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SYNTHESIS, INFRARED, MÖSSBAUER, NMR SPECTROSCOPIC CHARACTERISATION AND X-RAY STRUCTURE OF $[(Ph_3Sn)_2O_4Se]1.5H_2O$, $[(Me_3Sn)_2O_4Se](OH_2)_2$ and $[Me_3SnO_2AsMe_2]0.5H_2O$.

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Résumé : $[(Ph_3Sn)_2O_4Se]1.5H_2O$ (**1**), $[(Me_3Sn)_2O_4Se](OH_2)_2$ (**2**) et $[Me_3SnO_2AsMe_2]0.5H_2O$ (**3**) ont été synthétisés et caractérisés par spectroscopies infrarouge, Mössbauer et RMN. Les structures de ces composés ont aussi été déterminées par diffraction aux rayons X. Les différentes techniques spectroscopiques utilisées ont permis de montrer la présence d'étain dans un environnement bipyramidal trigonal dans tous les composés. Dans le cristal de **1** les résidus Ph_3Sn sont reliés dans des chaînes infinies par des ions séléniate pontants. Les séléniates sont à leur tour reliés à des groupes $Ph_3Sn(OH_2)$. Les différentes chaînes sont liées par des liaisons hydrogènes entre l'oxygène libre des séléniates et les molécules d'eau. La structure moléculaire de **2** est constituée d'unités de $[(Me_3Sn)_2O_4Se]$ discrètes, liées par des ponts hydrogènes. La structure de **3** est constituée de chaînes infinies contenant des ligands diméthylarséniates pontants, les différentes chaînes sont liées par des liaisons hydrogènes par l'intermédiaire de molécules d'eau.

Mots clés : Infrarouge ; Mössbauer; RMN, Rayons X ; trimétylétain ; triphenylétain ; séléniate ; diméthylarséniate.

Summary: $[(Ph_3Sn)_2O_4Se]1.5H_2O$ (**1**), $[(Me_3Sn)_2O_4Se](OH_2)_2$ (**2**) and $[Me_3SnO_2AsMe_2]0.5H_2O$ (**3**) were synthesized and characterised by infrared, Raman, Mössbauer and NMR techniques and their crystal structures determined by x-ray diffraction. Infrared and Mössbauer spectroscopies, in the solid state, and NMR spectroscopy, in solution, reveal the presence of trigonal bipyarmidal tin centres in all derivatives. In the structure of **1**, Ph_3Sn moieties are bridged together in polymeric chains by means of the selenate anions, each selenate being also bonded to a pendant hydrated $Ph_3Sn(OH_2)$ group. Cross-linking is provided by hydrogen bonds between the water molecules of one chain and the free oxygen atom of the selenate groups of adjacent chains. The structure of **2** consists of discrete units of bis[aquatrimethyltin(IV)]selenate in which the selenate anion behaves as a bidentate ligand. The different units are connected via a network of hydrogen bonds. The structure of **3** consists of one-dimensional polymeric chain involving Me_3Sn moieties axially bridged through dimethylarsonate ligands. Parallel chains are linked via hydrogen bonds.

Keywords: Infrared, Mössbauer; NMR; X-ray; trimethyltin(IV); triphenyltin(IV) derivatives; selenate; dimethylasonate.

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I. INTRODUCTION

The interest in synthesising new organotin derivatives is related to their biological and pharmaceutical applications in different fields (agrochemicals, surface disinfectants, wood preservatives, and marine-antifouling paints) [1]. Structural and bonding details of organotin derivatives have received wide attention these last years in searching to correlate the structural parameters with physical and chemical properties of these compounds. Reports on structure determinations or spectroscopic characterisations of trimethyl- and triphenyltin(IV) derivatives with mono- and polybasic oxyanions (XO_m^{n-} ; X=Cr, Se, S, P, Cl, Se, N; m=3, 4 and n=1, 2, 3) show that the oxyanions behave mainly as polydentate ligands involving a one-dimensional polymeric, bi- or tridimensional network structure [2]. These derivatives exhibit a rich diversity of geometries even if small changes in the structure of the group around the central tin atom are made. Examples of this feature are the related compounds, $[(Ph_3Sn)(H_2OSnPh_3)SO_4]_n$[3], $[Me_3SnO_2P(OH)(Me)]_n$ and $[Me_3SnO_2As(OH)(Ph)]_n$ [4], $[Et_4N][(Me_3Sn)_7(O_3As(OH))_4]$ [5]; in each case the structure consists of a one or three-dimensional, polymeric array involving R_3Sn (R = Me, Ph) moieties axially-bridged through either sulphate, methylphosphonate, phenylarsonate or monohydrogenoarsonate ligands. The tin atoms in each case are in a *trans*- O_2SnC_3 trigonal bipyramidal environment. Hydrogen bonds ensure the compactness of the structures featuring the presence of cavities that can be occupied by cations.[5] A one dimensional polymeric layered structure has also been obtained in the cases of $[(H_2OSnPh_3)_2SO_4]_n$ [6], $[(Me_3SnO_3Se)(H_2OSnMe_3)]$ [7] and $[(H_2OSnMe_3)_2C_2O_4]_n$ [8]. As a continuation of our work on the elucidation of structures of organotin derivatives containing tetrahedral or pseudo-tetrahedral oxyanions we report here a spectroscopic characterisation and the crystal structures of [triphenyltin(IV)][aquatriphenyltin(IV)]selenate, bis(aquatrimethyl)selenate and trimethyltin(IV) dimethylarsonate.

