Synthesis, Characterization and Reactivity of a Diorganotin Thiocarboxylate: Dimethyl(thioacetato)-tin(IV) Chloride and its Reactions with Nucleophiles Exhibiting Desulfurization

Neetu Singh[a], Subrato Bhattacharya[a], Heinrich Nöth[b], and Peter Mayer[b]

[a] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India
[b] Department of Chemistry, University of Munich, Butenandtstraße 5 – 13, D-81377 Munich, Germany

Reprint requests to Dr. S. Bhattacharya. Fax: +91-542-2368127. E-mail: s_bhatt@bhu.ac.in or Prof. Dr. H. Nöth. Fax: +4989-2180-77455. E-mail: H.Noeth@lrz.uni-muenchen.de

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

Dimethyl(thioacetato)tin chloride (**1**) was synthesized by the reaction of dimethyltin dichloride with thioacetic acid in the presence of triethylamine. Compound **1** was subjected to hydrolysis under different reaction conditions in order to obtain sulfido/hydrosulfidotin compounds. Except for one case where the product was hexamethyl-1,3,5-trithia-2,4,6-tristannacyclohexane, $(Me_2SnS)_3$ (**4**), all other reactions led to desulfurization, and the products obtained were organostannoxane compounds, dinuclear tetramethyl-oxo-dichloroditin, $\{Me_2SnCl_2.Me_2SnO\}_2$ (**2**), and tetraacetatodioxotetra(dimethyltin), $(Me_2Sn)_4O_2(O_2CMe)_4$ (**3**). These complexes have been characterized by ^1H, ^{13}C, ^{119}Sn NMR and FTIR spectroscopy, and compounds **2** – **4** also by X-ray crystallography. Density functional calculations were performed to explain the structure and reactivity of the compounds.

Key words: Organotin Compounds, Stannoxane, Thiocarboxylate, Hydrolysis, Desulfurization

Introduction

Organostannoxane chemistry has always attracted interest of chemists due to the synthetic challenges [1, 2], unique structural features ranging from monomeric compounds [3, 4] to cluster networks [2, 5], and a wide range of catalytic applications [6]. Thiocarboxylates constitute an interesting class of ligands having both soft and hard donor sites. These ligands are known to exhibit a variety of bonding modes [7]. Hampden-Smith and coworkers have shown that thioacetate complexes are excellent single source precursors of the corresponding metal sulfide materials [8]. Organotin thiocarboxylates are not very common most likely due to their thermal instability and the lability of the RC(O)S ligands. We have earlier reported a few monoorganotin(IV) thioacid compounds [9] which are in general mononuclear though a few binuclear compounds were also obtained having Sn–O–Sn linkages. In these complexes the thiocarboxylate group usually binds to tin atoms monodentately through sulfur, however, a bidentate bonding was also observed when the Lewis acidity of the tin(IV) center was increased. It may be noted that organostannathianes still remain almost unexplored, and to the best of our knowledge no tin thiocarboxylate is known having Sn–S–Sn linkages. The chemistry of organotin thioacetates is quite different from that of the corresponding acetates. Organotin carboxylates are associated molecules, their hydrolysis is quite fast and thus difficult to control. On the other hand, tin thioacetates are discrete molecules, and their hydrolysis is expected to be slower due to the thiophilic nature of tin(IV). In this paper we report on the synthesis of a diorganotin thioacetate, dimethyl(thioacetato)tin(IV) chloride and its hydrolysis under different experimental conditions attempted in order to develop a convenient route for the formation of a new structure type with Sn–S linkages.

Result and Discussion

Compound $Me_2SnCl(SCOCH_3)$ (**1**), was obtained by the reaction of Me_2SnCl_2 with thioacetic acid in 1 : 1 molar ratio in the presence of an equimolar amount of triethyl amine. The compound is a yel-

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low crystalline solid which is quite stable not only in the solid state but also in solution in the absence of moisture. Although colorless crystals of suitable size and shape were obtained, their quality was not good enough for an X-ray structure determination.

