopyridine to give the unexpected 4-dimethylaminopyridinium $[\{\{[Sn(Cl)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\{\{[Sn(OH)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2\text{-}O_2\}\cdot H_2O\cdot Cl]^-$ (**28**) (Figure 5). The molecular structure of compound **28** is characterised by two 20-membered rings linked together to form a double ladder structure.



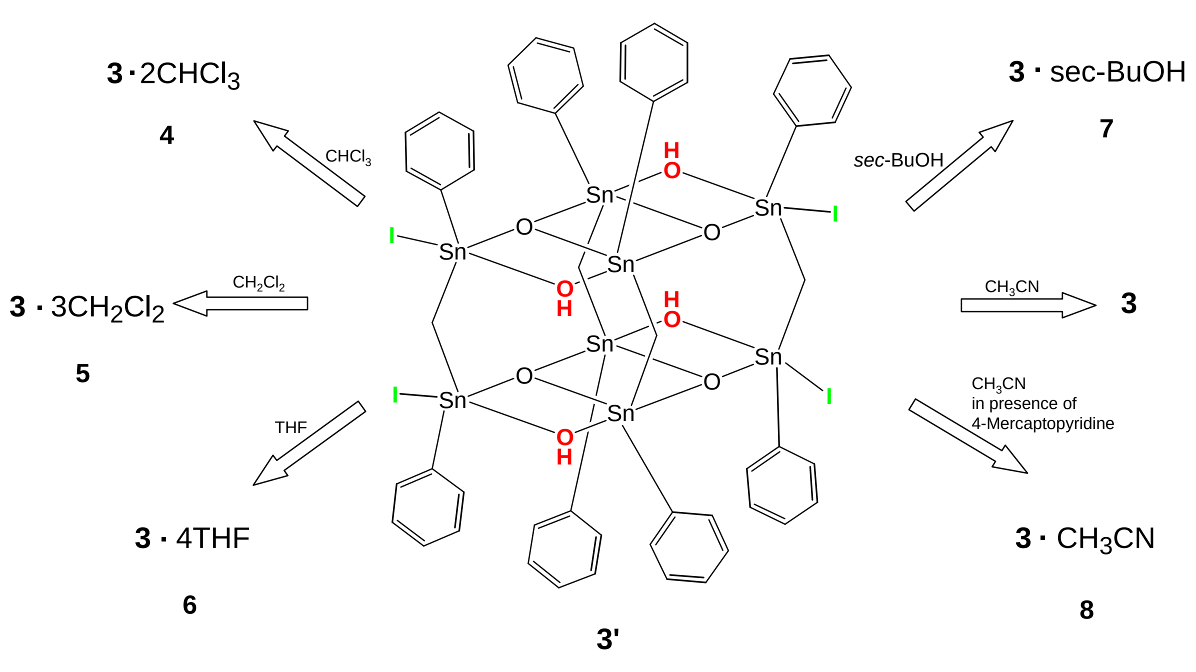
**28**

**Figure 5** 4-dimethylaminopyridinium $[\{\{[\mathrm{Sn(Cl)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)}]\text{-}(\mathrm{CH_2})_3\}_2\mathrm{O_2}\}\{\{[\mathrm{Sn(OH)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)}](\mathrm{CH_2})_3\}_2\text{-}\mathrm{O_2}\}\cdot\mathrm{H_2O}\cdot\mathrm{Cl}]^-$ (**28**).

## Chapter 2

Aim of the second part of this work was the synthesis of methylene-bridged double ladders.

A simple approach to assemble organotin oxo clusters is the hydrolysis of $[PhSn(I_2)]_2CH_2$ in a $MeOH/H_2O/NEt_3$ mixture affording in this way the oxo cluster $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4$ (**3’**). Subsequent crystallisation of derivative **3’** from different solvents afforded building blocks as solvent-adducts. On the other hand, crystallisation of derivative **3’** from $CH_3CN$ provided the solvent-free double ladder **3** (Scheme 1). Otherwise crystallisation from $CHCl_3$, $CH_2Cl_2$, THF and *sec*-BuOH gave the corresponding solvent-adducts **4**, **5**, **6** and **7** (Scheme 1). Somewhat surprisingly, when the residue **3’** is dissolved in $CH_3CN$ and treated with 4-mercaptopyridine, adduct **8** is obtained (Scheme 1). The novel organotin oxo clusters crystallise as one- and two-dimensional polymers. Furthermore, the aptitude of the solvent to form hydrogen bonds is the factor that determines the structure and controls in the solid state the association of the organotin oxo cluster.



