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► To cite this version:

Laurent Plasseraud. Organotin(IV) Complexes Containing Sn-O-Se Moieties: A Structural Inventory. Synthesis: Journal of Synthetic Organic Chemistry, 2018, 50 (18), pp.3653-3661. 10.1055/s-0037-1610164 . hal-03529646

HAL Id: hal-03529646

<https://hal.science/hal-03529646>

Submitted on 17 Jan 2022

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Organotin(IV) Complexes Containing Sn–O–Se Moieties: A Structural Inventory

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Dedicated to Professor Libasse Diop and his colleagues from the LACHIMIA laboratory (Dakar) for their contributions in this field.

Received:

Accepted:

Published

online:

DOI:

Abstract This review focuses on organotin compounds exhibiting Sn–O–Se moieties and whose the molecular structures were previously resolved by single-crystal X-ray diffraction analysis. Three distinct classes of compounds have been identified. Thus, the various modes of coordination of selenite, selenate and organoseleninate anions with tin atoms of organotin(IV) fragments are illustrated and detailed.

- 1 Introduction
- 2 Organotin(IV) Selenite Complexes
- 3 Organotin(IV) Selenate Complexes
- 4 Organotin(IV) Organoseleninate Complexes

Key words: X-ray crystallography, Structures, Organotin(IV), Oxoanions, Chalcogenites, Selenium, Coordination chemistry

1 Introduction

It is known for a long time that organotin(IV) compounds exhibit an interesting reactivity towards oxoacids (H_nEO_x). As early as 1924, Labourne reported on it, exploring the action of several protic acids on methylstannonic acid.¹ At the end of the 1980s, under the leadership of Holmes and his co-workers, this area of research generated a renewed interest.² Since then, this has led to the isolation of countless new organo-oxotin compounds, containing Sn–O–E moieties and highlighting various modes of coordination of oxoanions to tin. The literature on organotin compounds is therefore very abundant of examples reporting such reactions and involving in particular carboxylic acids, sulphonic acids, arsenic acid, phosphinic acids and phosphonic acids as reactants. Organotin(IV) precursors employed are generally halide,

hydroxide or oxide types. Sn–C bond cleavage reactions have also been considered as a possible access route for the synthesis of new organo-oxotins.³ From a structural point of view, these synthetic approaches have provided to an exceptional diversity of architectures, ranging from discrete mononuclear compounds to polynuclear clusters and more complex edifices (classified as: *ladder*, *O-capped*, *cube*, *prismanes*, *butterfly drum*, *football cage*, and *cyclic trimer*).⁴ This aspect has already been the subject of several articles and reviews, listing and discussing the fascinating shapes isolated in the solid state. Thus, for example, the resulting assemblies of di-organotin sulfonates⁵ and monorganotin(IV) phosphonates⁶ were intensively studied by the Chandrasekhar's group while the reactivity of aryl arsenic acids towards organotin(IV) compounds was investigated by Ma and coworkers.⁷ The chemistry of organotin triflates was also reviewed by Beckmann.⁸ More recently, the structural aspects of organotin(IV) dithiocarboxylates and carboxylates were the subject of a new contribution.⁹ Moreover, the study of the behavior of some of these species in solution, based on NMR studies, has also attracted much interest. This was particularly the case for the Sn_{12} -oxo cluster entity.¹⁰

Considering more specifically the elements of the chalcogens group (group 16), most published studies concern mainly sulfur-based derivatives and were achieved to extend the structural possibilities and also to confer potential catalytic and biological properties to the resulting compounds. However and to our knowledge, structural examples combining organotin compounds with selenium and tellurium derivatives, through Sn–O–Se,Te coordination, are much less common. Yet, there is a perceptible renewal of interest in this field and in general for the preparation of heterobimetallic oxides¹¹ which are admitted to be suitable precursors in materials science for the preparation of inorganic-organic hybrid materials¹² and oxide nanomaterials.¹³ Herein, only compounds containing Sn–O–Se moieties characterized by X-ray crystallographic analysis will be

considered. Tellurium-containing organo-oxotin derivatives and which also arouse a growing interest, are not included in this inventory. However, to date twenty-six X-ray crystallographic structures have been identified in the Cambridge Structural Data Base and which are mostly attributed to the four distinct research groups of Beckman¹⁴, Ma¹⁵, Merzweiler¹⁶ and Vij¹⁷.

