



Organotin(IV) selenate derivatives – Crystal structure of $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4 \cdot \text{CH}_3\text{OH}]_n$

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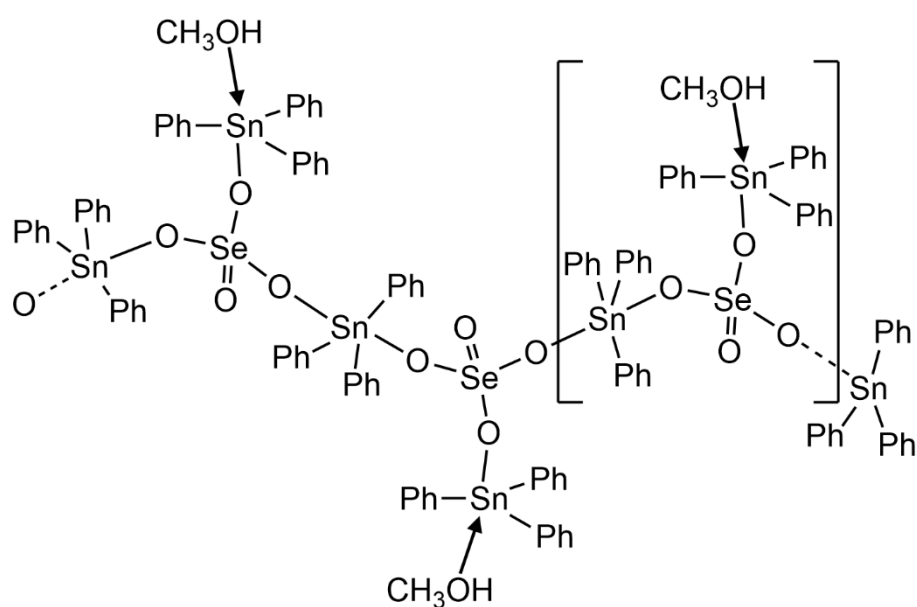
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16

17 **Abstract:** Crystallization of $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4]\cdot 1.5\text{H}_2\text{O}$ in methanol leads to the formation of
18 $[\{(\text{Ph}_3\text{Sn})_2\text{SeO}_4\}\cdot\text{CH}_3\text{OH}]_n$ (**1**) which constitutes a new specimen of organotin(IV) selenate
19 derivatives. In the solid state, complex **1** is arranged in polymeric zig-zag chains, composed of
20 alternating Ph_3Sn and SeO_4 groups. In addition, pendant $\text{Ph}_3\text{Sn}\cdot\text{CH}_3\text{OH}$ moieties are branched
21 along chains according to a syndiotactic organization and *via* $\text{Sn}-\text{O}-\text{Se}$ connections. From a
22 supramolecular point of view, intermolecular hydrogen bonds established between the selenate
23 groups (uncoordinated oxygen) and the hydroxyl functions (CH_3OH) of the pendant groups link
24 the chains together.

Keywords: organotin(IV), selenium, Sn–O–Se moiety, crystal structure, inorganic chain.

An inventory of crystallographic structures of organotin complexes exhibiting Sn–O–Se moieties was recently reviewed, highlighting the existence of a great diversity of compounds involving selenite, selenate and organoseleninate derivatives (Plasseraud, 2018). Based on bridging SeO_4^{2-} groups, the class of organotin(IV) selenate exhibits the predominance of polymeric structures, involving in particular inorganic chains, with tin atoms exhibiting trigonal bipyramidal geometries. Recently, we completed this category by characterizing a new trimethyltin(IV) selenate specimen, $[(\text{Me}_3\text{Sn})_3(\text{SeO}_4)(\text{OH})]_n$, isolated from the reaction of $[(\text{Me}_2\text{NH}_2)_2\text{SeO}_4]$ and Me_3SnCl in methanol (Diallo et al., 2018). Continuing our investigation in this field, we report herein the crystal structure of $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4] \cdot \text{CH}_3\text{OH}$ (**1**) resulting from the crystallization of $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4] \cdot 1.5\text{H}_2\text{O}$ in methanol. An X-ray diffraction study from a suitable single crystal revealed, in the solid state, an organization based on polymeric zig-zag chains with pendant $\text{Ph}_3\text{Sn} \cdot \text{CH}_3\text{OH}$ groups (Scheme 1).