**Scheme 1** Solvent-controlled different solid state structures of **3**.

# 4 Appendix

## 4A Crystal data and structure refinement

Crystal data and structure refinement for bis(iododiphenylstannyl)methane (**2**, chapter 1), bis(bromodiphenylstannyl)methane (**3**, chapter 1), bis{diiodo[(trimethylsylil)methyl]stannyl}methane (**7**, chapter 1), 1,1,3-triiodo-5,5,7,7-tetramethyl-3-phenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**11**, chapter 1), 1,3-dichloro-5,5,7,7-tetramethyl-1,3-di-phenyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**14**, chapter 1), 1,1,3,3,-tetraiodo-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**15**, chapter 1), 1,1,3,3,-tetrabromo-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane (**16**, chapter 1), 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-bis(dimethylsulfoxide) (**17**, chapter 1), 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-dimethylsulfoxide (**18**, chapter 1), 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane-bis(dimethyl-formamide) (**19**, chapter 1), 1,1,3,3,-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclo-octane-1,3-dimethylimidazolidin-2-one (**20**, chapter 1), bis(triiodostannyl)methane (**21**, chapter 1), bis(triiodostannyl)propane (**23**, chapter 1), bis(triiodostannyl)methane-bis(dimethylsulfoxide) (**24**, chapter 1), bis(triiodostannyl)methane-dimethylformamide (**25**, chapter 1), 4-dimethylaminopyridinium $\{\{[Sn(Cl)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\{\{[Sn(OH)CH_2Si(Me_2)OSi(Me_2)CH_2Sn(Cl)](CH_2)_3\}_2O_2\}\cdot H_2O\cdot Cl]^-$ (**28**, chapter 1), $\{[Ph(HO)SnCH_2Sn(I)\text{-}Ph]O\}_4$ (**3**, chapter 2), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 2CHCl_3$ (**4**, chapter 2), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 3CH_2Cl_2$ (**5**, chapter 2), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot 4THF$ (**6**, chapter 2), $\{[Ph(HO)SnCH_2Sn(I)Ph]O\}_4 \cdot$ *s*-BuOH (**7**, chapter 2) and $\{[Ph(HO)Sn\text{-}CH_2Sn(I)Ph]O\}_4 \cdot CH_3CN$ (**8**, chapter 2) are listed in Tables 1 - 11.

Intensity data for the orange crystals of compounds **3**, **15**, **23** (chapter 1) and for the colourless crystals of **3**, **4**, **5**, **6**, **7** (chapter 2) were collected on a Nonius KappaCCD diffractometer with graphite-monochromated MoK$\alpha$ radiation at 173 K.

Intensity data for the colorless crystals of **2**, **7**, **11**, **14**, **16**, **17**, **18**, **19**, **20**, **28** (chapter 1) and **8** (chapter 2) were collected on a Nonius KappaCCD diffractometer with graphite-monochromated MoK$\alpha$ radiation, for the orange crystals of **21**, **24**, **25** (chapter 1) on a Nonius CAD4 diffractometer with graphite-monochromated AgK$\alpha$ radiation, at 291 K.

The structures were solved by direct methods SHELXS97[1] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97[2].

The H atoms were placed in geometrically calculated positions using a riding model with $U_{iso}$ constrained at 1.2 times $U_{eq}$ of the carrier atom.

## References

(1) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(2) Sheldrick, G. M. Göttingen University **1997**.

**Table 1** Crystal data and structure refinement for compounds **2**, **3** and **7** (chapter 1).

| | **2** | **3** | **7** |
|---|---|---|---|
| formula | $C_{25}H_{22}I_2Sn_2$ | $C_{25}H_{22}Br_2Sn_2$ | $C_9H_{24}I_4Sn_2Si_2$ |
| formular weight | 813.61 | 719.63 | 933.44 |
| crystal system | *monoclinic* | *orthorhombic* | *monoclinic* |
| crysal. size, mm | 0.15 x 0.15 x 0.13 | 0.14 x 0.13 x 0.13 | 0.22x 0.22 x 0.20 |
| space group | $P2_1/c$ | *Pbca* | $P2_1/c$ |
| $a$, Å | 9.5181(2) | 20.9041(8) | 10.2571(2) |
| $b$, Å | 12.2184(3) | 10.1334(4) | 9.9756(2) |
| $c$, Å | 22.4020(4) | 23.7107(8) | 23.1185(5) |
| $\alpha$, ° | 90 | 90 | 90 |
| $\beta$, ° | 101.7673(12) | 90 | 98.2012(9) |
| $\gamma$, ° | 90 | 90 | 90 |
| $V$, Å$^3$ | 2550.51(9) | 5022.6(3) | 2341.31(8) |
| $Z$ | 4 | 8 | 4 |
| $\rho_{calcd.}$, g·cm$^{-3}$ | 2.119 | 1.903 | 2.648 |
| $\mu$, mm$^{-1}$ | 4.388 | 5.180 | 7.496 |
| $F(000)$ | 1512 | 2736 | 1672 |
| $\theta$ range, ° | 3.04 – 27.48 | 3.39 – 27.48 | 2.91 – 27.48 |
| index ranges | $-12 \le h \le 12$<br>$-15 \le k \le 15$<br>$-29 \le l \le 28$ | $-27 \le h \le 27$<br>$-13 \le k \le 13$<br>$-30 \le l \le 30$ | $-13 \le h \le 13$<br>$-12 \le k \le 12$<br>$-30 \le l \le 29$ |
| number of reflections collected | 19973 | 30592 | 22396 |
| completeness to $\theta_{max}$ | 0.996 | 0.993 | 0.987 |
| number of independent reflections/$R_{int}$ | 5824 / 0.027 | 5708 / 0.058 | 5298 / 0.048 |
| number of reflections observed with ($I > 2\sigma(I)$) | 4364 | 2513 | 2976 |
| number of refined parameters | 262 | 202 | 160 |
| GOF ($F^2$) | 0.861 | 0.878 | 0.710 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0240 | 0.0497 | 0.0299 |
| $wR2$ ($F^2$) (all Data) | 0.0396 | 0.1353 | 0.0455 |
| $(\Delta/\sigma)_{max.}$ | 0.001 | < 0.001 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 0.676 / -0.655 | 1.027 / -1.663 | 0.756 / -1.015 |