Regarding the selenium oxoanions, two types are known, (i) selenites (SeO_3^{2-}) and (ii) selenates (SeO_4^{2-}), which are differentiated by the oxidation state of selenium, +IV and +VI, respectively. The corresponding oxoacids are selenic (H_2SeO_4) and selenous acids (H_2SeO_3), respectively. These acids are the main source of selenium for the preparation of selenites and selenates of organotin(IV) compounds. In some cases, selenium dioxide, SeO_2 , is also used. Se oxoanions and parent acids related to this review are shown in Scheme 1. The scheme 2 summarizes the possible bonding modes leading to Sn–O–Se moieties.

The first two sections of this review deal with organotin derivatives of these oxoanions, while the last one is devoted to the structures of organotin organoseleninate complexes. These latter derivatives are prepared from organoseleninic acids, RSeO_2H , where R, organic, can be easily modified and functionalized (in general it is an arene group), thus offering a larger modularity in synthesis and of structures. Therefore, this family is currently the most represented in terms of crystallographic reports.

Scheme 1 Molecular representations of Se oxoanions and parent acids

Scheme 2 Possible bonding modes of Se oxoanions toward tin: (a) of the selenite type, (b) of the organoseleninate type and (c) of the selenate type.

2 Organotin(IV) Selenite Complexes

These compounds are rather rare since to date there are only five X-ray crystallographic structures relating to this type of complex. Interestingly, in 2011, Diop and Molloy reported a unique example of an organotin hydrogen selenite complex by reacting SnMe_2Cl_2 with H_2SeO_3 (1:2 ratio) in ethanol.¹⁸ $\text{HSeO}_3\text{SnMe}_2\text{Cl}$ (**1**), obtained in 60% yield, consists of

a one-dimensional polymeric chain in which the tin atoms describe a distorted octahedral geometry. The methyl groups are *trans*-arranged and the $[\text{HSeO}_3]^-$ anions are tridentate. The skeleton of the chains can be viewed as composed of two types of rings, (i) four-atoms Sn_2O_2 ring and (ii) eight-atoms $[\text{SeO}_2\text{Sn}]_2$ ring, which are adjacent (Figure 1). From a supramolecular point of view, the OH group of each $[\text{HSeO}_3]^-$ anion is involved in O–H...Cl hydrogen bonds which brings the chains together and leads to the formation of sheets. To the best of our knowledge this is the only example of organotin hydrogen selenite complex characterized up to now by X-ray crystallography.

Figure 1 Molecular structure of **1** (MERCURY view) [Sn dark grey, O red, Se orange, Cl green, C grey, H white]. Hydrogen atoms of methyl groups are omitted for clarity.

The reaction of $(\text{Me}_4\text{N})_2\text{SeO}_3 \cdot 2\text{H}_2\text{O}$ with SnMe_3Cl in ethanol leads to the formation of $(\text{Me}_3\text{Sn})_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ (**2**) which crystallized by slow evaporation of an acetonitrile solution (Eq. 1).¹⁹ The structure of **2** can be described as a polymeric zig-zag chain consisting of SnMe_3 moieties bridged by selenite anions. Pendant $\text{SnMe}_3(\text{H}_2\text{O})$ groups are also connected to the chain, according to a syndiotactic modes, and *via* Sn–O–Se bonds (Figure 2). All tin atoms adopt a trigonal bipyramidal geometry and selenito ligands are triply-bridging. In solution (CDCl_3), the ^{119}Sn NMR spectrum exhibits only one resonance located at -23.4 ppm.

Equation 1 Synthesis of **2**.¹⁹

Figure 2 Molecular structure of **2** (MERCURY view) [Sn dark grey, O red, Se orange, C grey]. Hydrogen atoms are omitted for clarity.