Compound **1** exhibits two ^{1}H NMR signals at 1.12 and 2.45 ppm. The ratio between the two methyl groups, one attached to the Sn atom and the other to the thioacetate group is 2 : 1 as expected. The ^{119}Sn NMR spectrum of compound **1** in $CDCl_3$ solution exhibits a single peak at +16.80 ppm, characteristic for compounds with tetra-coordinated tin. In the IR spectrum, a strong peak due to the carbonyl stretching vibration is observed at 1597 cm^{-1}.

Diorgano(acetato)tin chlorides have generally a one-dimensional polymeric structure. One of the oxygen atoms of the acetate group bridges between two tin centers. Unlike the carboxylates, thiocarboxylates usually are discrete monomeric molecules in the solid state.

The structure of the triorganotin thiocarboxylate $Ph_3Sn(4\text{-}CH_3C_6H_4COS)$ has been reported by Tani *et al.* [10]. The molecule is monomeric, and the thiocarboxylate ion is bonded to the metal through its sulfur atom. However, there is a weak intramolecular Sn–O interaction. A similar bonding mode was also observed in the case of the organotin tris-thiobenzoate, *n*-$BuSn(SOCPh)_3$ [9]. From the IR data it is evident that the bonding of the thiobenzoic group is certainly through sulfur, but a lowering of 99 cm^{-1} in ν(C=O) as compared to free thioacetic acid indicates a weak bonding interaction between the tin and oxygen atoms. It may be noted that in the case of $Cl_2Sn(SCOPh)_2$ the ligand acquires a bidentate bonding mode due to the increased Lewis acidity of the tin center [9]. Similarly, the presence of one Cl atom may also induce some +I effect, thereby increasing the positive charge on tin. As a result, the electron density on O may be polarized to a considerable extent.

Quantum chemical calculations also corroborate these spectral features. The molecular geometry was fully optimized within the framework of DFT at the B3LYP/6-31+G* (C,H,O,Cl) and 3-21G* (Sn) level using the finite field procedure included in the GAUSSIAN03W package [11]. Vibrational analysis was performed at the same level in order to establish the presence of a global minimum on the potential energy surface. One important result is that the charge localization is quite high in this molecule. The Sn, Cl and O atoms possess +1.75, −0.51 and −0.59 charges, respectively (Fig. 1). Possibly due to these charges the molecule exists as a dimer as evidenced by its FAB mass spectrum (Fig. 2). Even species with masses higher than the dimer, though in low concentration, are observed. Our attempts to optimize the dimeric structure did not succeed due to convergence failure. Although both the O and the Cl atoms possess almost equal negative charges, the bridging between the two Sn centers is possibly through the Cl atoms due to its lesser electronegativity and higher polarizability as compared to oxygen. Thus the molecule can be viewed at as an S-thioester of tin.

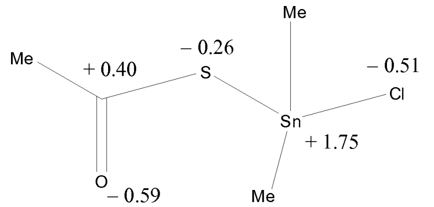

Fig. 1. Calculated charges of **1**.

As organic S-thioesters are known to undergo hydrolysis and alcoholysis one can expect that the tin thioester also will undergo similar reactions. The product of such a reaction is expected to contain a hydrosulfido group bonded to tin:

$$R_3CSC(O)R' + H_2O \rightarrow R_3CSH + R'COOH$$

$$R_3SnSC(O)R' + H_2O \rightarrow R_3SnSH + R'COOH$$

Slow diffusion of water at r. t. into a chloroform solution of compound **1** afforded $[Me_2SnCl_2{\cdot}Me_2SnO]_2$ (**2**), which is a colorless crystalline solid quite stable in air, and it was thus easy to obtain it in pure form and in good yields. In the ^{1}H NMR spectrum two very close and sharp signals with approximately the same intensity were recorded at 1.15 and 1.25 ppm. Both signals are due to the methyl protons directly attached to tin. Expectedly, the ^{119}Sn NMR also shows two sharp signals at −60.83 and −115.67 ppm, indicating the presence of different stereochemical environments around the two tin atoms. From the chemical shift values one can tentativly conclude that both the tin atoms are penta-coordinated.