Scheme 1. Molecular representation of **1** (Ph = C₆H₅) showing its zig-zag chain arrangement.

In the past, some of us reported the synthesis and the characterization of [(Ph₃Sn)₂SeO₄]·1.5H₂O which was prepared from H₂SeO₄ and triphenyltin hydroxide in ethanol (Diop et al., 2007). The recrystallization of [(Ph₃Sn)₂SeO₄]·1.5H₂O in methanol causes the displacement of H₂O and leads to the growth of colorless prism-shaped crystals characterized as the new triphenyltin(IV) selenate, [{(Ph₃Sn)₂SeO₄}·CH₃OH]_n (**1**). The crystal structure of **1** was resolved by the X-ray diffraction. Selected crystallographic data and refinement details are reported in Table 1. An OLEX2 view with selected bond lengths and angles [Å, °] is shown in Figure 1. The asymmetric unit of **1** contains two distinct tin(IV) atoms, each bearing three coplanar phenyl groups [Sn1–C13 = 2.119(4), Sn1–C1 = 2.119(4), Sn1–C7 = 2.123(4), Sn2–C26 = 2.119(4), Sn2–C32 = 2.130(4), and Sn2–C20 = 2.122(4) Å]. The two Sn atoms are *trans*-coordinated by two oxygen atoms and adopt a trigonal bipyramidal geometry (TBP). Values of O–Sn–O angles are almost linear [O2–Sn1–O1 = 178.55(10) and O5–Sn2–O4ⁱ = 176.48(9)°]. The structural indexes τ values of the Addison parameter (Addison et al., 1984) determined for Sn1 and Sn2 (0.950 and 0.919, respectively) indicate a distorted character for each TBP, which is consistent with earlier reports (Parvez et al., 2000). The apical positions of Sn2 are occupied by two oxygen atoms of two distinct tetrahedral selenate groups acting as tridentate and triply bridging ligand [O5–Sn2 = 2.230(2) and O4ⁱ–Sn2 = 2.285(2) Å]. For Sn1, one apical position is occupied by one oxygen atom of SeO₄²⁻ [Sn1–O2 = 2.213(3) Å], and the second by the oxygen atom of a coordinated CH₃OH molecule [Sn1–O1 = 2.320(3) Å]. The Sn–O(Se) distances of **1** are in the range of those already reported for triphenyltin(IV) selenates [2.15–2.31 Å] (Plasseraud, 2018). Regarding the Ph₃Sn–O(H)CH₃ distance [Sn1–O1 = 2.320(3) Å], a comparable value was recorded for [(Ph₃Sn)₂CrO₄]·CH₃OH [2.361(3) Å] which is structurally similar to **1**. [(Ph₃Sn)₂CrO₄]·CH₃OH was previously characterized as polymer

chains resulting from the association of Ph_3Sn moieties linked to tridentate CrO_4 groups, and bearing also pendant $\text{Ph}_3\text{Sn}-\text{O}(\text{H})\text{CH}_3$ units (Diallo et al., 2007).

In the crystal lattice, $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4]\cdot\text{CH}_3\text{OH}$ (**1**) is organized in infinite zig-zag chains, propagating along the *a*-axis and whose structure is based on alternating Ph_3Sn^+ and SeO_4^{2-} building-blocks (Figure 2). In addition, non-coordinated oxygen atoms of selenate anions are involved in intermolecular hydrogen bonding interactions with hydroxyl groups of methanol molecule of neighboring chains [$\text{O}\cdots\text{H}-\text{O} = 2.663 \text{ \AA}$]. This results in the propagation of a grid-shaped three-dimensional network depicted in Figure 3.