A comparable framework was obtained for $\text{SeO}_3(\text{SnPh}_3)_2$ (**3**) prepared from triphenyltin hydroxide and selenous acid.²⁰ Single crystals suitable for an X-ray crystallographic analysis were grown in ethanol in the presence of Et_4NI . In agreement with the ^{119}Sn NMR spectrum measured in the solid state (two resonances given at $\delta = -69$ and -99 ppm), two distinct geometries are also observed for the tin atoms: (i) trigonal bipyramidal and (ii) tetrahedral. In comparison to the methylated compound **2**, the tin atoms of the pendant moieties in **3** are not terminally coordinated by a water molecule of and

therefore there are no interactions between adjacent zig-zag chains (Figure 3).

Figure 3 Molecular structure of **3** (MERCURY view) [Sn steel blue, O red, Se orange]. Phenyl groups are omitted for clarity.

As part of their work on the N→Sn intramolecularly coordinated organotin(IV) compounds, Dostál and Jambor reported a dinuclear organotin(IV) selenite derivative, $[L(Ph)SnSeO_3]_2$ (**4**) ($L = 2,6-(Me_2NCH_2)_2C_6H_3^-$), by reacting $L(Ph)SnCO_3$ with SeO_2 (89% yield, Eq. 2).²¹ The release of CO_2 leads to an unusual structure which consists of two $[L(Ph)Sn]$ moieties bridged by two selenito $-O,O'$ groups generating the formation of an eight-membered inorganic ring. The two tin atoms are hexacoordinated (Figure 4). The authors argue that the coordination around the tin atoms is maintained in solution, supported in particular on the chemical shift measured by ^{119}Sn NMR spectroscopy, in $CDCl_3$ ($\delta = -270.7$ ppm), which corroborates the crystallographic data.

Equation 2 Synthesis of **4**.²¹

Figure 4 Molecular structure of **4** (MERCURY view) [Sn steel blue, O red, Se orange, N mauve, C grey]. Hydrogen atoms are omitted for clarity.

orange, N mauve, C grey]. Hydrogen atoms are omitted for clarity.

Figure 5 Molecular structure of **5** (MERCURY view) [W blue, Sn steel blue, O red, Se orange, Na violet, C grey]. Hydrogen atoms and $[C_2H_8N]^+$ are omitted for clarity.

Recently Qin and Liu reported an unusual dimethyl-functionalized polyoxotungstate polyanion, characterized as $[\{Sn(Me)_2\}_{10}\{Sn(Me)_2(H_2O)\}_6Se_{11}W_{56}O_{211}(OH)_8]^{18-}$ (**5**) and incorporating organotin(IV) selenito moieties.²² Negative charges are compensated by $[C_2H_8N]^+$ and Na^+ cations. In an unpredictable and remarkable way, the Sn–O–Se moieties can be considered as the keystones of a tetrameric "closed" ring-shaped architecture (Figure 5). According to the authors, **5** can be considered as the first example of dimethyltin-functionalized organic-inorganic hybrid selenotungstate.

By way of comparison, the Table 1 summarizes the lengths of the Sn–O and Se–O bonds and the Sn–O–Se angles recorded in the organotin(IV) selenite complexes previously listed. It appears that the Sn–O(Se) and Se–O(Sn) bonds show significant variability from one compound to another, ranging almost from 2.0–2.6 Å and 1.6–1.80 Å, reflecting the impact of the coordination mode of the selenite anion (doubly- or triply-bridging) and the nature of the tin-connected substituents. The values of the Sn–O–Se angles also exhibit significant variations in this class of compounds.

Table 1 Comparison of Sn–O and Se–O bond lengths (Å), and Sn–O–Se angles (deg) in organotin(IV) selenite complexes.