II. EXPERIMENTAL

2.1 Materiel and Methods

$SnMe_3Cl$, KOH, Ph_3SnOH and the acids $(HO)_2SeO_2$ and $(HO)As(O)(CH_3)_2$ were purchased from Aldrich Chemicals and used without further purification. Me_3SnOH was obtained by reacting $SnMe_3Cl$ with KOH in methanol and filtering the precipitate of KCl.

Details of our infrared and Mössbauer spectrometers and data collection procedures are reported elsewhere [9-10]. The Raman spectrum of a polycrystalline sample sealed in glass tube was obtained on a T 800 CODERG triple monochromator using 5154 Å line of a Spectraphysics Ar^+ laser. NMR spectra for **1**, **2** and **3** were recorded as saturated CD_3OD (**1**) and $CDCl_3$ (**2**, **3**) at room temperature, using a Bruker 300 MHz spectrometer. The ^1H, ^{13}C and ^{119}Sn NMR were measured at 300.13, 75.47 and 111.92 MHz, respectively. ^1H and ^{13}C NMR chemical shifts and $\delta(^{119}Sn)$ NMR are given in ppm and are referred respectively to TMS and $SnMe_4$ all set to 0.00 ppm; the coupling constants are in Hz. Elemental analyses of **1**, **2,** and **3** were performed using an Exeter Analytical CE 440 analyser. Infrared data are given in cm^{-1}. Abbreviations: br = broad, s = strong, vs = very strong, m = medium, sh = shoulder, w = weak. Mössbauer parameters are given in mms^{-1}: QS = quadrupole splitting, IS = isomer shift, Γ = FWHH (full width at half-height).

2.2 Synthesis

Compounds **1-3** were obtained by the condensation, in ethanol, of the appropriate acid with triphenyltin hydroxide (**1**) or trimethyltin hydroxide (**2**, **3**) in 1:2 (**1**, **2**) or 1:1 (**3**) ratio. The mixtures were stirred for several hours at room temperature and slow solvent evaporation gives crystals suitable for X-ray analysis. Colourless crystals were obtained for **1** (53%) **2** (43 %) and **3** (46 %).

2.3 Spectroscopic characterisation

[triphenyltin(IV)][aquatriphenyltin (IV)]selenate $[(Ph_3Sn)_2O_4Se]1.5H_2O$ (1): Analytical data: [%Found (%calcd.) For $C_{72}H_{64}O_{10.5}Se_2Sn_4$] C 54.31 (54.38), H 3.77 (3.71), Sn 22.15 (22.21). Infrared data *(cm^{-1})*: 3520 br νH_2O, 1650m δH_2O, 904 sh, 845 w, 825 sh (ν_3); 407 w (ν_4), 277vs $\delta_{as}SnC_3$, 231sh $\delta_{as}SnC_3$, 214sh ν_sSnC_3, 177s δ_sSnC_3. Mössbauer data *(mm/s)*: IS=1.69, QS=3.72, Γ=0.97. NMR data [CD_3OD; δ(ppm); ^nJ (Hz)]: ^{1}*H NMR*: δ(phenyl protons): [7.90 - 6.90 (m) H]. ^{13}*C NMR:* 141.2[C-i, $^1J(^{119}Sn-^{13}C)$=784.0], 137.6 [C-o, $^2J(^{119}Sn-^{13}C)$=46.8], 130.8 C-p, 129.8 [C-m, $^3J(^{119}Sn-^{13}C)$=69.76]. ^{119}Sn NMR: δ(^{119}Sn) =-213.0

bis-(aquatrimethyltin(IV))selenate *$[(Me_3Sn)_2O_4Se](H_2O)_2$ (2)* : Analytical data: [%Found (%calcd.) For $C_6H_{22}O_6SeSn_2$] C 14.31 (14.25), H 4.47 (4.34). Infrared data *(cm^{-1})*: 3514 br νH_2O, 1647m δH_2O, 910 sh, 878 w, 845 sh (ν_3); 450 m (ν_4), 570 $\nu_{as}SnC_3$, 508 trace ν_sSnC_3. Mössbauer data *(mm/s)*: IS=1.42, QS=3.92, Γ=0.93. NMR data [$CDCl_3$ δ(ppm); ^nJ (Hz)]: ^{1}*H NMR*: 0.53 [s, $Sn(CH_3)_3$; $^2J(^{119,117}Sn-C-H)$ = 71.4, 69.1]. ^{13}*C NMR*: 3.0 [s, $Sn(CH_3)_3$; $^1J(^{119,\ 117}SnC)$ = 570.8, 510.5]. ^{119}*Sn NMR*: -27.5.