**Table 2** Crystal data and structure refinement for compounds **11** and **14** (chapter 1).

| | **11** | **14** |
|---|---|---|
| formula | $C_{13}H_{23}I_3OSn_2Si_2$ | $C_{19}H_{28}Cl_2OSn_2Si_2$ |
| formula weight, g·mol$^{-1}$ | 869.57 | 636.87 |
| crystal system | *triclinic* | *monoclinic* |
| crysal. size, mm | 0.10 x 0.08 x 0.08 | 0.12 x 0.07 x 0.07 |
| space group | $P$-1 | $P2_1/c$ |
| $a$, Å | 9.203(1) | 19.930(1) |
| $b$, Å | 10.119(1) | 6.241(1) |
| $c$, Å | 13.613(1) | 21.853(1) |
| $\alpha$, ° | 95.337(1) | 90 |
| $\beta$, ° | 95.317(1) | 109.702(1) |
| $\gamma$, ° | 98.554(1) | 90 |
| $V$, Å$^3$ | 1240.9(2) | 2559.0(4) |
| $Z$ | 2 | 4 |
| $\rho_{calcd.}$, Mg·m$^{-3}$ | 2.327 | 1.653 |
| $\mu$, mm$^{-1}$ | 5.839 | 2.261 |
| $F$(000) | 792 | 1248 |
| $\theta$ range, ° | 3.02 – 25.33 | 3.19 - 25.00 |
| index ranges | $-11 \leq h \leq 11$<br>$-12 \leq k \leq 12$<br>$-15 \leq l \leq 15$ | $-23 \leq h \leq 23$<br>$-6 \leq k \leq 6$<br>$-25 \leq l \leq 24$ |
| number of reflections collected | 14195 | 29049 |
| completeness to $\theta_{max}$ | 0.926 | 0.945 |
| number of independent reflections/$R_{int}$ | 4195 / 0.0260 | 4268 / 0.0280 |
| number of reflections observed with ($I > 2\sigma(I)$) | 3348 | 3071 |
| number of refined parameters | 196 | 241 |
| GOF ($F^2$) | 1.078 | 0.896 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0298 | 0.0237 |
| $wR2$ ($F^2$) (all Data) | 0.0826 | 0.0514 |
| $(\Delta/\sigma)_{max.}$ | 0.001 | < 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 0.428 / -1.184 | 0.440 / -0.411 |

**Table 3** Crystal data and structure refinement for compounds **15** and **16** (chapter 1).

| | **15** | **16** |
|---|---|---|
| formula | $C_7H_{18}I_4OSn_2Si_2$ | $C_7H_{18}Br_4OSn_2Si_2$ |
| formula weight, g·mol$^{-1}$ | 919.37 | 731.41 |
| crystal system | *monoclinic* | *triclinic* |
| crysal. size, mm | 0.15 x 0.15 x 0.15 | 0.12 x 0.10 x 0.10 |
| space group | $P2_1/c$ | $P$-1 |
| $a$, Å | 17.6649(2) | 13.4166(2) |
| $b$, Å | 14.6371(2) | 17.9978(3) |
| $c$, Å | 18.9242(2) | 18.8209(3) |
| $\alpha$, ° | 90 | 61.8575(8) |
| $\beta$, ° | 115.7426(4) | 89.9073(7) |
| $\gamma$, ° | 90 | 85.6996(7) |
| $V$, Å$^3$ | 4407.48(9) | 3993.16(11) |
| $Z$ | 8 | 8 |
| $\rho_{calcd.}$, Mg·m$^{-3}$ | 2.771 | 2.433 |
| $\mu$, mm$^{-1}$ | 7.965 | 10.611 |
| $F(000)$ | 3264 | 2688 |
| $\theta$ range, ° | 2.91 – 27.47 | 2.94 – 27.48 |
| index ranges | $-22 \leq h \leq 22$<br>$-18 \leq k \leq 18$<br>$-24 \leq l \leq 22$ | $-17 \leq h \leq 17$<br>$-23 \leq k \leq 23$<br>$-24 \leq l \leq 24$ |
| number of reflections collected | 39796 | 52373 |
| completeness to $\theta_{\max}$ | 0.976 | 0.979 |
| number of independent reflections/$R_{\text{int}}$ | 9854 / 0.04 | 17931 / 0.081 |
| number of reflections observed with ($I > 2\sigma(I)$) | 6576 | 9324 |
| number of refined parameters | 289 | 593 |
| GOF ($F^2$) | 1.006 | 0.945 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0385 | 0.0642 |
| $wR2$ ($F^2$) (all Data) | 0.0643 | 0.1734 |
| $(\Delta/\sigma)_{\max.}$ | 0.001 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 1.219 / -1.546 | 4.704 / -1.309 |

**Table 4** Crystal data and structure refinement for compounds **17** and **18** (chapter 1).

| | **17** | **18** |
|---|---|---|
| formula | $C_{11}H_{30}Cl_4O_3S_2Sn_2Si_2$ | $C_9H_{24}Cl_4O_2SSn_2Si_2$ |
| formula weight, g·mol$^{-1}$ | 709.83 | 631.70 |
| crystal system | *triclinic* | *triclinic* |
| crysal. size, mm | 0.18 x 0.15 x 0.15 | ? |
| space group | *P*-1 | *P*-1 |
| *a*, Å | 10.1167(9) | 7.2814(3) |
| *b*, Å | 11.1881(10) | 11.5166(4) |
| *c*, Å | 11.7529(12) | 13.8406(6) |
| $\alpha$, ° | 93.555(4) | 93.2678(14) |
| $\beta$, ° | 94.524(4) | 91.2862(13) |
| $\gamma$, ° | 91.822(4) | 105.0540(19) |
| *V*, Å$^3$ | 1322.7(2) | 1118.14(8) |
| *Z* | 2 | 2 |
| $\rho_{calcd.}$, Mg·m$^{-3}$ | 1.782 | 1.876 |
| $\mu$, mm$^{-1}$ | 2.549 | 2.910 |
| *F*(000) | 696 | 612 |
| $\theta$ range, ° | 3.12 – 25.37 | 2.95 – 27.45 |
| index ranges | $-12 \le h \le 12$<br>$-13 \le k \le 13$<br>$-14 \le l \le 13$ | $-9 \le h \le 9$<br>$-14 \le k \le 14$<br>$-17 \le l \le 17$ |
| number of reflections collected | 11164 | 11134 |
| completeness to $\theta_{max}$ | 0.981 | 0.980 |
| number of independent reflections/$R_{int}$ | 4758 / 0.134 | 5004 / 0.032 |
| number of reflections observed with ($I > 2\sigma(I)$) | 2233 | 2758 |
| number of refined parameters | 217 | 187 |
| GOF ($F^2$) | 1.121 | 0.655 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.1328 | 0.0290 |
| $wR2$ ($F^2$) (all Data) | 0.3885 | 0.0515 |
| $(\Delta/\sigma)_{max.}$ | < 0.001 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 4.571 / -1.884 | 0.592 / -0.495 |