Compounds	Sn–O(Se)	Se–O(Sn)	Se–O	Se–O(H)	Sn–O–Se	CSD Entry Deposition Number	Ref.
$HSeO_3SnMe_2Cl$ (1)	2.235(5) 2.546(5) 2.285(6)	1.677(5) 1.645(6)		1.767(6)	110.4(3) 134.5(3) 174.2(4)	BOFBF 782622	18
$(Me_3Sn)_2SeO_3 \cdot H_2O$ (2)	2.263(6) 2.293(6) 2.139(6)	1.655(6) 1.675(6) 1.707(6)			128.0(3) 140.4(4) 124.3(3)	NIVXIZ 1221026	19
$SeO_3(SnPh_3)_2$ (3)	2.193(3) 2.252(3) 2.030(3)	1.681(3) 1.678(3) 1.724(3)			128.76(18) 121.71(17) 126.10(19)	HIBLOU 622160	20
$[L(Ph)SnSeO_3]_2$ (4)	2.052(3) 2.069(3)	1.731(3) 1.721(3)	1.633(3)		121.80(2) 130.16(3)	TELGOI 903804	21

$[\{\text{Sn}(\text{Me})_2\}_{10}\{\text{Sn}(\text{Me})_2(\text{H}_2\text{O})\}_6\text{Se}_{11}\text{W}_{56}\text{O}_{211}(\text{OH})_8\}^{18-} \text{ (5)}$	2.06(3)	1.65(4)			123(1)	LOXHUD 1028651	22
	2.19(3)	1.72(3)			128(2)		
	2.20(2)	1.74(2)			129(2)		
	2.30(3)	1.79(3)					

L = 2,6-(Me₂NCH₂)₂C₆H₃[−]

3 Organotin(IV) Selenate Complexes

Like the previous one, this family consists only of five compounds, isolated in the solid state as single-crystals. Four of which contain a triphenyltin(IV) moiety and one, a trimethyltin(IV) moiety. They result mainly from studies carried out in Senegal (Dakar) within the Diop's group, in collaboration with various European teams. Initially, in 2001, they shown that the reactions of $[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Se}\cdot\text{H}_2\text{O}]$ with tetraphenylphosphonium bromide or chloride led to the formation of polymeric complexes $\{\text{Ph}_4\text{P}[(\text{SeO}_4)(\text{SnPh}_3)(\text{SnPh}_3\text{X})]\}_n$ [X = Br (**6**) or Cl (**7**)].²³ Both derivatives describe a comparable framework which can be described as a main zig-zag polymer chain alternating $[\text{SnPh}_3]^+$ and $[\text{SeO}_4]^{2-}$ fragments (Figure 6). Pendant SnPh_3X fragments are positioned along the chain. The tin atoms are in a pentacoordination geometry environment. In solution, the ¹¹⁹Sn NMR spectra reveal two resonances at −115 ppm and −69 (**6**) or −65 ppm (**7**). Selenium atoms are tetrahedrally coordinated and involved in three Se–O–Sn bonds. One oxygen atom of each selenates is not coordinating.

Figure 6 Molecular structure of **7** (MERCURY view) [Sn steel blue, O red, Se orange, Cl green]. Phenyl groups are omitted for clarity.

A similar polymeric structure was solved for $\{[(\text{Ph}_3\text{Sn})_2\text{O}_4\text{Se}]\cdot 1.5\text{H}_2\text{O}\}_n$ (**8**) prepared from H₂SeO₄ and triphenyltin hydroxide in ethanol.²⁴ In this case, the pendant organotin fragments are $\text{SnPh}_3(\text{H}_2\text{O})$. This results in the propagation of hydrogen interactions between adjacent chains, involving the free oxygen of the selenates and the water molecules, and leading to a three-dimensional network, consisting of cavities.

Under the same conditions, interestingly, when SnMe_3Cl is used as precursor of tin, a discrete complex is preferentially formed, characterized as $[(\text{Me}_3\text{Sn})_2\text{O}_4\text{Se}](\text{H}_2\text{O})_2$ (**9**).²⁴ Two Me_3Sn moieties are bridged by a bidentate SeO_4 unit which exhibits a nearly tetrahedral geometry (Figure 7). The two tin atoms have a trigonal bipyramidal geometry. The apical positions are occupied by two oxygen atoms, from the selenate ligand and a water molecule, respectively. The two uncoordinated oxygen atoms of each SeO_4 unit are involved in hydrogen interactions with aqua ligands of surrounding complexes of **9** leading to a supramolecular three-dimensional network.

In solution, respectively in CD₃OD and CDCl₃, compounds **8** and **9** are characterized by ¹¹⁹Sn resonances located at $\delta = -213$ and -27.5 ppm.