trimethyltin(IV)dimethylarsonate monohydrate $[Me_3SnO_2AsMe_2]0.5H_2O$ (2): Analytical data: [%Found (%calc. for $C_{10}H_{32}As_2O_5Sn_2$)]: C 18.93 (19.02), H 5.04 (5.12). Infrared data *(cm^{-1})*: 3482 br νH_2O; 1619 w νH_2O; 880 s, 751 s νAsO_3; 634 s, 600 m νAsC_2; 468 m, 391 s δAsO_3; 544vs $\nu asSnC_3$; 511 trace $\nu sSnC_3$. Mössbauer data *(mm/s)*: I.S. =1.25, Q.S. =3.84, Γ = 0.80. NMR data [$CDCl_3$ δ(ppm); ^nJ (Hz)]: ^{1}*H NMR*: 0.46 [s, $Sn(CH_3)_3$; $^2J(^{119,117}Sn-C-H)$ = 72.0, 68.7]. ^{13}*C NMR*: 3.7 [s, $Sn(CH_3)_3$; $^1J(^{119},\ ^{117}SnC)$ = 568.2, 510.5]. ^{119}*Sn NMR*: -23.6.

2.4 X ray data collection:

General crystal and experimental details are reported in Table 1. Data collection was carried out at 150(2) K (for **1**, **2** and **3**) on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream crystal cooling apparatus. The data were corrected for Lorentz and polarisation effects and for absorption (except **1**). The structures were solved using direct-methods (SHELXS-86) [11] and each refined by a full-matrix least-squares procedure based on F^2 using

Table I: *Crystal data for* $[(Ph3SnO_4Se)(H_2OPh_3Sn)]0.5H_2O$ (**1**) $[(Me_3Sn)_2O_4Se](OH_2)_2$ (**2**) *and* $[Me_3SnO_2AsMe_2]0.5H_2O)$ (**3**).

	1	**2**	**3**
Empirical formula	$C_{72}H_{64}O_{10.5}Se_2Sn_4$	$C_6H_{22}O_6SeSn_2$	$C_{10}H_{32}As_2O_5Sn_2$
Formula weight	1629.92	506.58	619.58
Crystal size, mm	0.30 x 0.30 x 0.25	0.3 x 0.3 x 0.25	0.30 x 0.30 x 0.15
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	orthorhombic	Monoclinic
Space group	$P2_12_12_1$	P n c a	$P\ 2_1/n$
a (Å)	16.9510(1)	10.67500(10)	10.9350(1)
b (Å)	19.8020(1)	11.42400(10)	14.3350(1)
c (Å)	20.02300(10)Å	12.9310(2)	13.7640(1)
β (°)			107.5330(10)
V (Å^3)	6720.99(6)	1576.95(3)	2057.32(3)
Z	4	4	4
Theta range (°)	3.13 to 30.06	4.09 to 25.02	3.91 to 30.08
Independent reflections	19641 [R(int) = 0.0561]	1359 [R(int) = 0.0348]	5992 [R(int) = 0.0740]
Reflections observed $I>2\sigma(I)$	17795	1356	5678
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.025$ $wR_2 = 0.046$	R1 = 0.020, wR2 = 0.051	$R_1 = 0.031$, $wR_2 = 0.080$
R indices (all data)	$R_1 = 0.033$ $wR_2 = 0.048$	R1 = 0.021, wR2 = 0.051	$R_1 = 0.033$, $wR_2 = 0.082$
Largest diff. Peak and hole (eÅ^3)	0.737 and -0.727	0.457 and -0.633	1.065 and -1.308
Deposition number	CCDC 241567	CCDC 283468	CCDC 241566

SHELXL-97 [12] with anisotropic displacement parameters for all non-H atoms.

III. RESULTS AND DISCUSSION

3.1 Spectroscopic studies

3.1.1Infrared spectroscopy

In the case of the selenato derivative (**1**), the non splitting of the antisymmetrical stretching vibration (ν_2) of the SeO_4^{2-} anions which appears as a strong band centered at 845 cm^{-1} (in the case of **1**) and at 878 cm^{-1} (in the case of **2**) and the absence of a band due to ν_1 allow to conclude to the presence of tetrahedral oxyanion in these compounds, according to Nakamoto col. [13].

According to previous studies [14-19] on triorganotin (IV) compounds, two strong or medium absoption bands are generally present in the 600-500 cm^{-1} region (trimethyltin) and 200-300 cm^{-1} region (triphenyltin). They are due to $\nu_{as}SnC_3$ and ν_sSnC_3 vibrations and their presence is consistent with C_{3v} symmetry of the SnC_3 groups (in this case the SnC_3 groups are not planar). The presence of a single band due to the Sn-C stretching vibrations ($\nu_{as}SnC_3$) in the 600-550 cm^{-1} region (trimethyltin) and around 275 cm^{-1} (triphenyltin) is consistent with D_{3h} sylmetry for the SnC_3 groups (in this case the SnC_3 groups are planar). The trace at 508 cm^{-1} in the infrared spectrum of **2,** due to ν_sSnC_3, can be interprtate by the presence of an almost planar SnC_3 framework while the presence of ν_sSnC_3, as a shoulder in the spectrum of **1** at 214 cm^{-1}, indicate the presence of non planar SnC_3 groups.

