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Synthesis, Spectroscopic Studies and Crystal Structures of $[Et_2Sn(O_2AsMe_2)_2]$ and $[Ph_2Sn(O_2AsMe_2)(\mu\text{-}OMe)]_2$

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Abstract. $[Et_2Sn(O_2AsMe_2)_2]$ (**1**) and $[Ph_2Sn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**2**) were synthesized by treatment of Et_2SnO and Ph_2SnS with HO_2AsMe_2 in Methanol, respectively. The compounds were characterized by elemental analyses, vibrational spectroscopy and mass spectrometry. According to X-ray diffraction measurements compound **1** crystallizes monoclinic in space group $P2_1/n$ with cell parameters $a = 804.89(3)$, $b = 987.11(5)$, $c = 966.42(4)$ pm, $\beta = 113.354(3)°$. The unit cell parameters of **2**, which crystallizes in the same space group, are $a = 974.4(1)$, $b = 1463.3(1)$, $c = 1228.9(1)$ pm, $\beta = 111.324(3)°$. The $(SnOAsO)_4$ rings of **1** are linked and form a two-dimensional network with the SnEt groups pointing into the holes of the next layer. Compound **2** occurs as a dimer with internal $Sn(OMe)_2Sn$ bridges in the $(SnOAsO)_2$ rings. The vibrational and mass spectra are given and discussed.

1 Introduction

The reactions of diorganotin dichlorides R_2SnCl_2 with HO_2AsMe_2 in methanol at ambient temperature produce $[R_2ClSn(O_2AsMe_2)]$ (R_2 = Me_2, Et_2,[1] Bu_2[2]). Meanwhile $[Ph_3Sn(O_2AsMe_2)]$ and the dimer $[PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ were formed by the reaction of NaO_2AsMe_2 with Ph_3SnCl and Ph_2SnCl_2 respectively.[2] Crystalline $[Bu_2Sn(O_2AsMe_2)_2]$ was synthesized by the reaction of Bu_2SnO and HO_2AsMe_2.[3] X-ray diffraction studies of $[R_2ClSn(O_2AsMe_2)]$ and $[Ph_3Sn(O_2AsMe_2)]$ show that the O_2AsMe_2 groups behave as bidentate bridging ligands between the tin atoms, thus forming polymeric chain structures.[1,2] A two-dimensional polymeric structure with $(SnOAsO)_4$ sixteen-membered rings was reported for $[Bu_2Sn(O_2AsMe_2)_2]$.[3] An analogous polymeric structure with $(SnOPO)_4$ rings was found in $[Et_2Sn(O_2PMe_2)_2]$.[4] In addition, the tetramers $[Me_3Sn(O_2PPh_2)]_4$,[5] $[Me_3Pb(O_2PPh_2)]_4$,[6] and $[Bu_3Sn(O_2Pcyc)]_4$ (cyc = 1,1,2,3,3-pentamethyltrimethylene)[7] show also sixteen-membered ring structures with bridging phosphinato ligands between the metal atoms. Continuing our work on the preparation and structural studies of organotin dimethylarsinates, we describe here the synthesis and crystal structures of $[Et_2Sn(O_2AsMe_2)_2]$ (**1**) and $[Ph_2Sn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**2**). The vibrational and mass spectra are given and discussed.

2 Results and Discussion

The reaction of Et_2SnO with HO_2AsMe_2 in a 1:2 molar ratio in refluxing methanol leads to the formation of $[Et_2Sn(O_2AsMe_2)_2]$ (**1**). Treatment of Ph_2SnS with HO_2AsMe_2 in methanol at ambient temperature afforded $[Ph_2Sn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**2**) according to the following equation.

$$2Ph_2SnS + 2HO_2AsMe_2 + 2HOMe \rightarrow [Ph_2Sn(O_2AsMe_2)(\mu\text{-}OMe)]_2 + 2H_2S$$

The reactions of Ph_2SnCl_2 with NaO_2AsMe_2 and with HO_2PPh_2 in methanol produce also dimers containing MeO groups $[PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ and $[PhClSn(O_2PMe_2)(\mu\text{-}OMe)]_2$, which indicate that methanol behaves as solvent and reactant. X-ray diffraction studies show that **2** and $[PhClSn(O_2AsMe_2)(\mu\text{-}OMe)]_2$[2] are centrosymmetric dimers involving hexacoordinate tin atoms connected by two bridges of O_2AsMe_2 and two bridges of OMe groups forming $Sn_2O_4As_2$ eight-membered and Sn_2O_2 four-membered rings. A similar structure has been found for the analogous phosphorus-containing dimer $[PhClSn(O_2PMe_2)(\mu\text{-}OMe)]_2$.[8] Furthermore, $[Ph_2Sb(\mu\text{-}O)(O_2AsMe_2)]_2$, which was prepared by treatment of $(Ph_2SbBrO)_2$ with NaO_2AsMe_2 in CH_2Cl_2 shows a similar quadruply bridged structure with $Sb_2O_4As_2$ eight-membered and Sb_2O_2 four-membered rings.[9] It is worth noting, that $[(Me_2SnOSAsMe_2)_2O]_2$ was obtained by the reaction of Me_2SnS with HO_2AsMe_2 in methanol at ambient temperature.[3]