Figure 7 Molecular structure of **9** (MERCURY view) [Sn steel blue, O red, Se orange, C grey, H white].

More recently the reaction of H₂SeO₄ and SnPh_3OH , in ethanol and in the presence of *n*-Bu₂NH, led to the isolation of $[\text{n-Bu}_2\text{NH}_2]_3[\text{SnPh}_3(\text{SeO}_4)]$ (**10**) (Figure 8).²⁵ The synthetic route requires two steps, first with the *in situ* preparation of $[\text{n-Bu}_2\text{NH}_2][\text{HSeO}_4]$. $(\text{Ph}_3\text{Sn})_2\text{O}$ is co-produced with the complex **10**. Its structure consists to a SnPh_3 moiety *trans*-coordinated by two SeO_4^{2-} . The negative charges of $[\text{SnPh}_3(\text{SeO}_4)]^{3-}$ are compensated by the presence of three surrounding $[\text{n-Bu}_2\text{NH}_2]^+$ cations. From a supramolecular point of view, the uncoordinated O atoms $[\text{SnPh}_3(\text{SeO}_4)]^{3-}$ participate to N–H⋯O interactions leading to a three-dimensional network. An astonishing organization based on trinuclear macrocyclic rings has thus been highlighted. In solution in CD₃OD, the ¹¹⁹Sn NMR spectrum of **10** reveals one resonance at $\delta = -232$ ppm which corroborates with the *trans* trigonal bipyramidal geometry environment, recorded in the solid state for **10**.

Figure 8 Molecular structure of **10** [Sn steel blue, O red, Se orange, C grey]. Hydrogen atoms and $[\text{n-Bu}_2\text{NH}_2]^+$ cations are omitted for clarity (MERCURY view).

A Comparison of Sn–O and Se–O bond lengths (Å), and Sn–O–Se angles (deg) recorded in the organotin (IV) selenate complexes previously described is reported in Table 2. For **10**, in which two monodentate selenato ligands coordinate a SnPh_3 moiety, the Sn–O(Se) distances are shorter than those reported for complexes in which SeO_4^{2-} acts as a bidentate and tridentate ligand [Sn–O(Se) distances are between 2.20 and 2.32 Å]. In all compounds, the Se–O(Sn) distances are quite similar [1.64 Å (mean value)]. Non-coordinating Se–O(Sn) bonds also display

weak variation in length. With regard to the Sn–O–Se angles, the complex **10** exhibits values close to linearity whereas for the

other organotin(IV) Selenate compounds, they are all almost in the range 130–150°.

Table 2 Comparison of Sn–O and Se–O bond lengths (Å), and Sn–O–Se angles (deg) in organotin(IV) selenate complexes.

Compounds	Sn–O(Se)	Se–O(Sn)	Se–O	Sn–O–Se	CSD Entry Deposition Number	Ref.
{Ph ₄ P[(SeO ₄)(SnPh ₃)(SnPh ₃ Br)]} (6)	2.215(3) 2.276(3) 2.284(5)	1.640(3) 1.630(3) 1.644(3)	1.603(3)	139.0(2) 142.2(2) 149.7(2)	QENRUW 146133	23
{Ph ₄ P[(SeO ₄)(SnPh ₃)(SnPh ₃ Cl)]} (7)	2.208(7) 2.276(6) 2.313(7)	1.611(7) 1.648(6) 1.658(6)	1.582(7)	138.6(4) 141.2(4) 149.7(4)	QENQUV 146132	23
{[(Ph ₃ Sn) ₂ O ₄ Se]·1.5H ₂ O} _n (8)	2.2032(18) 2.2169(17) 2.2457(17) 2.2505(17) 2.2793(17) 2.3095(17)	1.6386 1.6388 1.6390 1.6436 1.6488 1.6601	1.6106 1.6207	133.40(9) 135.2(1) 140.2(1) 141.2(1) 143.7(1) 146.9(1)	QOTCIM 241567	24
{[(Me ₃ Sn) ₂ O ₄ Se](H ₂ O) ₂ } (9)	2.252(2) 2.300(3)	1.644(2)	1.631(2)	129.2(1)	QOTCOS 283468	24
[n-Bu ₂ NH ₂] ₃ [SnPh ₃ (SeO ₄)] (10)	2.152(9) 2.182(8)	1.599(9) 1.632(8)	1.598(8) 1.603(10) 1.618(8) 1.627(8) 1.632(8) 1.639(9)	170.7(9) 170.8(6)	UDOMOR 933485	25

^a Insert table footnotes here.