**Table 5** Crystal data and structure refinement for compounds **19** and **20** (chapter 1).

| | **19** | **20** |
|---|---|---|
| formula | $C_{14}H_{34}Cl_6N_2O_3Sn_2Si_2$ | $C_{12}H_{28}Cl_4O_2N_2Sn_2Si_2$ |
| formula weight, g·mol$^{-1}$ | 784.69 | 667.72 |
| crystal system | *triclinic* | *monoclinic* |
| crysal. size, mm | 0.25x 0.23 x 0.20 | 0.25x 0.25 x 0.20 |
| space group | $P$-1 | $P2_1/n$ |
| $a$, Å | 9.5005(1) | 11.5862(2) |
| $b$, Å | 11.4438(2) | 13.0954(2) |
| $c$, Å | 14.4861(2) | 16.3114(3) |
| $\alpha$, ° | 81.3642(6) | 90 |
| $\beta$, ° | 73.1686(6) | 100.8093(9) |
| $\gamma$, ° | 85.0752(7) | 90 |
| $V$, Å$^3$ | 1488.90(4) | 2430.95(7) |
| $Z$ | 2 | 4 |
| $\rho_{calcd.}$, Mg·m$^{-3}$ | 1.750 | 1.824 |
| $\mu$, mm$^{-1}$ | 2.314 | 2.602 |
| $F$(000) | 772 | 1304 |
| $\theta$ range, ° | 2.94 – 27.46 | 2.98 – 27.49 |
| index ranges | $-12 \leq h \leq 12$<br>$-14 \leq k \leq 14$<br>$-17 \leq l \leq 18$ | $-15 \leq h \leq 15$<br>$-17 \leq k \leq 17$<br>$-21 \leq l \leq 20$ |
| number of reflections collected | 19628 | 22683 |
| completeness to $\theta_{max}$ | 0.996 | 0.993 |
| number of independent reflections/$R_{int}$ | 6788 / 0.032 | 5533 / 0.037 |
| number of reflections observed with ($I > 2\sigma(I)$) | 5369 | 4439 |
| number of refined parameters | 270 | 223 |
| GOF ($F^2$) | 0.978 | 0.995 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0230 | 0.0226 |
| $wR2$ ($F^2$) (all Data) | 0.0477 | 0.0484 |
| $(\Delta/\sigma)_{max.}$ | 0.001 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 0.375 / -0.703 | 0.524 / -0.842 |

**Table 6** Crystal data and structure refinement for compounds **21** and **23** (chapter 1).

| | **21** | **23** |
|---|---|---|
| formula | $CH_2I_6Sn_2$ | $C_3H_6I_6Sn_2$ |
| formula weight, g·mol$^{-1}$ | 1012.81 | 1040.86 |
| crystal system | *monoclinic* | *monoclinic* |
| crysal. size, mm | 0.1 x 0.075 x 0.025 | 0.15 x 0.15 x 0.13 |
| space group | $P2_1/c$ | $P2_1/n$ |
| $a$, Å | 11.570(1) | 12.2952(8) |
| $b$, Å | 10.137(2) | 11.5202(11) |
| $c$, Å | 13.438(3) | 13.8712(12) |
| $\alpha$, ° | 90 | 90 |
| $\beta$, ° | 90.72(2) | 115.985(5) |
| $\gamma$, ° | 90 | 90 |
| $V$, Å$^3$ | 1576.0(5) | 1766.1(7) |
| $Z$ | 4 | 4 |
| $\rho_{calcd.}$, Mg·m$^{-3}$ | 4.269 | 3.914 |
| $\mu$, mm$^{-1}$ | 7.870 | 13.281 |
| $F(000)$ | 1704 | 1768 |
| $\theta$ range, ° | 3.17 – 21.97 | 2.95 – 25.36 |
| index ranges | $-15 \leq h \leq 15$<br>$-13 \leq k \leq 13$<br>$-17 \leq l \leq 17$ | $-14 \leq h \leq 14$<br>$-13 \leq k \leq 13$<br>$-16 \leq l \leq 15$ |
| number of reflections collected | 7910 | 10239 |
| completeness to $\theta_{max}$ | 0.997 | 0.993 |
| number of independent reflections/$R_{int}$ | 3907 / 0.0786 | 3220 / 0.05 |
| number of reflections observed with ($I > 2\sigma(I)$) | 1966 | 1441 |
| number of refined parameters | 83 | 100 |
| GOF ($F^2$) | 0.952 | 0.573 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0464 | 0.0261 |
| $wR2$ ($F^2$) (all Data) | 0.0738 | 0.0441 |
| $(\Delta/\sigma)_{max.}$ | 0.001 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 1.076 / -0.901 | 0.752 / -0.667 |