Vibrational Spectroscopy

Selected IR and Raman frequencies (Table 1) are assigned by comparison with the vibrational spectra of related organotin dimethylarsinates.[1–3] In agreement with bridging bidentate O_2AsMe_2 groups, the vibrational spectra of **1** and **2** exhibit

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ν(AsO_2) vibrations in the range between 790–900 cm^{-1}. The frequencies due to $\nu_{as}(AsC_2)$ and $\nu_s(AsC_2)$ appear in the region between 580–650 cm^{-1}.[10]

Table 1. Selected IR and Raman frequencies /cm^{-1} of **1** and **2**.

$[Et_2Sn(O_2AsMe_2)_2]$ (**1**)		$[Ph_2Sn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**2**)		Assignment
IR	Raman	IR	Raman	
		1018 s		ν(O-CH_3)
			999 vs	Ph ring breathing
897 vs	888 vw	900 w		ν(AsO_2)
	855 vs			ν(AsO_2)
	852 vs		851 w	ν(AsO_2)
819 vs	821 m-s	837 vs	817 vw	ν(AsO_2)
638 s	637 m	648 m	646 m	$\nu_{as}(AsC_2)$
		620 vw	620 w	(C-C-C) Ph bend
605 m	607 s-vs		611 m-s	$\nu_s(AsC_2)$
525 m				$\nu_{as}(SnC_2)$
		494 m	470 vw	ν(Sn-O-Sn)
	472 s-vs			$\nu_s(SnC_2)$
	429 m	450 vs	445 m	ν(Sn-OAs)
417 s	418 m			ν(Sn-OAs)
			258 w	$\nu_{as}(SnPh_2)$
			215 m	$\nu_s(SnPh_2)$

A comparison of the vibrational spectra of $[Et_2Sn(O_2AsMe_2)_2]$ (**1**) and the structural analogue $[Bu_2Sn(O_2AsMe_2)_2]$[3] shows that decreasing the size of the alkyl groups has little effect on the frequencies of the O_2AsMe_2 ligands.

The vibrational spectra of **1** show $\nu_{as}(SnC_2)$ at 525 cm^{-1} (IR) and $\nu_s(SnC_2)$ at 472 cm^{-1} (Raman), which is in agreement with a linear C–Sn–C arrangement. The bands at 494 cm^{-1} (IR) and 470 cm^{-1} (Raman) in the vibrational spectra of **2** are assigned to ν(Sn–O–Sn) vibrations. At 999 cm^{-1}, the Raman spectrum of **2** exhibits the characteristic and very strong band due to phenyl ring breathing.

Mass Spectrometry

Table 2 gives the characteristic ions in the EI mass spectra (70 eV) of compounds **1** and **2**. The mass spectrum of **1** shows the $[M - Et]^+$ ion (m/e = 423) in considerable abundance whereas the $[M - Ph]^+$ ion (m/e = 805) appears in the mass spectrum of **2** with low abundance. However the ion $Ph_3Sn_2(O_2AsMe_2)_2O^+$ (**2** minus Me_2O and Ph-group, m/e = 759) appears in high abundance. In agreement with the polymeric nature of **1**, the mass spectrum exhibits ions with masses greater than the molecular mass of the monomer. The peaks at 527 and 511 in the mass spectrum of **1** are assigned to $EtHSn_2O_4As_2Me_3^+$ and $EtHSn_2O_3As_2Me_3^+$ respectively. These ions may be formed by β-hydrogen elimination. The ion $Et_2Sn_2O_4As_2Me_3^+$ (m/e = 555) which appears in the spectrum of **1** has also been observed in the spectrum of $[Et_2ClSn(O_2AsMe_2)]$.[1] The spectra of **1** and **2** display the tin(II)-containing ion $Sn(O_2AsMe_2)^+$, which seems to be a characteristic feature in the mass spectra of organotin dimethylarsinates.[1–3] The mass spectrum of **2** shows the ions Ph_3Sn^+, Ph_2Sn^+, $PhSn^+$ in relatively high abundance. The appearance of Ph_3Sn^+ indicates a phenyl group transfer.