4 Organotin(IV) Organoseleninate complexes

This type of derivatives also exhibiting Sn–O–Se moieties, is the most represented by the number of structures identified on the Cambridge Structural Database. To date, thirty five X-ray structures have been reported. The presence of an organic substituent linked to the selenium atom significantly increases the range of available reagents. However, most of them are areneseleninate derivatives.

To the best of our knowledge, the first crystallographic report of organotin(IV) organoseleninate complexes dates from 1978,²⁶ in which Lindner reported the resolution of the structure of [Me₃Sn(O₂SeMe)]_n (**11**). Synthetically, **11** was prepared from Me₃SnCl and MeSeO₂Na (65% yield, Eq. 3) and suitable crystals were obtained in a chloroform solution. Compound **11** consists to a polymeric seleninato-*O,O'* complex describing an organization of zig-zag chains. The unit cell contains two symmetrical independent chains (Figure 9).

Equation 3 Synthesis of **11**.²⁶

Figure 9 Molecular structure of **11** (MERCURY view) [Sn dark grey, O red, Se orange, C grey].

More than a decade later, Chandrashekar and Tiekink published the isolation and X-ray structure of [Ph₃Sn(O₂SePh)]_n (**12**), described as the first example of an organotin ester of phenylseleninic acid.²⁷ Prepared from bis(triphenyltin)oxide and phenylseleninic acid (Eq. 4), **12** is also organized according to a zig-zag chain-type polymer structure in which PhSeO₂ units act as bridging ligands. Tin atoms display a trigonal bipyramidal geometry. The apical positions are occupied by two oxygen atoms from two distinct phenylseleninate ligands. Three phenyl ligands complete the coordination by defining the basal plane (Figure 10).

Equation 4 Synthesis of **12**.²⁷

Figure 10 Molecular structure of **12** [Sn dark grey, O red, Se orange, C grey]. Hydrogen atoms are omitted for clarity (MERCURY view).

In 2009, a comparable chain structure was obtained for [Ph₃Sn(O₂SeOCH₂CH₃)]_n (**13**) synthesized from [(C₆H₅)₃SnCl, selenium oxide (SeO₂) and ethanol (Eq. 5).²⁸ To our knowledge, this is only the second example of organotin (IV) organoseleninate complexes for which the organic group R linked to Se is not of the arene type (the first being the Lindner's

complex). The chain displays a more rectilinear character compare to areneseleninate derivatives (Figure 11).

Equation 5 Synthesis of **13**.²⁸

Figure 11 Molecular structure of **13** [Sn dark grey, O red, Se orange, C grey]. Hydrogen atoms are omitted for clarity (MERCURY view).

Since then, numerous X-ray structures of triorganotin(IV) organoseleninate compounds exhibiting a comparable organization in one-dimensional zig-zag chain, have been solved and published. They vary according to the nature of organic ligands bound to tin (exclusively phenyl and methyl derivatives) and also to selenium (mainly arene derivatives):

$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-2-Me})]_n$, ²⁹	$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Me})]_n$, ³⁰
$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-}t\text{-Bu})]_n$, ³⁰	$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-}i\text{-Pr})]_n$, ³¹
$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Cl})]_n$, ³⁰	$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Et})]_n$, ³²
$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-2-Et})]_n$, ³²	$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-OMe})]_n$, ³¹
$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-F})]_n$, ³³	$[\text{Ph}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-2-CF}_3)]_n$, ³⁴
$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_5)]_n$, ³⁵	$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Me})]_n$, ³⁰
$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Me})]_n$, ³¹	$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Et})]_n$, ³²
$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-}i\text{-Pr})]_n$, ³¹	$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-}t\text{-Bu})]_n$, ³⁰
$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Cl})]_n$, ³⁰	$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-OMe})]_n$, ³¹
$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-F})]_n$, ³³	$[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_3\text{-3,4-F}_2)]_n$, ³⁶