When compound **1** dissolved in benzene was treated with powdered sodium hydroxide a compound $[Me_8Sn_4O_2(O_2CMe)_4]$ (**3**), was obtained as a product. Its two ^{1}H NMR signals at 1.05 and 1.15 ppm are due to methyl groups attached to the metal atoms which are present in two different environments around the tin

Table 1. Crystal structure data for **2**–**4**.

Compound	**2**	**3**	**4**
Formula	$C_4H_{12}Cl_2OSn_2$	$C_{16}H_{36}O_{10}Sn_4$	$C_6H_{18}S_3Sn_3$
M_r	384.42	863.21	271.23
Crystal size, mm^3	$0.54 \times 0.25 \times 0.11$	$0.22 \times 0.2 \times 0.1$	$0.18 \times 0.14 \times 0.11$
Crystal system	monoclinic	monoclinic	tetragonal
Space group	$P2_1/c$	Pc	$P4_32_12$
a, Å	7.188(1)	11.139(2)	9.622(1)
b, Å	18.34(1)	7.735(2)	9.622(1)
c, Å	8.704(2)	8.704(2)	17.188(3)
β, deg	109.38(3)	109.38(3)	90
V, Å^3	1082.6(4)	1376.0(5)	1591.1(5)
Z	4	2	8
$D_{calcd.}$, g cm^{-3}	2.359	2.359	2.264
$\mu(MoK_\alpha)$, mm^{-1}	5.048	3.630	5.029
$F(000)$, e	712	824	1008
hkl range	$-9 \le h \le 9$	$-14 \le h \le 14$	$-12 \le h \le 12$
	$-23 \le k \le 23$	$-9 \le k \le 10$	$-12 \le k \le 11$
	$-11 \le l \le 11$	$-21 \le l \le 21$	$-22 \le l \le 22$
2θ range, deg	6.40–55.00	6.46–54.92	6.36–54.96
Refl. meas./unique	17195/2239	21683/5752	27329/1725
R_{int}	0.0407	0.0399	0.0365
Param. refined	83	261	57
$R(F)/wR(F^2)$ (all refl.)	0.0264/0.0575	0.0325/0.0677	0.0221/0.0456
x(Flack)	–	0.015(2)	0.01(4)
GOOF (F^2)	1.111	1.124	1.169
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.689 / –0.656	1.056 / – 1.983	0.481 / – 0.571

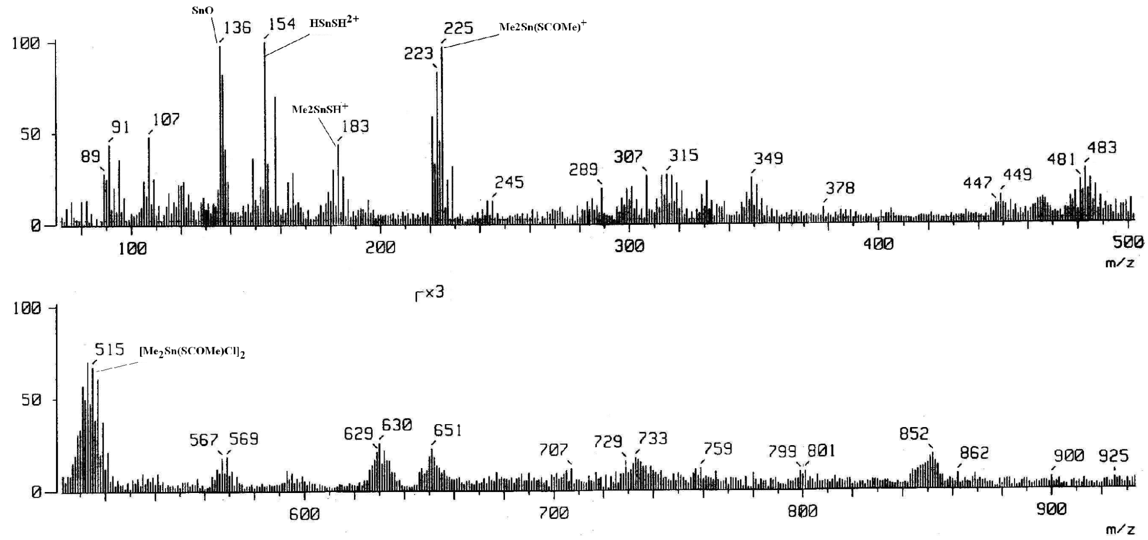

Fig. 2. FAB mass spectrum of compound **1** showing the presence of fragments of even higher masses than the dimer.

atoms. A sharp signal at 2.45 ppm is recorded for the methyl group of the acetate ligand.