Structural Results

Sixteen-membered rings $(SnOAsO)_4$ occur as part of layered two-dimensional networks in **1** (Figure 1) and $[Bu_2Sn(O_2AsMe_2)_2]$.[3] Other examples of this structural arrangement are reported with phosphinate[4] and fluorosulfate bridging ligands.[11] Some characteristic properties of these layer compounds are listed in Table 3. The interlayer distance is shown to depend mainly on the organic tin substituent, and the mesh size to vary with the nature of the bridging ligand and layer folding. The planarity of the sheets as expressed in the deviation of the bridging atoms from the tin atom plane, is found equally high for the phosphinate and the arsinates. Severe folding in the fluorosulfate ligand is the reason for a small

Table 2. Characteristic ions formed in the 70 eV mass spectra of **1** and **2** (m/e /%).

	$[Et_2Sn(O_2AsMe_2)_2]$ (**1**)	$[Ph_2Sn(O_2AsMe_2)(\mu\text{-}OMe)]_2$ (**2**)
$Ph_3Sn_2(O_2AsMe_2)_2(OMe)_2^+$		805 (2)
$Ph_3Sn_2(O_2AsMe_2)_2O^+$		759 (90)
$PhSn_2(O_2AsMe_2)_2O^+$		605 (7)
$Et_2Sn_2O_4As_2Me_3{}^+$	555 (70)	
$EtHSn_2O_4As_2Me_3{}^+$	527 (18)	
$EtHSn_2O_3As_2Me_3{}^+$	511 (13)	
$Et_3SnO_2As_2Me_4{}^+$	449 (33)	
$EtSn(O_2AsMe_2)_2{}^+$	423 (14)	
$Ph_2Sn(O_2AsMe_2){}^+$		411 (9)
$EtSnO_2As_2Me_4{}^+$	391 (92)	
Ph_3Sn^+		351 (77)
Ph_2SnOMe^+		305 (18)
Ph_2Sn^+		274 (66)
$Sn(O_2AsMe_2){}^+$	257 (50)	257 (5)
$PhSn^+$		197 (65)
AsO_2^+	107 (92)	107 (100)
AsO^+	91 (100)	91 (46)

Table 3. Some characteristic properties of similar layer structures (rounded values).

	Space group	interlayer distance /pm	max. ring atom dev. of tin atom plane /pm	mesh size r(Sn–Sn)$_{\text{diag}}$ /pm
$[Et_2Sn(O_2PMe_2)_2]$[4]	$P2_1/n$	737	16	985/974
$[Et_2Sn(O_2AsMe_2)_2]$ (**1**) a)	$P2_1/n$	727	22	982/987
$[Bu_2Sn(O_2AsMe_2)_2]$[3]	*Pbca* (HT)	983	43	1003/975
$[Me_2Sn(O_2SOF)_2]$[11]	$P2_1/c$	695	153	814/834

a) Measured at 193 K. All other data taken from RT measurements.

mesh opening, and the low volumes of methyl group and bridging ligand are responsible for the shorter distance between the sheets.

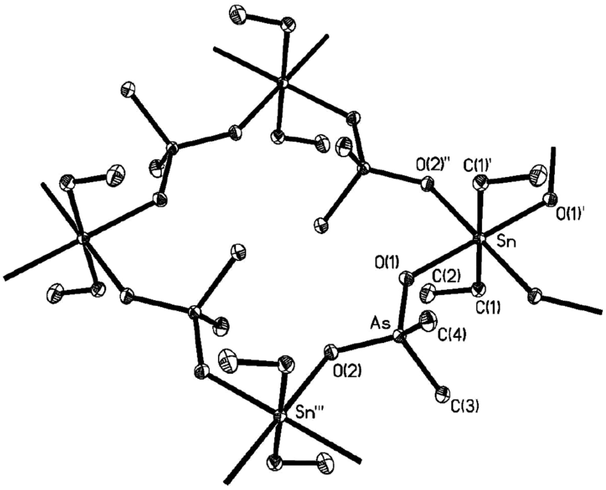

Figure 1. Perspective view[17] of a $(SnOAsO)_4$ mesh in the polymeric network **1** with the atomic numbering scheme. Thermal ellipsoids are shown at 50 % probability level.