Interestingly, two triorganotin(IV) organoseleninate complexes exhibit a tetranuclear macrocyclic geometry instead of an infinite one-dimensional chain: $[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Et})]_4$ (**14**) and $[\text{Me}_3\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-2-CF}_3)]_4$ (**15**) (Figure 12).^{32,34} Both complexes were prepared from trimethyltin chloride used as triorganotin precursor, and 4-ethylbenzeneseleninic acid and 2-trifluoromethylbenzeneseleninic, respectively. The structure of these derivatives can be described as 16-membered $\text{Sn}_4\text{Se}_4\text{O}_8$ tetranuclear macrocycles formed by trimethyltin and organoseleninate fragments alternately linked. The resulting cavities size is reported in the range of 6–8 Å. Moreover, the presence of intermolecular interactions (C–H...O and C–H... π) leads to the propagation of supramolecular networks.

In solution, and based on ^{119}Sn NMR data recorded in CDCl_3 for **14** and **15** (δ = 92.6 and 23.3 ppm, respectively), four-coordinate geometries are suggested for tin atoms, thereby inconsistent with the macrocyclic structures isolated in the solid state.

Figure 12 Molecular structure of **15** [Sn dark grey, O red, Se orange, C grey, F green]. Hydrogen atoms are omitted for clarity (MERCURY view).

Examples of diorganotin(IV) organoseleninate complexes are less common. To date, only five X-ray crystallographic structures have been resolved: $[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-2-CF}_3)_2]_n$ (**16**),³⁴ $[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_5\text{-2-OMe})_2]_n$ (**17**),³⁷ $[\text{Me}_2\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-2-CF}_3)_2]_n$ (**18**),³⁴ $[\text{Me}_2\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-}i\text{-Pr})_2]_n$ (**19**),³⁷ $[\text{Me}_2\text{Sn}(\text{O}_2\text{SeC}_6\text{H}_4\text{-4-Et})_2]_n$ (**20**).³⁷ These compounds were synthesized from $n\text{-Bu}_2\text{SnCl}_2$ and Me_2SnCl_2 , respectively, by reacting with four distinct areneselenenic acids: 2-trifluoromethylbenzeneseleninic, 2-methoxybenzeneseleninic, 4-isopropylbenzeneseleninic, and 4-ethylbenzeneseleninic acid, respectively, and in the presence of sodium ethoxide. All describe a comparable polymeric structure which can be viewed as the linear propagation of $\text{Sn}_2\text{O}_4\text{Se}_2$ eight-membered rings describing an infinite 1D-helical double-chain structure. Tin atoms systematically display a six-coordinate geometry environment, linked through Sn–O–Se connections to four distinct bridging areneseleninate ligands (Figure 13). In solution in CDCl_3 , the ^{119}Sn NMR spectra of **17**, **19**, and **20** reveals only one resonance located between –220 and –282 ppm which is consistent with the crystallographic data. For **16** and **18**, on the other hand, ^{119}Sn NMR chemical shifts of less than –200 ppm are recorded, which would tend to suggest a penta-coordination geometry in solution for the tin atoms.

Figure 13 Molecular structure of **19** [Sn dark grey, O red, Se orange, C grey]. Hydrogen atoms are omitted for clarity (MERCURY view).

Sn–O and Se–O bond lengths (Å), and Sn–O–Se angles (deg) recorded in organotin(IV) organoseleninate complexes are listed in Table 3. In general, for all these compounds, few variations in distances are observed from one complex to another, leading to the following mean values: Sn–O(Se) = 2.24 Å, Se–O(Sn) = 1.68 Å and Se–C = 1.96 Å. With regard to Sn–O–Se angles, the values are between 120 and 135° for diorganotin derivatives (compounds **11–15**), and between 125 and 140° for triorganotin derivatives (compounds **16–20**).