Infrared spectroscopy analysis of **1** mainly shows the absorption bands corresponding to νSeO_4 at 818, 727, and 693 cm^{-1} (Baran et al., 1997; Soukrata et al., 2014; Ben Hassen et al., 2014). In solution, despite the difficulties of solubilization in usual solvents, we were able to obtain the ^{119}Sn NMR fingerprint of **1** in CD_3OD showing two broad resonances at $\delta -193.6$ and $\delta -215.1$ ppm. The synthetic precursor, $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4]\cdot 1.5\text{H}_2\text{O}$, exhibited only one resonance at $\delta -213.0$ ppm (Diop et al., 2017). These values of chemical shift, are consistent with five-coordinated tin(IV) atoms in a *trans* trigonal bipyramidal geometry environment (Holeček et al., 1983) and support for **1** the preservation of the structure in solution. For comparison, the chromato structural analogue of **1**, $[(\text{Ph}_3\text{Sn})_2\text{CrO}_4]\cdot\text{CH}_3\text{OH}$, exhibits in CDCl_3 only one resonance at $\delta -44$ ppm, which was explained by the disruption of the polymeric chains and reflecting the four-coordination environment of tin atoms in solution (Diallo et al., 2007). Regarding the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1**, carbon atoms of the phenyl groups exhibit chemical shifts comparable to $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4]\cdot 1.5\text{H}_2\text{O}$ (Diop et al., 2007), however the resonance corresponding to the *ipso* carbon is not visible.

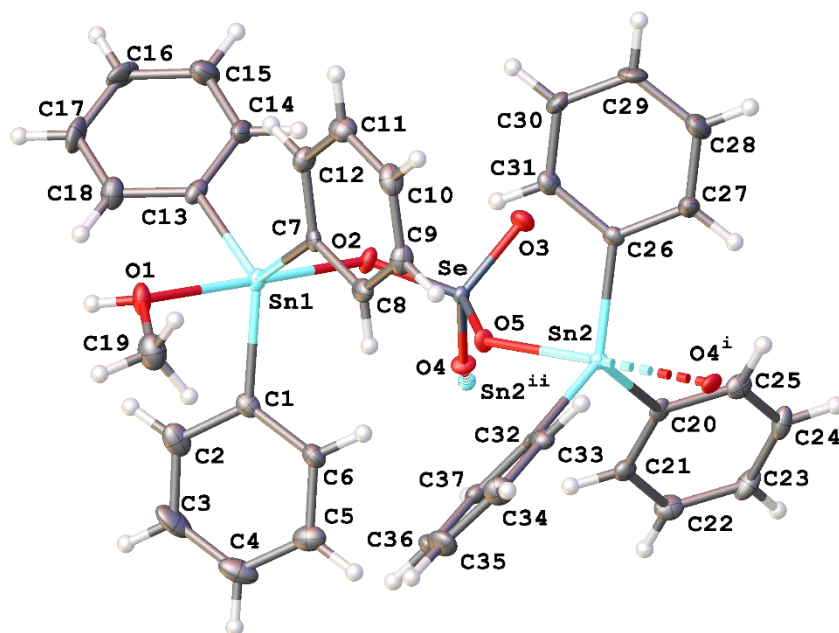
In summary, the complex of $[\{(\text{Ph}_3\text{Sn})_2\text{SeO}_4\} \cdot \text{CH}_3\text{OH}]_n$ (**1**) constitutes a new specimen of triorganotin(IV) selenate and thus extends this class of compounds predisposed to lead to the development of inorganic polymer networks.

Table 1. Crystal data and structure refinement of **1**.

Formula	$\text{C}_{37}\text{H}_{34}\text{O}_5\text{SeSn}_2$
Formula weight, $\text{g} \cdot \text{mol}^{-1}$	874.98
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a , Å	12.6189(3) Å
b , Å	15.4979(4) Å
c , Å	17.1412(4) Å
α , °	90
β , °	90
γ , °	90
V , Å ³	3352.24(14)
Z	4
ρ_{calcd} , $\text{g} \cdot \text{cm}^{-3}$	1.734
T , K	115
μ (Mo $K\alpha$), mm^{-1}	2.618 mm^{-1}
$F(000)$	1720
θ range, °	2.40–27.49
Index ranges	$-12 \leq h \leq 16$
	$-20 \leq k \leq 20$,
	$-22 \leq l \leq 22$