The ^{119}Sn NMR spectrum exhibits only one peak at −47.51 ppm, characteristic of a class of compounds where the tin atoms are penta-coordinated. The absence of a second peak at a higher field due to a hexa-coordinated tin(IV) atom indicates the change in structure from the solid state to solution.

Compound **4** resulted by the same reaction as described above using a polar solvent (methanol) in place of a nonpolar one (benzene). This led to the trinuclear compound, $(Me_2SnS)_3$, which is an already reported molecule [14]. The ^{119}Sn NMR of compound **4** shows a sharp peak at 134.22 ppm. This chemical shift is typical for tetra-coordinate tin compounds.

Table 2. Selected bond length (Å) and angles (deg) for **2**, **3** and **4** with estimated standard deviations in parentheses.

	2	**3**	**4**
Sn1–C1	2.100(3)	2.106(6)	2.131(4)
Sn2–C2	2.110(3)	2.104(6)	–
Sn1–Cl1	2.688(1)	–	–
Sn1–O1	2.100(3)	2.238(4)	–
Sn1–O2	2.046(2)	2.001(4)	–
Sn2–O2	2.035(2)	2.097(4)	–
Sn2–O3	–	2.125(4)	–
Sn2–O4	–	2.380(4)	–
Sn1–S3	–	–	2.403(1)
Sn2–S3	–	–	2.430(1)
C1–Sn1–C2	134.8(1)	137.7(3)	113.1(3)
O1–Sn1–C1	112.4(1)	84.4(2)	–
O–Sn1–O	74.59(9)	91.6(2)	–
Sn1–Cl1–Sn2	82.42(2)	–	–
S3–Sn1–Sn3(A)	–	–	104.83(2)
S2–Sn1–S3	–	–	106.64(3)

As mentioned earlier, the attack of nucleophiles on thioesters occurs at the carbonyl carbon, and the same can be expected in the case of tin thioesters. However, in the present study we found that compounds **2** and **3** are generated by desulfurization as a result of the removal of the thioacid ligand from the complex. The nucleophile preferentially attacks the tin atom rather than the carbonyl carbon atom because of the higher positive charge at the tin center. The nucleophile water attacks at the tin atom of **1** cleaving the Sn–S bond with elimination of thioacetic acid generating compound **2**. On the other hand, when sodium hydroxide is used as the nucleophile, the attack takes place at the Sn center as well as at the carbonyl carbon with formation of compound **3** precipitating the S^{2-} ion in the form of Na_2S. The acetate ion is well known to bridge between two metal centers, and this results in the polymeric structure of compound **3**.

When the hydrolysis of **1** was carried out in methanolic medium in the presence of stoichiometric amounts of NaOH, the concentration of the free OH^- ions is much higher than in the aforementioned two cases due to partial dissociation of NaOH in methanol. It should, therefore, attack both electrophilic centers, the tin as well as the carbonyl carbon. However, the solvation of the tin(IV) atom decreases its electrophilic character considerably, and the nucleophile therefore attacks at the carbonyl carbon only.

Molecular structures of ***2*** *–* ***4***

The molecular structures of compounds **2**–**4** (see Figs. 3–6) have been determined by X-ray crystallography. The crystallographic data for these compounds are summarized in Table 1. Selected bond lengths and bond angles for **2**, **3**, and **4** are listed in Table 2.