Table 3 Comparison of Sn–O and Se–O bond lengths (Å), and Sn–O–Se angles (deg) in organotin(IV) organoseleninate complexes.

Compounds	Sn–O(Se)	Se–O(Sn)	Se–OR	Se–C	Sn–O–Se	CSD Entry Deposition number	Ref.
[Me ₃ Sn(O ₂ SeMe)] _n (11)	2.23(2) 2.24(2) 2.26(2) 2.28(2)	1.67(2) 1.68(2) 1.76(2)		1.91(4) 1.92(3)	120.4(3) 122.7(1) 129.6(10)	MSNSEL 1214525	26
[Ph ₃ Sn(O ₂ SePh)] _n (12)	2.223(4) 2.225(5)	1.682(5) 1.696(5)		1.929(8)	128.8(3) 133.7(3)	KUTRAS 1201626	27
[Ph ₃ Sn(O ₂ SeOCH ₂ CH ₃)] _n (13)	2.147(9) 2.262(10)	1.599(10) 1.684(11)	1.721(12)		131.3(6) 134.6(6)	VUQXUB 698175	28
[Me ₃ Sn(O ₂ SeC ₆ H ₄ -4-Et)] ₄ (14)	2.269(19) 2.28(2)	1.683(19) 1.70(2) 1.71(2)		1.95(3) 2.04(3)	126(2) 131(2)	POHZOD 928636	32
[Me ₃ Sn(O ₂ SeC ₆ H ₄ -2-CF ₃)] ₄ (15)	2.235(6) 2.236(6) 2.246(6) 2.243(6) 2.256(6) 2.284(6) 2.290(6)	1.661(7) 1.666(6) 1.668(6) 1.675(8)		1.95(1) 1.96(1)	126.7(3)	ADEFEX 1061825	34
[<i>n</i> -Bu ₂ Sn(O ₂ SeC ₆ H ₄ -2-CF ₃)] ₂ (16)	2.226(4) 2.231(3)	1.676(4) 1.681(4)		1.985(5)	127.0 139.6	ADEFUN 1061828	34
[<i>n</i> -Bu ₂ Sn(O ₂ SeC ₆ H ₅ -2-OMe)] ₂ (17)	2.217(3) 2.225(3)	1.686(3) 1.687(3)		1.958(5)	140.40(17)	XEHVOX 837259	37
[Me ₂ Sn(O ₂ SeC ₆ H ₄ -2-CF ₃)] _n (18)	2.206(4) 2.219(4)	1.668(4) 1.689(4)		1.987(6)	126.5 139.6	ADEFOH 1061827	34
[Me ₂ Sn(O ₂ SeC ₆ H ₄ -4- <i>i</i> -Pr)] _n (19)	2.232(7) 2.239(7)	1.692(7) 1.723(7)		1.953(10)	138.9	XEHVUD 841668	37
[Me ₂ Sn(O ₂ SeC ₆ H ₄ -4-Et)] ₂ (20)	2.235(13) 2.237(14)	1.665(13) 1.708(14)		1.94(1)	123.2 124.6	XEHWAK 841669	37

In summary, this structural inventory of organotin(IV) complexes containing Sn–O–Se groups revealed an interesting diversity of architectures, as well as various coordination modes. Three distinct classes of compounds have been highlighted, ranging from discrete complexes to polymeric edifices. From a supramolecular point of view, organotin(IV) selenite and selenate derivatives preferentially generate one-dimensional chain-based organizations while organoseleninate complexes lead to the formation of macrocyclic derived structures. Thus, these successive examples show and confirm that selenium-based oxoanions exhibit also a significant reactivity toward organotin(IV) precursors. The reaction conditions, the number and the nature of the ligands bound to the tin atom (but also to the selenium atom in the case of organoseleninate derivatives) play significant structural roles. To date, the published work has focused mainly on structural characterization, but these compounds would certainly be of interest to consider for their chemical, catalytic and biological properties.

Acknowledgment

The University of Bourgogne Franche-Comté (UBFC) and the Centre de la Recherche Scientifique (CNRS) are thanked for their supports. LP also wishes to thank the anonymous reviewers for their pertinent suggestions that contributed to improving the content of this article.

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Biosketches

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