In the case of the pseudo tetrahedral substituted oxyanion, $Me_2AsO_2^-$, it is not possible to correlate the point group symmetry with the number of bands observed in the infrared spectrum, according to Nakamoto col. [13]. The main structural information that can be obtained from the infrared spectrum of (**3**) is the absence of band due to ν_sSnC_3 in the 500-600 cm^{-1} region which correlates with the presence of a planar SnC_3 moiety (symmetry D_{3h}) in (**3**).

3.1.2 Mössbauer spectroscopy

The Mössbauer spectra of the derivatives (**1**), (**2**) and (**3**) show, in each case, a slightly asymmetric quadrupole split doublet with an isomer shift value [1.69 mm/s (**1**), 1.25 mm/s (**2**) and 1.42 mm/s (**3**)] in the normal range for organometallic tin(IV) derivatives. The quadrupole splitting values [3.72 mm/s (**1**), 3.92 mm/s (**2**) and 3.84 mm/s (**3**)] are consistent with *trans*-coordinated R_3Sn residues (R= Ph, Me), accordind to Davis and col. [20].

3.1.3 NMR spectroscopy

The values of $\delta(^{119}Sn)$ and those observed for $^nJ(^{119}Sn-^{13}C)$ coupling constants are consistent with five coordinated tin(IV) centres in all derivatives. The chemical shift value in (**1**), $\delta(^{119}Sn)$ (-213 ppm) and $^1J(^{119}Sn-^{13}C)$ (784 Hz) indicate the presence of unambiguously *trans*-coordinated Ph_3Sn residues in solution [21]. In the cases of the trimethyltin derivatives (**2** and **3**), $\delta(^{119}Sn)$ = -27.5 ppm (**2**) and -23.6 ppm (**3**), these values of chemical shift and those of the coupling constants, [$^1J(^{119,\ 117}Sn-^{13}C)$ = 570.1 and 511.8 Hz and $^2J(^{119,\ 117}Sn-C-H)$ = 71.4 and 69.1 Hz (**2**)] and [$^1J(^{119,\ 117}Sn-^{13}C)$ = 568.2 and 510.5 Hz and $^2J(^{119,\ 117}Sn-C-H)$ = 72.0 and 68.7 Hz (**3**)], are consistent with the presence of *trans*-O_2SnC_3 moieties in solution. In the cases of Me_3SnCl and the isomeric trimethyltin(IV) 1- and-2naphtoates, where the environment around the tin centre is tetrahedral, $\delta(^{119}Sn)$ values are 50, 138 and 139 ppm, respectively [20, 22].

Both infrared and Mössbauer data in the solid state and the NMR data, in solution, of the derivatives (**1**-**3**) are consistent with trigonal bipyramidal environment around the tin centres.

3.2 X-rays structures

3.2.1 Description of the structure of [triphenyltin(IV)][aquatriphenyltin(IV)] selenate (1)

Figure 1 shows the asymmetric unit with the labelling scheme used in the text and a view of the crystal packing with the hydrogen bonds network in Figure 2. The asymmetric unit, indicated by unprimed atoms in Figure 1, consists of four triphenyltin moieties, two selenates and three water molecules. The lattice structure consists of polymeric chains of triphenyltin(IV)-O-selenato $SnPh_3OSeO_3$

groups with pendant aqua triphenylstannyl(IV) groups, $SnPh_3OH_2$ or $SnPh_3(OH_2)_{1.5}$.