**Table 7** Crystal data and structure refinement for compounds **24** and **25** (chapter 1).

| | **24** | **25** |
|---|---|---|
| formula | $C_5H_{14}I_6O_2S_2Sn_2$ | $C_4H_9I_6ONSn_2$ |
| formula weight, g·mol$^{-1}$ | 1169.11 | 1085.90 |
| crystal system | *orthorhombic* | *monoclinic* |
| crysal. size, mm | 0.3 x 0.25 x 0.3 | 0.2 x 0.15 x 0.4 |
| space group | *Pbca* | $P2_1/c$ |
| *a*, Å | 17.470(3) | 8.3290(10) |
| *b*, Å | 14.577(3) | 13.514(2) |
| *c*, Å | 18.679(4) | 17.943(3) |
| $\alpha$, ° | 90 | 90 |
| $\beta$, ° | 90 | 100.55(2) |
| $\gamma$, ° | 90 | 90 |
| *V*, Å$^3$ | 4756.8(16) | 1985.5(5) |
| *Z* | 8 | 4 |
| $\rho_{calcd.}$, Mg·m$^{-3}$ | 3.181 | 3.633 |
| $\mu$, mm$^{-1}$ | 5.314 | 6.258 |
| *F*(000) | 3936 | 1864 |
| $\theta$ range, ° | 3.00 – 21.96 | 3.00 – 21.97 |
| index ranges | $-22 \leq h \leq 22$<br>$-19 \leq k \leq 19$<br>$-24 \leq l \leq 0$ | $-10 \leq h \leq 9$<br>$-16 \leq k \leq 16$<br>$-22 \leq l \leq 22$ |
| number of reflections collected | 11541 | 9657 |
| completeness to $\theta_{max}$ | 0.996 | 0.976 |
| number of independent reflections/$R_{int}$ | 5888 / 0.0490 | 4807/0.0463 |
| number of reflections observed with ($I > 2\sigma(I)$) | 3666 | 3245 |
| number of refined parameters | 164 | 128 |
| GOF ($F^2$) | 1.011 | 1.002 |
| *R*1 (*F*) ($I > 2\sigma(I)$) | 0.0392 | 0.0335 |
| *wR*2 ($F^2$) (all Data) | 0.0872 | 0.0832 |
| $(\Delta/\sigma)_{max.}$ | 0.002 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 1.904 / -1.145 | 1.066 / -1.103 |

**Table 8** Crystal data and structure refinement for compound **28** (chapter 1).

| | **28** |
|---|---|
| formula | $C_{26}H_{84}Cl_8O_2N_8Sn_4Si_4$ |
| formula weight, g·mol$^{-1}$ | 1411.73 |
| crystal system | *monoclinic* |
| crysal. size, mm | 0.13x 0.13 x 0.10 |
| space group | $P2_1/c$ |
| $a$, Å | 19.3720(2) |
| $b$, Å | 21.1173(2) |
| $c$, Å | 23.0845(3) |
| $\alpha$, ° | 90 |
| $\beta$, ° | 110.7838(4) |
| $\gamma$, ° | 90 |
| $V$, Å$^3$ | 8828.98(17) |
| $Z$ | 4 |
| $\rho_{calcd.}$, Mg·m$^{-3}$ | 1.062 |
| $\mu$, mm$^{-1}$ | 1.435 |
| $F(000)$ | 2816 |
| $\theta$ range, ° | 2.99 – 27.48 |
| index ranges | $-24 \leq h \leq 24$<br>$-27 \leq k \leq 27$<br>$-29 \leq l \leq 28$ |
| number of reflections collected | 74163 |
| completeness to $\theta_{max}$ | 0.987 |
| number of independent reflections/$R_{int}$ | 19987 / 0.036 |
| number of reflections observed with ($I > 2\sigma(I)$) | 13206 |
| number of refined parameters | 778 |
| GOF ($F^2$) | 0.940 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0291 |
| $wR2$ ($F^2$) (all Data) | 0.0456 |
| $(\Delta/\sigma)_{max.}$ | 0.002 |
| largest diff peak/hole, e/ Å$^3$ | 1.159 / -0.941 |

**Table 9** Crystal data and structure refinement for compounds **3** and **4** (chapter 2).

| | **3** | **4** |
|---|---|---|
| formula | $C_{52}H_{52}I_4O_8Sn_8$ | $C_{54}H_{54}I_4Cl_6O_8Sn_8$ |
| formular weight | 2262.06 | 2500.79 |
| crystal system | *monoclinic* | *triclinic* |
| crysal. size, mm | 0.10 x 0.10 x 0.08 | 0.15 x 0.15 x 0.13 |
| space group | $P2_1/n$ | $P$-1 |
| $a$, Å | 15.8313(4) | 14.3743(3) |
| $b$, Å | 18.5471(5) | 15.3717(3) |
| $c$, Å | 21.8859(7) | 17.0095(3) |
| $\alpha$, ° | 90 | 85.1994(11) |
| $\beta$, ° | 105.5531(9) | 87.9058(12) |
| $\gamma$, ° | 90 | 72.6028(11) |
| $V$, Å$^3$ | 6190.9(3) | 3573.61(12) |
| $Z$ | 4 | 2 |
| $\rho_{calcd.}$, g·cm$^{-3}$ | 2.427 | 2.324 |
| $\mu$, mm$^{-1}$ | 5.213 | 4.745 |
| $F$(000) | 4160 | 2312 |
| $\theta$ range, ° | 2.93 - 25.32 | 3.07 - 27.45 |
| index ranges | $-19 \leq h \leq 19$<br>$-22 \leq k \leq 22$<br>$-26 \leq l \leq 25$ | $-18 \leq h \leq 18$<br>$-18 \leq k \leq 19$<br>$-21 \leq l \leq 22$ |
| number of reflections collected | 40285 | 44900 |
| completeness to $\theta_{\max}$ | 0.986 | 0.977 |
| number of independent reflections/$R_{\text{int}}$ | 11147 / 0.061 | 15969 / 0.049 |
| number of reflections observed with ($I > 2\sigma(I)$) | 5688 | 8582 |
| number of refined parameters | 649 | 739 |
| GOF ($F^2$) | 0.947 | 0.836 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0538 | 0.0333 |
| $wR2$ ($F^2$) (all Data) | 0.0923 | 0.0570 |
| $(\Delta/\sigma)_{\text{max.}}$ | 0.001 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 1.746 / -0.971 | 1.003 / -1.081 |