116	No. of reflections collected	22656
117	Completeness to θ_{\max}	99.00%
118	No. of independent reflections	7638
119	No. of observed reflections with $[I > 2 \sigma(I)]$	6939
120	No. of refined parameters	410
121	Goodness of fit on (F^2)	0.967
122	$R1(F) [I > 2\sigma(I)]$	0.0238
123	$wR2(F2)$ (all data)	0.0367
124	(Δ/σ) max	0.001
125	Largest diffraction peak/hole, e/ Å ³	0.479/-0.403

126



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Figure 1. Crystal structure of **1** showing 50% probability ellipsoids and the crystallographic numbering scheme (OLEX2 view). Selected bond lengths and angles [\AA , $^\circ$]: Sn1–O1 2.320(3), Sn1–O2 2.213(3), Sn1–C1 2.119(4), Sn1–C7 2.123(4), Sn1–C13 2.119(4), Sn2–O5 2.230(2), Sn2–O4ⁱ 2.285(2), Sn2–C20 2.122(4), Sn2–C26 2.119(4), Sn2–C32 2.130(4), Se–O2 1.650(3), Se–O3 1.616(3), Se–O4 1.636(3), Se–O5 1.651(2), C19–O1 1.464(5); C13–Sn1–C7 117.07(16), C1–Sn1–C7 120.93(14), C1–Sn1–C13 121.54(14), C26–Sn2–C32 121.34(15), C26–Sn2–C20 119.84(15), C20–Sn2–C32 118.59(16), Se–O2–Sn1 139.91(14), Se–O5–Sn2 133.94(14), O4–Se–O5 107.04(13), O4–Se–O2 108.48(13), O2–Se–O5 107.71(13), O3–Se–O5 110.65(12), O3–Se–O4 113.23(13), O3–Se–O2 109.55(14), C19–O1–Sn1 115.4(2), [Symmetry operation: ⁱ = $\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$; ⁱⁱ = $-\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$].

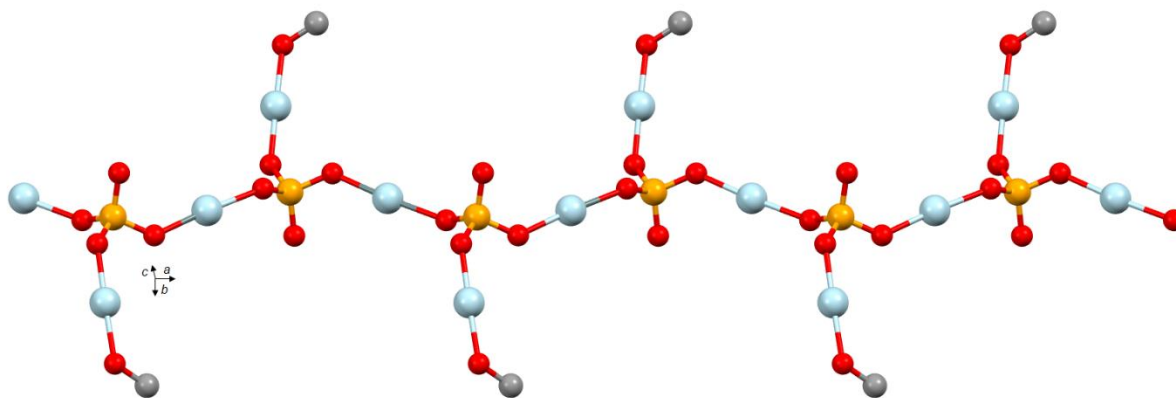


Figure 2. The infinite chain of **1** propagating along the *a*-axis (MERCURY view) [Sn (light blue), Se (yellow), O (red), C (grey)]. Hydrogen atoms and phenyl groups are omitted for clarity.