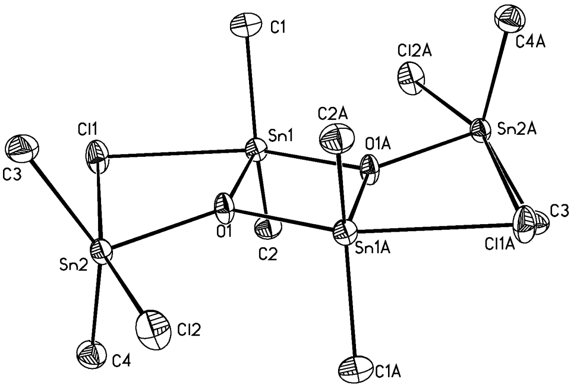

Fig. 3. Molecular structure of the dimeric unit of compound $(Me_2Sn)_2OCl_2$ (**2**).

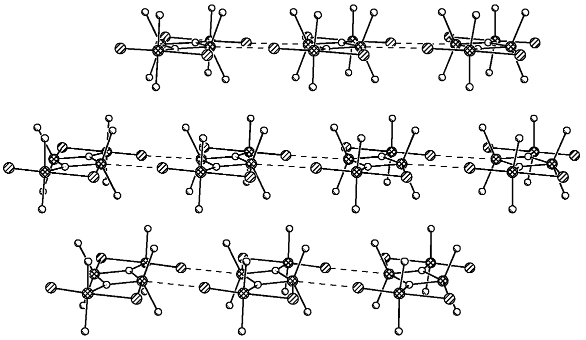

Fig. 4. Arrangement of the dimeric units of compound **2** in the unit cell. The view down the crystallographic *b* axis shows the intramolecular Sn–Cl–Sn interactions. Bond lengths Cl2–Sn2 and Sn2–Cl1 (intermolecular) are 2.245(1) and 3.987(1) Å, respectively. The Sn1–Cl2–Sn2 angle is 177.3(2)°.

The molecular structure of **2** is shown in Fig. 3, and the packing in the unit cell in Fig. 4. The structure shows a ladder type of arrangement [12] involving a net combination of two molecules of Me_2SnCl_2 and a dimer of Me_2SnO. Structural reports for a large number of distannoxane compounds are available in the literature [13], and generally a few interesting features of the Sn–O bonding are notable for these compounds. The Sn–O bonds of covalent character range in lengths between 2.07 to 2.15 Å, and in some cases the two Sn–O bond lengths are equal. In compound **2**, the distannoxane ring exhibits two different Sn–O bond lengths, 2.046(2) and 2.117(2) Å for Sn1–O and Sn1A–O, respectively, which are within the above mentioned range. However, the third Sn–O

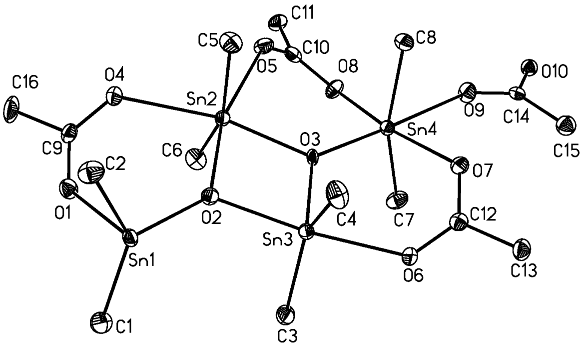

Fig. 5. The asymmetric unit of the compound $Me_8Sn_4(OCOMe)_8O_2$ (**3**).

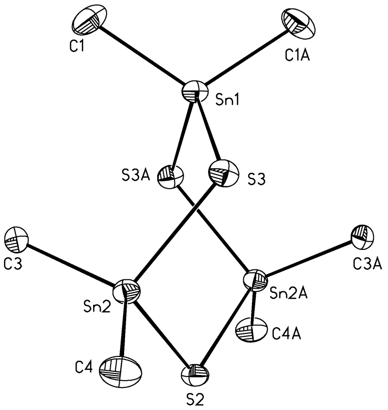

Fig. 6. The molecular structure of compound **4** in the crystal. Its crystallographic C_2 axis runs through the atoms S2 and Sn1.

bond (Sn2–O) is shorter at 2.035(2) Å. A better description of the molecule would be as a dimer of the formula $[(Me_2SnCl)_2O]_2$. The two chlorine atoms are non-equivalent. The terminal one makes supramolecular connectivity involving a tin atom of a neighboring molecule. As expected, the terminal Sn2–Cl2 bond [2.045(1) Å] is shorter than the bridging Sn–Cl-bonds [Cl1–Sn1 2.688(1), Sn2–Cl1 2.792(1) Å].