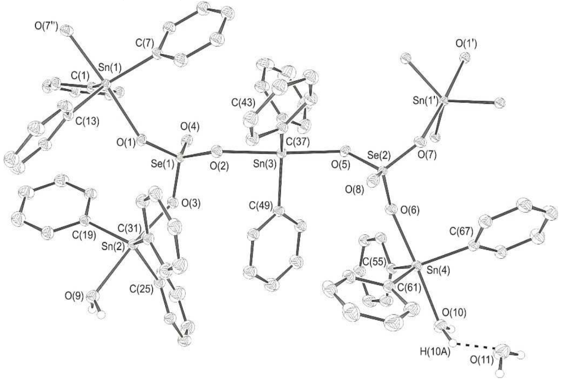

Figure 1: The asymmetric unit of $[(SnPh_3)_2O_4Se]1.5H_2O$ showing the labelling scheme used in the crystallographic tables (the H atoms have been omitted for clarity). Selected bond distances (Å) and angles (˚): Sn1-O1 2.3095(17), Sn1-O7 2.2505(17), Sn2-O3 2.2032(18), Sn2-O9 2.3502(19), Sn3-O2 2.2793(17), Sn3-O5 2.2457(17), Sn4-O6 2.2169(17), Sn4-O10 2.2972(19), Se1-O1 1.6390, Se1-O2 1.6436, Se1-O3 1.6601, Se1-O4 1.6106, Se2-O5 1.6488, Se2-O6 1.6388, Se2-O7 1.6386, Se2-O8 1.6207. C1-Sn1-C7 116.65(10), C1-Sn1-C13 117.14(10), C7-Sn1-C13 126.13(10), C19-Sn2-C25 112.20(10), C19-Sn2-C31 124.63(10), C25-Sn2-C31 122.33(10), C37-Sn3-C43 119.30(10), C37-Sn3-C49 118.14(10), C43-Sn3-C49 122.52(10), C55-Sn4-C61 123.78(10), C55-Sn4-C67 115.61(10), C61-Sn4-C67 120.55(10), O1-Sn1-O7 175.94(7), O3-Sn2-O9 173.89(7), O2-Sn3-O5 176.73(7), O6-Sn4-O10 177.34(8).

The structure contains two types of tin centres in a trigonal bipyramidal environment: Sn1, Sn3 (involved in the chain) and Sn2, Sn4 (of the pendant aquatriphenyltin). The trigonal planes of the two types of tin centres are defined by the three ipso carbon atoms of the phenyl groups. While the axial positions of the tin(IV) atoms in the chain are occupied by two oxygen atoms of the selenates anions [O1, O7 (Sn1) and O2, O5 (Sn3)] and those of the tin centres in the pendant aquatriphenyltin(IV) by one oxygen atom derived from the selenate anions and the oxygen atom of the coordinated water molecules [O3, O9 (Sn2) and O6, O10 (Sn4)]. The sum of the C-Sn-C angles around the four tin centres is very close to 360° and the O-Sn-O angles deviate only slightly from linearity (O7-Sn1-O1=175.94(7)°, O3-Sn2-O9 = 173.89(7)°, O5-Sn3-O2=176.73(7)° and O6-Sn4-O10 = 176.0(5)°). The Sn-O distances are not equivalent, the largest difference is observed in the pendant aquatriphenyltin(IV)-O-selenato groups, [Sn2-O3 (selenate)= 2.2032 Å and the corresponding Sn2-O9 (water)= 2.3502 Å]. The Sn-O bond lengths in the aquatriphenylstannyl (Sn2-O9 and Sn4-O6) are in the normal range of those reported for $Sn-OH_2$ [2.14-2.47] [6]. The Se1-O bond distances (1.6390 and 1.6436 Å), which form part of the O_2SnC_3 group in the chain, are almost equivalent and slightly shorter than the Se1-O3 linked to the aquatriphenylstannyl groups (Se1-O3=1.6601 Å). The interaction of a second water molecule with the $Ph_3Sn(OH_2)$ probably shortens the Se-O bond distance (Se1-O3=1.6601 and Se2-O6=1.6388 Å). Of the Se-O bonds, the distance between the non-tin coordinated oxygen and the Se atoms are the shorter (Se1-O4=1.6106

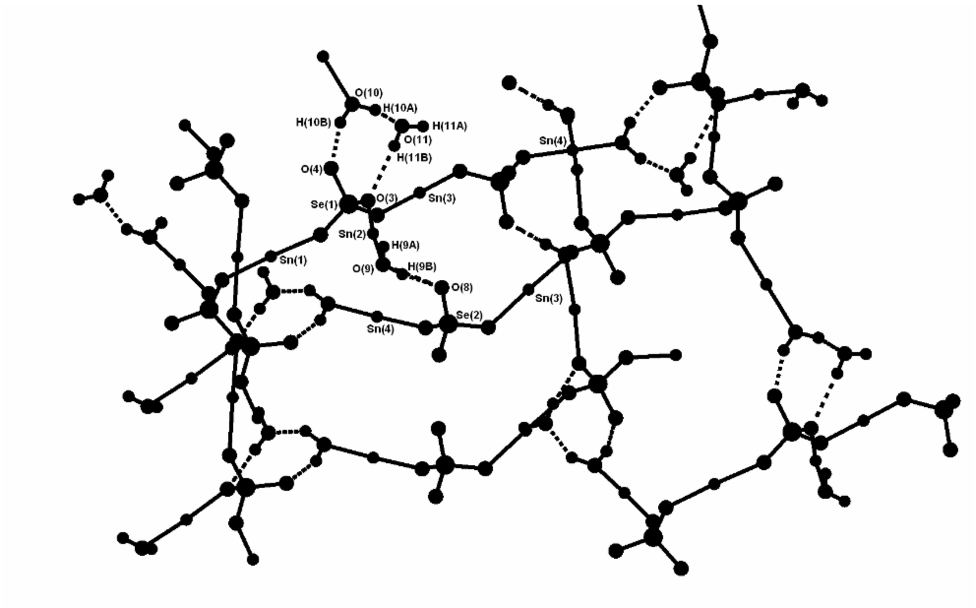

Figure 2: Three-dimensional propagation of the [(SnPh$_3$)$_2$O$_4$Se]1.5H$_2$O showing the hydrogen bonds network.