Bond lengths and angles of compound **1** are summarized in Table 4. Octahedral configuration at the tin atom (max. deviation of 2.13° from 90°) and tetrahedral surrounding of the arsenic atom (max. dev. 2.39° from tetrahedral angle) are approximately realized. By comparing compound **1** with its isostructural phosphorus analogue,[4] it is obvious that the angles O–P–O and O–P–Sn in the ring are significantly wider than the corresponding angles in **1**. This is not only a sign of steric stress, but also hints enhanced multiple bond character in the short P–O bonds giving also rise to an increase in the Sn–O bond length (222.4(1)/221.8(1) pm vs. 218.5(1)/218.2(1) pm in the arsinate).

Table 4. Selected bond lengths /pm and angles /° for $[Et_2Sn(O_2AsMe_2)_2]$ (**1**).

Sn–C(1)	215.2(2)	O(1)–Sn–O(2)'	87.87(5)
Sn-O1, Sn–O(2)''	218.2(1),218.5(1)	O(1)–As–O(2)	107.42(7)
As–O(1), As–O(2)	168.3(1),168.3(1)	O(1)–As–C(3)	110.76(8)
As–C(3), As–C(4)	190.6(2), 190.9(2)	O(1)–As–C(4)	108.61(8)
		O(2)–As–C(3)	111.10(8)
As–O(1)–Sn	129.71(8)	O(2)–As–C(4)	111.89(8)
As–O(2)–Sn'''	131.70(7)	C(3)–As–C(4)	107.07(9)

Symmetry transformations used to generate equivalent atoms:
El' : $-x, -y + 1, -z + 1$;
El'': $x - 1/2, -y + 1/2, z - 1/2$;
El''' : $-x + 1/2, y - 1/2, -z + 3/2$

Compound **2** forms a centrosymmetric dimer consisting of $(Sn–O–As–O)_2$ eight-membered rings, in which the tin atoms are linked by two MeO^- bridges (Figure 2). An analogue configuration has been found for an arsinate[2] and a phosphinate,[8] in which the tin atoms are asymmetrically substituted by a chloride and a phenyl group causing the bridge to be strongly asymmetric on account of the different *trans*-positioned ligands. Bond lengths and bond angles (Table 5) correspond well with the values found in the above arsenate,[2] except for the angles O–As–O and Sn–O–Sn in the almost symmetrical MeO^- bridge, which are by 3° wider. This is in accordance with the greater Sn–Sn distance in **2** (347.97(2) pm as compared to 340.84(2) pm in the phenyl-chloro-substituted compound) and is due to the steric needs of the two phenyl groups. The two SnO_2 units within the eight-membered rings of the dimer are very neatly coplanar (max. deviation of the best plane 0.44 pm), and the arsenic atom is placed 44 pm from this plane. The configuration at the triply coordinated atom O(3) is pyramidal with an angular sum of 348°.

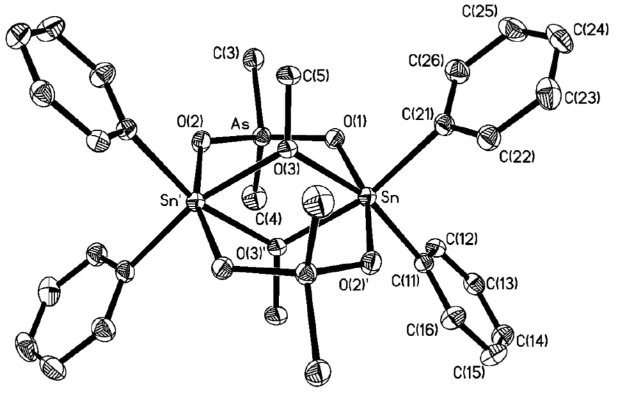

Figure 2. ORTEP[17] view of a dimeric molecule of **2** with displacement ellipsoids at 50 % probability level.

3 Experimental Section

The chemical reagents employed were obtained from commercial sources and were used without further purification. Sodium sulfide ($Na_2S\cdot xH_2O$, 60–62 %) was provided from Riedel-de Haën.

Ph_2SnS was prepared according to literature by treating Ph_2SnCl_2 with Na_2S.[12] Infrared spectra were measured using KBr pellets with a

Table 5. Selected bond lengths /pm and angles /° for [$Ph_2SnO_2AsMe_2(\mu$-OMe)]$_2$ (**2**).