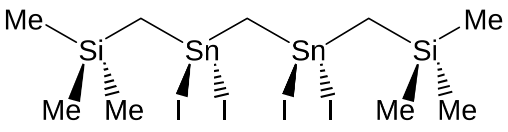
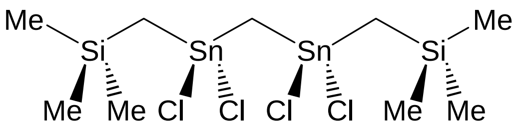
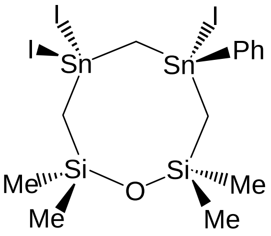
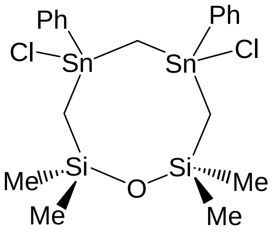
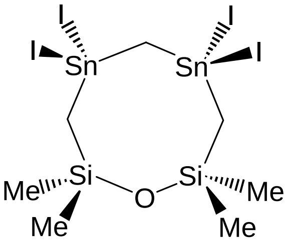
**Table 10** Crystal data and structure refinement for compounds **5** and **6** (chapter 2).

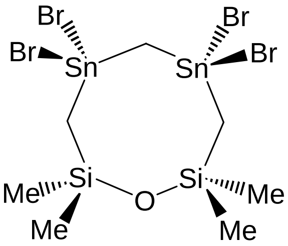
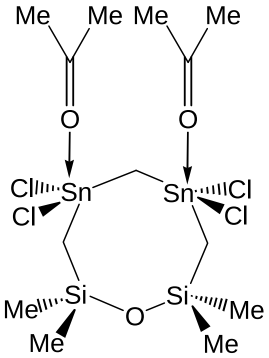
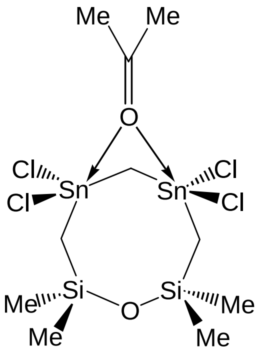
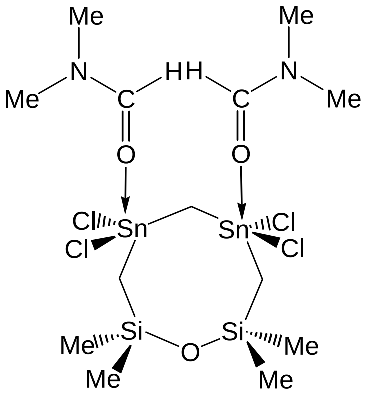
| | **5** | **6** |
|---|---|---|
| formula | $C_{55}H_{58}I_4Cl_6O_8Sn_8$ | $C_{68}H_{84}I_4O_{12}Sn_8$ |
| formular weight | 2516.83 | 2550.47 |
| crystal system | *monoclinic* | *monoclinic* |
| crysal. size, mm | 0.20 x 0.18 x 0.18 | 0.18 x 0.15 x 0.15 |
| space group | $P2_1/n$ | $C2/c$ |
| *a*, Å | 17.8847(2) | 27.7234(13) |
| *b*, Å | 19.7039(3) | 20.1467(11) |
| *c*, Å | 21.2582(2) | 15.6854(10) |
| $\alpha$, ° | 90 | 90 |
| $\beta$, ° | 105.4481(8) | 114.5854(17) |
| $\gamma$, ° | 90 | 90 |
| *V*, $Å^3$ | 7220.71(15) | 7966.6(8) |
| *Z* | 4 | 4 |
| $\rho_{calcd.}$, g·$cm^{-3}$ | 2.315 | 2.126 |
| $\mu$, $mm^{-1}$ | 4.697 | 4.068 |
| *F*(000) | 4664 | 4800 |
| $\theta$ range, ° | 2.98 - 27.49 | 3.31 - 25.00 |
| index ranges | $-23 \leq h \leq 23$<br>$-25 \leq k \leq 25$<br>$-27 \leq l \leq 26$ | $-32 \leq h \leq 32$<br>$-23 \leq k \leq 23$<br>$-18 \leq l \leq 16$ |
| number of reflections collected | 63211 | 30090 |
| completeness to $\theta_{max}$ | 0.988 | 0.994 |
| number of independent reflections/$R_{int}$ | 16361 / 0.0570 | 6985 / 0.049 |
| number of reflections observed with ($I > 2\sigma(I)$) | 9885 | 3892 |
| number of refined parameters | 730 | 394 |
| GOF ($F^2$) | 0.967 | 1.071 |
| *R*1 (*F*) ($I > 2\sigma(I)$) | 0.0462 | 0.0723 |
| *wR*2 ($F^2$) (all Data) | 0.0908 | 0.1878 |
| $(\Delta/\sigma)_{max.}$ | 0.001 | 0.001 |
| largest diff peak/hole, e/ $Å^3$ | 1.135 / -1.653 | 3.180 / -2.907 |