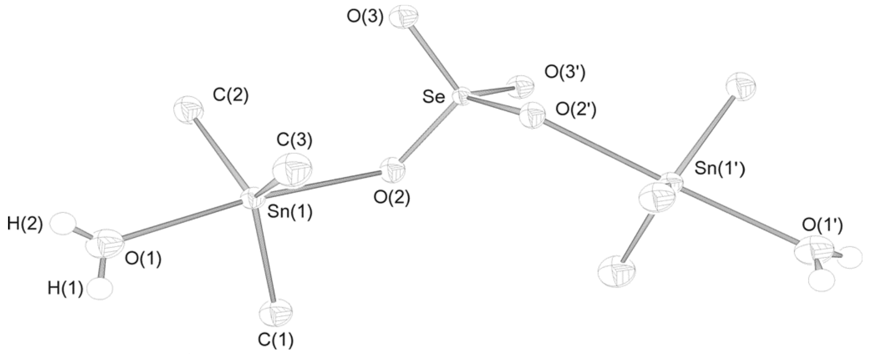

Figure 3: Asymmetric unit of [(Me$_3$Sn)$_2$O$_4$Se](OH$_2$)$_2$ (**2**) showing the labelling scheme used in the crystallographic table (the H atoms have been omitted for clarity). Selected bond distances (Å) and angles (˚): Sn-O1 2.300(3), Sn-O2 2.252(2), Se-O2 1.644(2), Se-O2' 1.644(2), Se-O3 1.631(2), Se-O3' 1.631(2). Symmetry transformations used to generate equivalent atoms: ' 1/2-x, 1-y, z. C1-Sn-C2 122.36(16), C1-Sn-C3 119.59(17), C2-Sn-C3 117.99(17), O1-Sn-O2 171.64(9), O2-Se-O3 110.27(11), O2-Se-O2' 109.80(17), O2-Se-O3' 106.58(11), O2'-Se-O3 106.58(11), O2'-Se-O3' 110.27(11), O3-Se-O3' 113.33(17). Symmetry transformations used to generate equivalent atoms: ' 1/2-x, 1-y, z.

and Se2-O8=1.6207 Å), probably these oxygen atoms are double bonded to the Se atom.

Hydrogen bonds between the two selenates anions of the asymmetric unit and the water molecules lead to the formation of cavities. The three water molecules have different behaviour: coordinated water O10 uses both hydrogens [O4…H10B-O10, symmetry operation –x, y-1/2, 3/2-z and O11…H10A-O10 of asymmetric unit]; coordinated water O9 uses only one hydrogen [O8…H9A-O9, symmetry operation +x, -y, 1-z] and the non coordinated water O11 acts as a donor through only one H [O3…H11B-O11, symmetry operation –x, +y, 3/2-z] and an acceptor to H10A, as above. Of the selenate oxygens, O4 and O8 are the primary H-bond acceptors, O3 is an acceptor to the water of solvation. A similar pattern of hydrogen bonds, ensuring the compactness of the structure, has already been observed in $SO_4(SnMe_3)_2.2H_2O$,[6] $SeO_3(SnMe_3)_2.H_2O$ [7] and $C_2O_4(SnMe_3)_2.2H_2O$ [8].

3.2.2 Description of the structure of bis(aquatrimethyltin)selenate.

The asymmetric unit of derivative (**2**) is shown in Figure 3. The structure of bis(aquatrimethyltin(IV))selenate consists of molecules in which a bidentate SeO_4 unit binds two Me_3Sn moieties.

The environment around the selenate atom is nearly tetrahedral (average of the O-Se-O angles = 109.98°). The two tin centres in the molecule have a trigonal bipyramidal environment and are bonded to two different oxygen atoms on the apical positions (one from the selenate, O2, and the other from the water molecule, O1). Such feature around tin has already been reported for analogous hydrates of trimethyltin sulphate[6], selenite [7], oxalate [8], nitrate [23]] and benzenesulphonate [24]. The tin atom coordinates the water molecule rather more weakly than the selenate [Sn1-O1 = 2.300(3) and Sn1-O2= 2.252(2),]. The coordinated solvent molecules (H_2O) plays an important role by generating a network of weak hydrogen bonds, as in the previous compound (**1**). O3 and O3' forms each one a pair of hydrogen bond as featured in Figure 4.