The asymmetric unit of compound **3** contains four tin atoms and four acetate groups which constitute one unit in its polymeric structure in the solid state as shown in Fig. 5. Each oxido group binds to three Sn atoms. The acetate groups are chelating and form six-membered rings comprising the acetate group and an Sn–O–Sn unit. Two of the four tin atoms are penta-coordinated, the other two show hexa-coordination. This does not correspond to the ^{119}Sn NMR spectrum of **3** which shows only a single signal for penta-coordinated Sn atoms. Thus, the structure of compound **3** is different in solution and in the solid state.

Another product of the hydrolysis of **1** is compound **4**, which is distinctly different from the other two hydrolysis products as it contains sulfido bridges. The X-ray structure analysis of this compound has been reported recently [14]. In the best reported structure the crystal system is monoclinic with space group $P2_1/n$. However, our analysis of the crystal led to a tetragonal crystal system with space group $P4_32_12$ and gave a much better result ($R1$ = 0.021, *cf.* earlier report $R1$ = 0.03 [14]). Its molecular structure as shown in Fig. 6 is similar to that of the earlier report, however, one small but remarkable difference is that the Sn(1) atom lies on a crystallographic C_2 axis of symmetry which is absent in the previously reported structure. The molecule has a twisted boat conformation. Conformational analyses using DFT method at B3LYP level confirmed our X-ray result. The skew-boat conformation is more stable than the chair conformation. The chair conformation would possess an axial methyl group, and this would result in an unstable conformation due to 1,3-diaxial interactions. The twisted-boat conformation reduces this steric effect.

Conclusion

In summary, we observe that in spite of the reported thermal instability of these complexes with thiocarboxylato ligands the dimethyl(thioacetato)tin chloride is quite stable, similar to its monoorganotin analog. However, hydrolysis of the thioacetate complex though facile is not very fast as to become uncontrollable like in the cases of corresponding thiocarboxylates and phosphinates. Although our attempts to obtain diorganotin hydrosulfides were unsuccessful, different compounds (organostannoxanes and dimethyltin sulfide) were obtained under different hydrolytic conditions. The reactivity of the thioacetato complex **1** and the rationale behind each reaction can be explained on the basis of DFT calculations.

Experimental Section

Dimethyltin dichloride and thioacetic acid were purchased from Sigma-Aldrich Chemicals and used without further purification. Solvents were stored over appropriate reagents and distilled prior to use. Elemental analyses were carried out by using the Exeter Model CE-440 CHN analyzer. IR spectra were recorded as KBr pellets on a Varian 3100 FT-IR spectrophotometer in the region 50 – 4000 or 400 – 4000 cm^{-1}. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Jeol AL300 FT NMR spectrometer in $CDCl_3$. The chemical shifts were referenced to tetramethylsilane (^{1}H) and tetramethyltin (^{119}Sn).

*(Dimethyl)thioacetatotin chloride [$Me_2Sn(Cl)SC(O)Me$] (**1**)*

Compound **1** was synthesized by addition of thioacetic acid (16.7 mmol, 1.27 g) and triethyl amine (16.7 mmol, 1.69 g) in THF (25 mL) to a stirred solution of dimethyltin dichloride (16.70 mmol, 3.682 g) in THF (25 mL) cooled by an ice bath. A white precipitate formed immediately. After stirring for 3 h the precipitated triethylammonium chloride was filtered off, and the solvent was removed from the filtrate under reduced pressure. The residue was then extracted with diethyl ether. Evaporation of the solvent yielded compound **1** which was dried *in vacuo* (5 mm/Hg) for 2 h. It was recrystallized from diethyl ether. Yield: 96 % (4.16 g), M. p. 58 – 60 °C. – SnC_4H_9ClOS (259.3): calcd. C 18.53, H 3.50; found C 19.17, H 3.40. – ^{1}H NMR ($CDCl_3$): δ = 1.12, 2.45. – ^{13}C NMR ($CDCl_3$): δ = 5.43, 32.24, 211.60. – ^{119}Sn NMR ($CDCl_3$): δ = 16.80 ppm. – IR: ν = 1597.19 cm^{-1} ν(CO). – MS: *m/z* = 519.