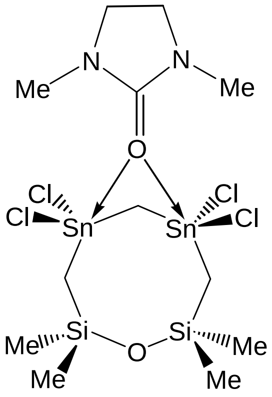
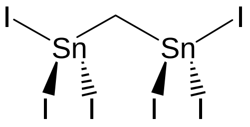
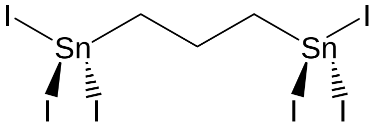
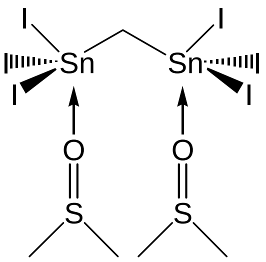
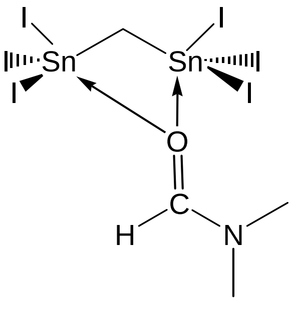
**Table 11** Crystal data and structure refinement for compounds **7** and **8** (chapter 2).

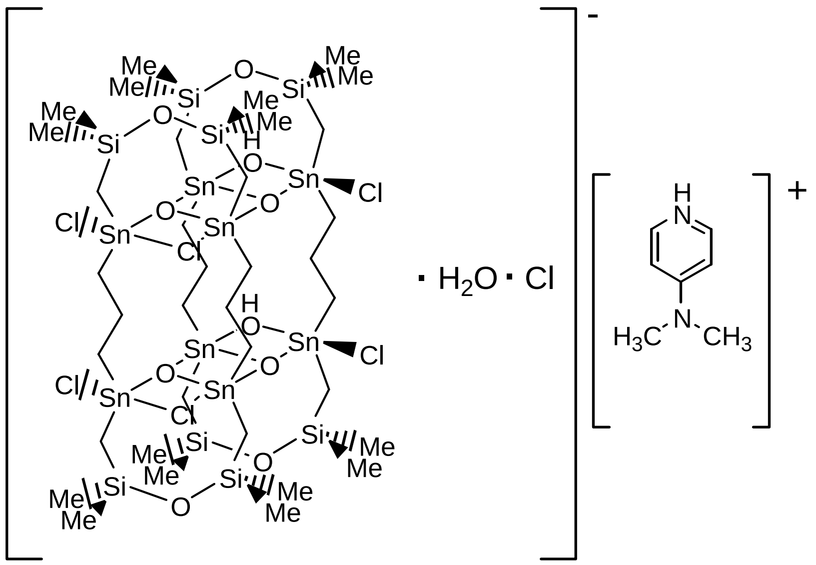
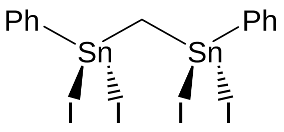
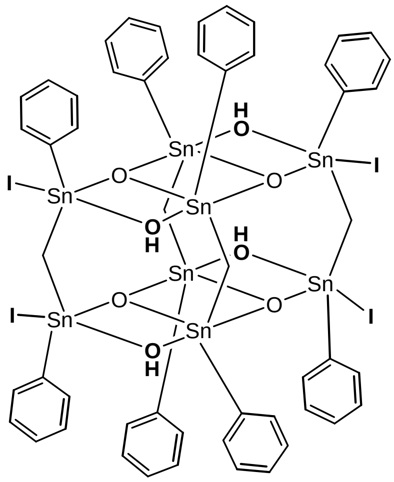
| | **7** | **8** |
|---|---|---|
| formula | $C_{56}H_{62}I_4O_9Sn_8$ | $C_{56}H_{58}I_4N_2O_8Sn_8$ |
| formular weight | 2500.79 | 2344.16 |
| crystal system | *monoclinic* | *monoclinic* |
| crysal. size, mm | 0.12 x 0.10 x 0.10 | 0.20x 0.18 x 0.18 |
| space group | $P2_1/c$ | $P2_1/n$ |
| $a$, Å | 12.7432(2) | 15.8172(3) |
| $b$, Å | 36.3427(6) | 20.4347(4) |
| $c$, Å | 15.7884(4) | 21.9804(5) |
| $\alpha$, ° | 90 | 90 |
| $\beta$, ° | 112.5854(6) | 104.5079(10) |
| $\gamma$, ° | 90 | 90 |
| $V$, Å$^3$ | 6751.2(2) | 6878.0(2) |
| $Z$ | 4 | 4 |
| $\rho_{calcd.}$, g·cm$^{-3}$ | 2.298 | 2.264 |
| $\mu$, mm$^{-1}$ | 4.786 | 4.698 |
| $F(000)$ | 4328 | 4336 |
| $\theta$ range, ° | 3.10 - 25.35 | 3.02 - 27.47 |
| index ranges | $-15 \leq h \leq 15$ | $-20 \leq h \leq 20$ |
| | $-43 \leq k \leq 43$ | $-25 \leq k \leq 24$ |
| | $-19 \leq l \leq 17$ | $-28 \leq l \leq 28$ |
| number of reflections collected | 12033 | 63046 |
| completeness to $\theta_{max}$ | 0.974 | 0.970 |
| number of independent reflections/$R_{int}$ | 39151 / 0.052 | 15283 / 0.058 |
| number of reflections observed with ($I > 2\sigma(I)$) | 6610 | 6057 |
| number of refined parameters | 688 | 704 |
| GOF ($F^2$) | 0.961 | 0.674 |
| $R1$ ($F$) ($I > 2\sigma(I)$) | 0.0508 | 0.0389 |
| $wR2$ ($F^2$) (all Data) | 0.0768 | 0.0692 |
| $(\Delta/\sigma)_{max.}$ | 0.001 | 0.001 |
| largest diff peak/hole, e/ Å$^3$ | 0.996 / -0.943 | 0.930 / -0.819 |