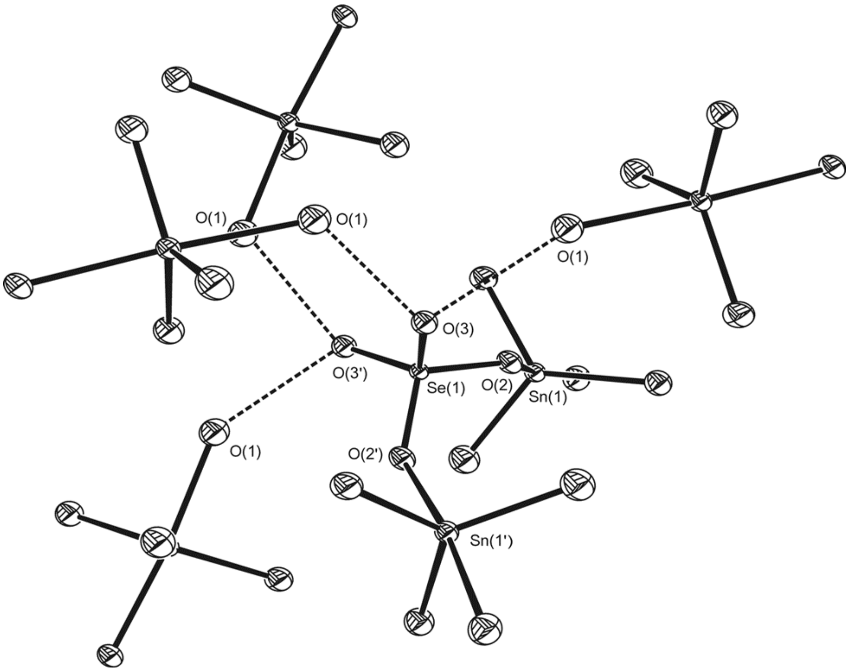

Figure 4: Three-dimensional propagation of the $[(Me_3Sn)_2O_4Se](OH_2)_2$ (**2**) showing the hydrogen bonds network.

3.2.3 Description of the structure of aquatrimethyltindimethylarsonate.

The asymmetric unit of (**3)** showing the labelling scheme used in the text and tables is shown in Figure 5. The crystal structure of $[Me_3SnO_2AsMe_2]0.5H_2O$ (**3**) consists of a one-dimensional polymeric chains along the *a* axis of the unit cell. The crystallographic asymmetric unit includes two independent Me_3Sn and two dimethylarsonato groups and one water molecule. Both tin atoms of the asymmetric unit are five-coordinated, the trigonal bipyramidal Me_3Sn units are axially bridged through the dimethylarsonato groups which behave as a bidentate ligand. The O2-Sn2-O3 and O1-Sn1-O4' angles [176.48(8), and 174.48(9)°] deviate slightly from linearity and the C-Sn-C angles are close to 120° (average sum of angles at tin 359˚). Three Sn-O bonds are almost equivalent (Sn1-O1 2.196(2) Å, Sn1-O4 2.219(2) Å, Sn2-O2 2.207(2) Å) and slightly shorter than Sn2-O3 (2.277(2) Å), which is involved in the hydrogen bond.

The As-O bond distances are essentially equivalent (As1-O1 1.672(2) Å, As1-O2 1.682(2) Å), the difference in the As-O bond is less than 0.015 Å in the two different AsO_2 groups. This allows us to conclude there is a redistribution of the negative charge equally between the two oxygen atoms rendering the As-O bonds equivalent. The geometry around the arsenic atom is approximately tetrahedral, although the three angles involving the oxygen atoms are markedly larger (by ca. 3°) than the C-As-C angles, this is due to the steric effect of the Me_3Sn groups. Unlike structures **1** and **2**, the water of solvation in **3** [O(5)] is not directly bonded to tin. Failure to locate the hydrogen atoms attached to O(5) precludes a detailed analysis of the hydrogen bonding pattern. However, O(5) is clearly hydrogen bonded to O(3) of one arsonate ligand (O3-O5 = 2.882 Å), and seems to play some role in linking adjacent chains by virtue of a long (3.651 Å)

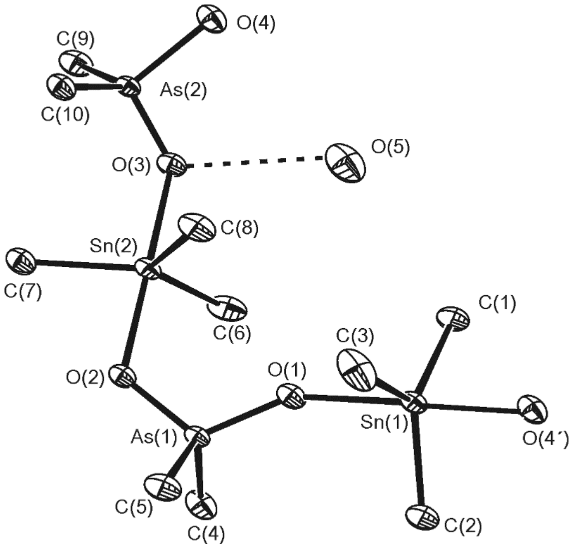

Figure 5: Asymmetric unit of $[Me_3SnO_2AsMe_2]0.5H_2O$ showing the labelling scheme used in the crystallographic table (the H atoms have been omitted for clarity). Selected bond distances (Å) and angles (˚): Sn1-O1 2.196(2), Sn1-O4 2.219(2), Sn2-O2 2.207(2), Sn2-O3 2.277(2), As1-O1 1.672(2), As1-O2 1.6822, As1-C4 1.909(3), As1-C5 1.913(3). C1-Sn1-C2 124.05(14), C1-Sn1-C3 118.37(16), C2-Sn1-C3 117.58(17), C6-Sn2-C8 120.00(14), C6-Sn2-C7 119.58(16), C7-Sn2-C8 120.26(15), O1-Sn2-O4 174.48(9), O2-Sn2-O3 176.48(8).

contact to symmetry related O(5) (1-x, 1-y, 1-z), which presumably also represents another weak hydrogen bonding interaction.