*Hydrolysis of **1** in neutral medium: Formation of 2-chloro-2,2,4,4-tetramethyl-1-oxa-3-chlora-2,4-distannacyclobutane dimer (**2**)*

A solution of **1** (3 mmol, 0. 778 g) in chloroform (10 mL) placed in a conical flask was put into a beaker containing some water at the bottom. The beaker was covered with parafilm and the arrangement left untouched. After 8 d a crystalline product could be isolated which was recrystallized form chloroform by slow evaporation of the solvent. Yield of **2**: 85 % (0.980 g). M. p. above 300 °C. – $Sn_4C_8H_{24}Cl_4O_2$ (384.4): calcd. C 12.50, H 3.15; found C 12.26, H 3.13. – ^{1}H NMR ($CDCl_3$): δ = 1.15, 1.25. – ^{13}C NMR ($CDCl_3$): δ = 12.39, 13.70. – ^{119}Sn NMR ($CDCl_3$): δ = −60.83, −115.67. – IR: ν = 381.87 ν(Sn–Cl), 464.72 ν(Sn–O), 278.79 ν(Sn–C) cm^{-1}.

*Hydrolysis of **1** in basic medium*

(A) Using a nonpolar solvent: *Formation of tetramethyl/-tetraacetato-bis(μ-oxo)distannane (**3**)*

Compound **3** was obtained by treatment of compound **1** (1.60 mmol, 0.415 g) with sodium hydroxide (1.60 mmol, 0.064 g) in 20 mL of benzene. Although the sodium hydroxide did not dissolve in benzene after stirring for 5 – 6 h, it has reacted completely. The filtered solution was subjected to crystallization. After few days disc-shaped single crystals appeared at the bottom of round-bottomed flask. Yield 80 % (1.104 g). M. p. 55 °C. – $Sn_4C_{16}H_{36}O_{10}$ (863.3): calcd. C 22.26, H 4.20; found C 22.35, H 4.24. – ^{1}H NMR ($CDCl_3$): δ = 1.05, 1.15, 2.45. – ^{13}C NMR ($CDCl_3$): δ = 3.61, 29.70, 33.24, 206.43. – ^{119}Sn NMR ($CDCl_3$): δ = −47.51. – IR: ν = 1611.37 ν(CO) cm^{-1}.

(B) Using a polar solvent: *Formation of hexamethyl-1,3,5-trithia-2,4,6-tristannacyclohexane (**4**)*

Compound **4** was obtained following a procedure similar to that used for **3**. Only the solvent was changed from benzene to methanol. Sodium hydroxide (5.78 mmol, 0.231 g) was added to a solution of **1** (5.78 mmol, 1.5 g) in 20 mL of methanol. $Sn_3C_6H_{18}S_3$ (542.5): calcd. C 13.28, H 3.34, S 17.73; found C 12.80, H 3.22, S 17.53. – ^{1}H NMR ($CDCl_3$): δ = 0.8. – ^{13}C NMR (CDCl3): δ = 4.77. – ^{119}Sn NMR ($CDCl_3$): δ = 134.22.

X-Ray structure determination

Selected single crystals were mounted under an atmosphere of dry N_2 onto a glass fiber with lithelene and placed on the goniometer head cooled with nitrogen gas to −60 °C. X-Ray diffraction data were collected using an Enraf Nonius Kappa CCD diffractometer operating with MoK_α radiation. The unit cell dimensions were calculated from the data on a series of frames, usually from 3 sets of 20 frames. Data were collected in the hemisphere mode and reduced by using the program SMART [15]. The data were corrected for absorption. The SHELX system of programs [16] was used for structure solution and refinement.

Absorption correction for compound **3** reduced the *R* value from 0.050 to 0.028. The Flack parameter, after structure refinement, was initially 0.78. After inversion of the structure the value was reduced to 0.015(2) which corresponds to the absolute configuration shown in Fig. 5.

CCDC 705286 – 705288 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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