Sn–O(1)/Sn–O(2)'	212.2(2)/211.3(2)	C(11)–Sn–C(21)	101.45(6)
Sn–O(3)/Sn–O(3)'	214.8(1)/215.7(1)	O(1)–Sn–O(2)'	163.00(6)
As–O(1)/As–O(2)	168.6(2)/167.8(2)	O(3)–Sn–O(3)'	72.15(6)
As–C(3)/As–C(4)	190.0(2)/190.9(2)	Sn–O(3)–Sn'	107.85(6)
Sn–C(11)/Sn–C(21)	218.2(2)/218.5(2)	O(2)–As–O(1)	116.08(7)
		C(3)–As–C(4)	109.5(1)
		As–O(1)–Sn	124.99(8)
		As–O(2)–Sn'	126.09(8)

Symmetry transformation used to generate equivalent atoms:
El' : $-x + 1, -y, -z + 1$

Bruker Instrument IFS 88. The Raman spectra were obtained using a Jobin Yvon Labram HR 800 instrument with 632.8 nm helium neon laser excitation. Mass spectra were recorded with a Finnigan MAT S (EI 70eV). The chemical analyses were carried out in the analytical laboratory of Fachbereich Chemie der Universität Marburg.

Synthesis of [$Et_2Sn(O_2AsMe_2)_2$] (1): Et_2SnO (0.39 g, 2 mmol) and HO_2AsMe_2 (0.55 g, 4 mmol) were mixed in methanol (50 mL). The reaction mixture was heated under reflux for 4h, filtered off and the mother liquor was set aside at ambient temperature in an open flask. After few days the formed precipitate was filtered off and recrystallized from methanol. The yield was 0.54 g.
$C_8H_{22}As_2O_4Sn$ (450.8): Calcd. C 21.31, H 4.92; found C 21.29, H 4.91

Synthesis of [$Ph_2Sn(O_2AsMe_2)(\mu$-OMe)]$_2$ (2): A solution of HO_2AsMe_2 (0.29 g, 2.1 mmol) in methanol (25 mL) was added to a solution of Ph_2SnS (0.30 g, 1.0 mmol) in 2:1 methanol/ethanol (150 mL). The mixture was set aside at ambient temperature in a closed flask. After 2d a small amount (yield 110 mg) of shiny crystals of **2** had formed and was filtered off.

X-ray Structural Investigations: The crystals of **1** and **2** were handled in oil, mounted on 0.2 mm cryoloops and measured at 193 K with a Stoe diffractometer IPDS I. After data reduction[13] both data sets were subjected to numerical absorption corrections. The structures were solved by direct methods and the models were refined by full-matrix least-squares methods.[14,15] Hydrogen positions were kept riding on calculated values. Crystal Data, experimental details, and details about structure solution and refinement may be taken from Table 6. The geometric calculations were made with PLATON.[16]

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nrs. CCDC-872551 (**1**) and -872550 (**2**). Details are available, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-Mail deposit@ccdc.cam.ac.uk).

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Table 6. Crystallographic and measurement data for the structures of **1** and **2**.

	1	**2**
Formula, *M*	[$Et_2Sn(O_2AsMe_2)_2$], 450.79	[$Ph_2SnO_2AsMe_2(\mu$-OMe)]$_2$, 881.82
Crystal size/mm	0.27 × 0.13 × 0.11	0.15 × 0.12 × 0.09
Space group	$P2_1/n$, $Z = 2$	$P2_1/n$ $Z = 2$
a /pm	804.89(3)	974.4(1)
b /pm	987.11(5)	1463.3(1)
c /pm	966.42(4)	1228.9(1)
β /°	113.354(3)	111.324(3)
Cell volume /m^3	704.93(5) × 10^{-30}	1632.2(1) × 10^{-30}
Density /Mg·m^{-3}	2.124	1.794
Absorption coefficient μ /mm^{-1}	6.465	3.581
Absorption corr. Type, T_{min}/T_{max}	numerical, 0.3575/0.6134	numerical, 0.5993/0.7787
Diffractometer type	IPDS I (Stoe)	
Radiation	Mo-K_α, graphite monochromator	
Measuring range *hkl*	$-10 \leq h \leq 11$ $-13 \leq k \leq 13$ $-13 \leq l \leq 12$	$-12 \leq h \leq 12$ $-18 \leq k \leq 18$ $-15 \leq l \leq 15$
Measuring range, max. Θ	29.14°	26.76°
Reflections (total)	10218	12438
Reflections unique/observed	1900/1780 >2σ(*I*)	3461/3071 >2σ(*I*)
Refined parameters	86	166
Programs used	SHELXS-97, SHELXL-97,[15] SHELXTL,[17] WINGX[14]	
Extinction coeff. (SHELXL)		0.0015(2)
$wR2(F^2)/R$(observed *F*)	0.0509/0.0201	0.0480/0.0191
Goodness of Fit *S*	1.061	1.020
final diff. electron density max./ min. /e·Å^{-3}	0.736/–0.717	0.602/–0.438

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