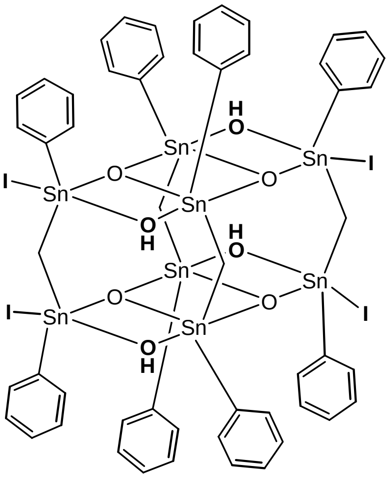
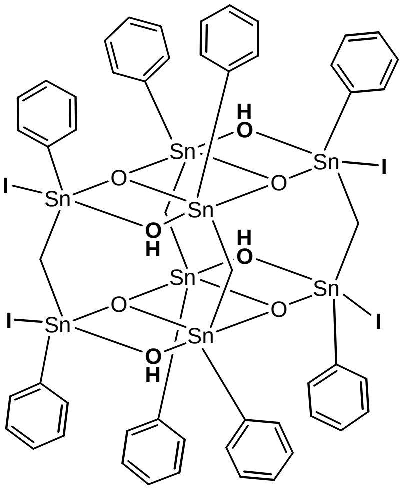
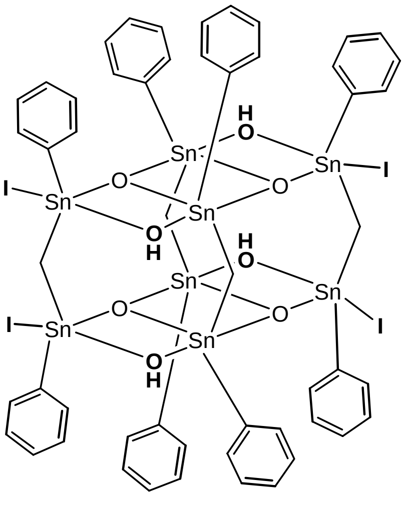
## 4B List of new compounds

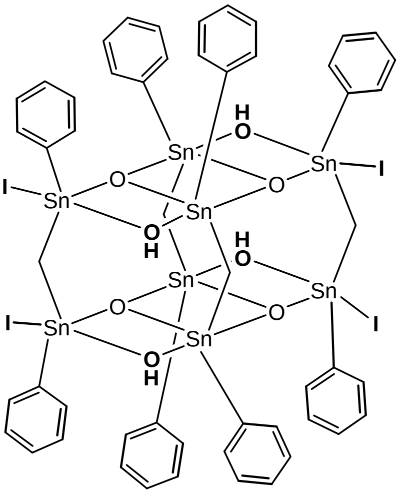
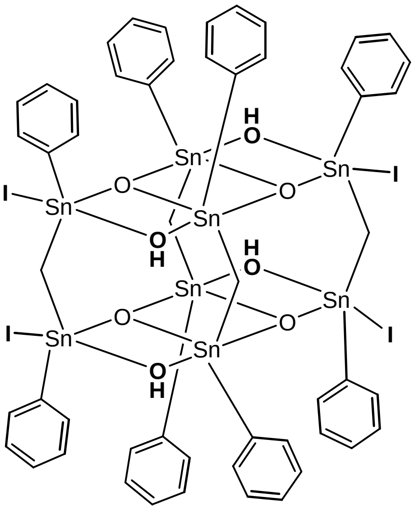
| Compound (Chapter 1) | Number |
|---|---|
|  | **7** |
|  | **8** |
|  | **11** |
|  | **14** |
|  | **15** |

| | |
|---|---|
|  | **16** |
|  | **17** |
|  | **18** |
|  | **19** |

| | |
|---|---|
|  | **20** |
|  | **21** |
|  | **23** |
|  | **24** |
|  | **25** |

| | |
|---|---|
|  | **28** |
| (Chapter 2) | |
|  | **2** |
|  | **3** |

| | |
|---|---|
|  · $2CHCl_3$ | **4** |
|  · $3CH_2Cl_2$ | **5** |
|  · 4THF | **6** |

| | |
|---|---|
|  · *sec*-BuOH | **7** |
|  · $CH_3CN$ | **8** |

# Curriculum vitae

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44147 Dortmund

## Personal informations

| | |
|---|---|
| Birthdate | 14.02.1975 |
| Birthplace | Palermo |
| Marital status | married |
| Nationality | Italian |

## Education

| | |
|---|---|
| 1980 - 1985 | primary school in Palermo |
| 1985 - 1988 | secondary school in Palermo |
| 1988 - 1993 | G. A. De Cosmi high school in Palermo |
| September 1993 | matriculation at the University of Palermo Department of Chemistry |
| October 1998 – June 1999 | University of Dortmund: Erasmus grant of the European community |
| July 1999 | graduate degree at the University of Palermo |
| September 1999 | begin of the PHD at the University of Dortmund “ Anorganische Chemie II “ by Prof. Dr. K. Jurkschat |