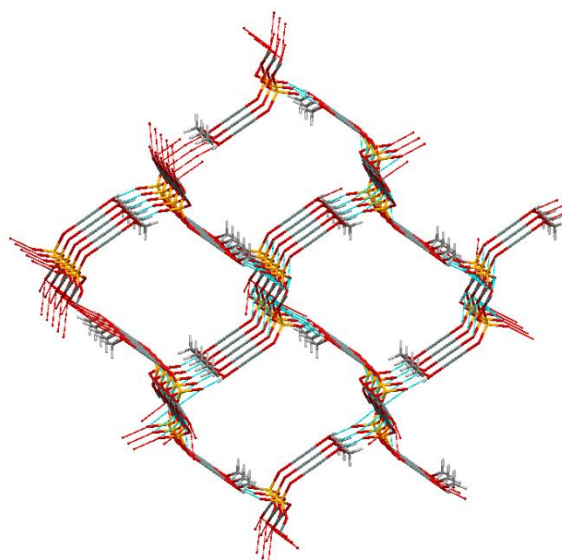


Figure 3. MERCURY view of the grid-shaped network resulting from the presence of intermolecular hydrogen bonds (blue dotted) between polymeric chains of **1**. Phenyl groups are omitted for clarity.

Experimental

General

[(Ph₃Sn)₂SeO₄].1.5H₂O was prepared according to a previously published procedure (Diop et al., 2007). Infrared spectra were recorded on a Bruker Vector 22 spectrometer (Wissenbourg, France) equipped with a Specac Golden GateTM ATR device. ¹H, ¹³C{¹H} and ¹¹⁹Sn{¹H} spectra were recorded on a Bruker Avance 300 spectrometer in CD₃OD. ¹H and ¹³C{¹H} chemical shifts (δ, ppm) were determined from the residual solvent signal (CH₃OH δ = 3.31 and CH₃OH δ = 49.00). ¹¹⁹Sn{¹H} chemical shifts (δ, ppm) were reported downfield from (CH₃)₄Sn used as external standard. Elemental analyses were performed at the “*Plateforme d’Analyse Chimique et de Synthèse Moléculaire de l’Université de Bourgogne* (PACSMUB)” on a Fisons EA 1108 CHNS-O apparatus.

Isolation of [{(Ph₃Sn)₂SeO₄}·CH₃OH]_n (1)

An amount of [(Ph₃Sn)₂SeO₄].1.5H₂O (0.3 g) was dissolved at room temperature in methanol (20 mL). Suitable colorless prism-shape crystals were obtained after few days of evaporation (37 % yield) and characterized by single-crystal X-ray diffraction as [{(Ph₃Sn)₂SeO₄}·CH₃OH]_n (**1**). Compound **1** is relatively stable over time and in ambient air (no significant degradation observed), which facilitated its handling and characterization.

¹H-NMR (ppm): δ = 7.75 [br, 12H, phenyl protons, *J*(^{117,119}Sn–H) = 63 Hz]; δ = 7.42 [br, 18H, phenyl protons], δ = 3.34 [s, 3H, CH₃OH]. ¹³C{¹H}-NMR (ppm): δ = 137.6, C(o) [*J*(^{117,119}Sn–C) = 46 Hz]; δ = 130.9, C(p), δ = 129.9, C(m) [*J*(^{117,119}Sn–C) = 70 Hz]. ¹¹⁹Sn{¹H}-NMR (ppm): –193.6; –215.1. IR (ATR, cm^{–1}): 3046 (w), 1622 (w), 1578 (w), 1480 (w), 1430 (m), 1075 (w), 1023 (w), 998 (w), 818 (s), 727 (s), 693 (s). Anal. Calc. for C₃₇H₃₄O₅SeSn₂ (804.04 g·mol^{–1}): Calc: C 50.79, H 3.92. Found: C 50.49, H 4.00.

X-ray crystallography

A suitable crystal of **1** was selected and mounted on a mylar loop with oil. Crystallographic

data collection was recorded with a Bruker Kappa Apex II diffractometer. The crystal ($0.33 \times 0.25 \times 0.12 \text{ mm}^3$) was kept at $T = 115 \text{ K}$ during data collection. Using OLEX2 (Dolomanov et al., 2009), the structure was solved with the XT (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of XL (Sheldrick, 2008) using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Programs used for the representation of the molecular and crystal structures: OLEX2 (Dolomanov et al., 2009), and MERCURY (Macrae et al., 2008).

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 2080826. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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Author contributions: Waly Diallo: conceptualization, investigation, writing – original draft; H  l  ne Cattey: investigation – crystal analysis, review; Laurent Plasseraud: supervision, writing – review and editing.

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