IV. CONCLUSION

In these compounds the oxyanions behave as multidentente ligands. From infrared study the selenate anions appear to have tetrahedral symmetry, this has been evidenced by crystallographical studies. All compounds feature a network of hydrogen bonds that ensure the compactness of the structure.

V. SUPPLEMENTARY MATERIEL

CCDC numbers 241567, 283468 and 241566 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. 11

BIBLIOGRAPHY

[1].a. A. G. Davies, P. J. Smith in Wilkinson G, Stone FGA, Abel EA 12
(Eds), Comprehensive Organometallic Chemistry. Pergamon Press. Oxford, 1982, p. 610. 13

b. M. H. Gitlitz, Adv. Chem. Ser., 157 (1976) 167.

[2].a. E. R. T Tiekink, J. Organomet. Chem., 302 (1986) C1.

b. J. Kummerlein, A. Sebald, H. Reuter, 14
J. Organomet. Chem., 427 (1993) 309.

c. P. G. Harrison, R. C. Philips, J.A. 15
Richards, J. Organomet. Chem., 114 (1976) 47.

d. C. Pelizzi, G. Pelizzi, P. Tarasconi, J. Chem. Soc. Dalton Trans, (1993) 2689.

e. C. A. K. Diop, M. Lahlou, L. Diop, B. Mahieu, U. Russo, Main Group Met. Chem., 20, 10 (1997) 683.

f. C. A. K. Diop, L. Diop, U. Russo, Main Group Met. Chem., 22, 4, (1999) 217.

[3]. C. A. K. Diop, L. Diop, R. A. Toscano Main Group Met. Chem., 25, 5, (2002)327

[4]. S. Bassène, C. A. K. Diop, M. Sidibé, A. Diasse-Sarr, L. Diop, K. C. Molloy, M. F. Mahon, R. A. Toscano. Main Group Met. Chem., 25: 1 (2002) 683.

[5]. A. Diassé-Sarr, A. H. Barry, T. Jouini, L. Diop, B. Mahieu, M. F. Mahon, K. C. Molloy, J. Organomet. Chem., 689, 12 (2004) 2087.

[6]. Molloy KC, Quill K, Cunningham D, McArdle P, Higgins T. J. Chem. Soc. Dalton Trans, (1989) 267.

[7]. A. Diassé-Sarr, L. Diop, K. C. Molloy, M. F. Mahon, Main Group Met. Chem., 20,4(1997) 223.

[8]. L.Diop, M.F. Mahon, K.C. Molloy, M.Sidibé, Main Group Met. Chem., 20,10,(1997) 649.

[9]. O. Gueye, H. Qamar, L. Diop, C.A. Diop, U. Russo, Polyhedron, 12 (1993) 1245.

[10]. Lahlou M, Diop L. Spectrochim. Acta, 47A, 12 (1991)1775.

[11]. Sheldrick GM SHELX 86. A Computer Program for Crystal Structure Determination, University of Gottingen, Gottingen. 1986.

[12]. Sheldrick GM, SHELX 97. A Computer Program for Crystal Structure Refinement, University of Gottingen, Gottingen.1997.

[13]. K. Nakamoto, in Willey Interscience (Eds), Infrared and Raman Spectra of inorganic and coordination compounds, Part B. J. Willey and Sons, Inc. 5th Edition, New York (1997) 79.

[14]. R. C. Poller and J.N.R. Ruddick, J. Chem. Soc., (1969) 2273.

[15]. K.L. Jaura, K. Chander and K.K. Sharma , *Z. Anorg. Allg. Chem.*, 376(1970)303

[16]. K. Yasuda, R. Okawara, J. Organomet. Chem., 3(1965) 76.

[17]. J. P. Clark and C. J. Wilkins, J. Chem. Soc., (A) (1966) 871.

[18]. R.J.H. Clark, A. G. Davies and R.J. Puddephatt, J. Chem. Soc., (A) (1968) 1828.

[19]. M. Sidibé M. Lahlou, L. Diop and B. Mahieu, Main Group Met. Chem., 21,10(1998) 65.

[20]. A. G Davies, P. J.Smith in: G. Wilkinson, F. G. A. Stone, E. A. Abel (Eds), Comprehensive Organometallic Chemistry. Pergamon Press. Oxford, (1982) 525.

[21]. J. Holecek, M. Nadvornik, K. Handlir, A. Lycka, J. Organomet. Chem., 241 (1982) 177.

[22]. J. Begley, D. B. Sowerby, P. Kapoor, P. Kapoor, Polyhedron, 14, 13-14 (1999) 1937.

[23]. R. E. Drew, F. W. B. Einstein, Acta Crystallogr. Sect. B., 28 (1972) 345.

[24]. P.G. Harrisson, R. P. Phillips, J. A. Richards, J. Organomet. Chem. 114 (1976) 47.