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Waly Diallo, H el ene Cattey, Laurent Plasseraud. Organotin(IV) selenate derivatives – Crystal structure of $[(\text{Ph}_3\text{Sn})_2\text{SeO}_4 \cdot \text{CH}_3\text{OH}]_n$. *Main Group Metal Chemistry*, 2021, 44 (1), pp.213-217. 10.1515/mgmc-2021-0023 . hal-03358015

HAL Id: hal-03358015

<https://hal.science/hal-03358015>

Submitted on 7 Oct 2021

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

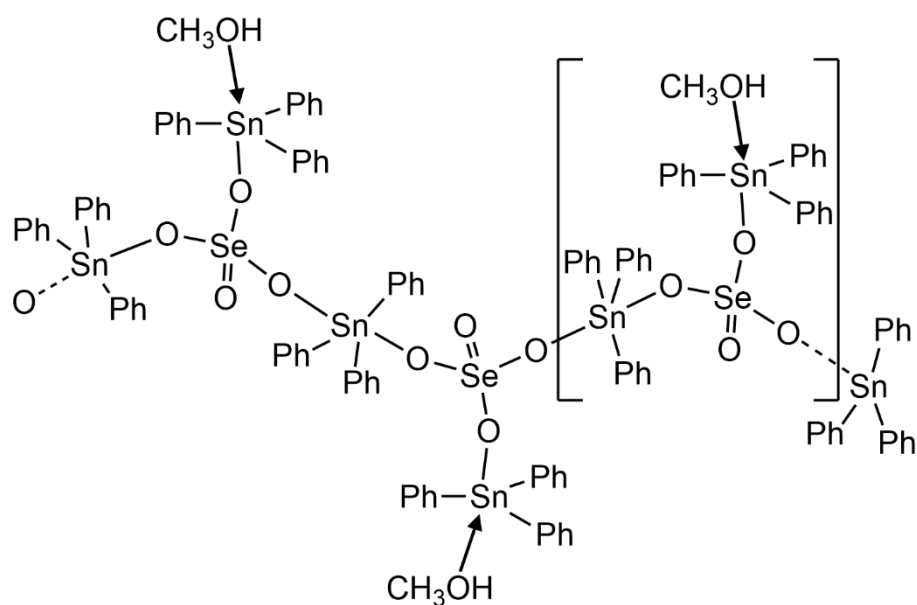
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26 **Keywords:** organotin(IV), selenium, Sn–O–Se moiety, crystal structure, inorganic chain.

27

28 An inventory of crystallographic structures of organotin complexes exhibiting Sn–O–Se
29 moieties was recently reviewed, highlighting the existence of a great diversity of compounds
30 involving selenite, selenate and organoseleninate derivatives (Plasseraud, 2018). Based on
31 bridging SeO_4^{2-} groups, the class of organotin(IV) selenate exhibits the predominance of
32 polymeric structures, involving in particular inorganic chains, with tin atoms exhibiting trigonal
33 bipyramidal geometries. Recently, we completed this category by characterizing a new
34 trimethyltin(IV) selenate specimen, $[(\text{Me}_3\text{Sn})_3(\text{SeO}_4)(\text{OH})]_n$, isolated from the reaction of
35 $[(\text{Me}_2\text{NH}_2)_2\text{SeO}_4]$ and Me_3SnCl in methanol (Diallo et al., 2018). Continuing our investigation
36 in this field, we report herein the crystal structure of $[\{(\text{Ph}_3\text{Sn})_2\text{SeO}_4\} \cdot \text{CH}_3\text{OH}]_n$ (**1**) resulting
37 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
38 from a suitable single crystal revealed, in the solid state, an organization based on polymeric
39 zig-zag chains with pendant $\text{Ph}_3\text{Sn} \cdot \text{CH}_3\text{OH}$ groups (Scheme 1).

40



41

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

43 In the past, some of us reported the synthesis and the characterization of
44 [(Ph₃Sn)₂SeO₄].1.5H₂O which was prepared from H₂SeO₄ and triphenyltin hydroxide in ethanol
45 (Diop et al., 2007). The recrystallization of [(Ph₃Sn)₂SeO₄].1.5H₂O in methanol causes the
46 displacement of H₂O and leads to the growth of colorless prism-shaped crystals characterized
47 as the new triphenyltin(IV) selenate, [(Ph₃Sn)₂SeO₄].CH₃OH]_n (**1**). The crystal structure of **1**
48 was resolved by the X-ray diffraction. Selected crystallographic data and refinement details are
49 reported in Table 1. An OLEX2 view with selected bond lengths and angles [Å, °] is shown in
50 Figure 1. The asymmetric unit of **1** contains two distinct tin(IV) atoms, each bearing three
51 coplanar phenyl groups [Sn1–C13 = 2.119(4), Sn1–C1 = 2.119(4), Sn1–C7 = 2.123(4),
52 Sn2–C26 = 2.119(4), Sn2–C32 = 2.130(4), and Sn2–C20 = 2.122(4) Å]. The two Sn atoms are
53 *trans*-coordinated by two oxygen atoms and adopt a trigonal bipyramidal geometry (TBP).
54 Values of O–Sn–O angles are almost linear [O2–Sn1–O1 = 178.55(10) and O5–Sn2–O4ⁱ =
55 176.48(9)°]. The structural indexes τ values of the Addison parameter (Addison et al., 1984)
56 determined for Sn1 and Sn2 (0.950 and 0.919, respectively) indicate a distorted character for
57 each TBP, which is consistent with earlier reports (Parvez et al., 2000). The apical positions of
58 Sn2 are occupied by two oxygen atoms of two distinct tetrahedral selenate groups acting as
59 tridentate and triply bridging ligand [O5–Sn2 = 2.230(2) and O4ⁱ–Sn2 = 2.285(2) Å]. For Sn1,
60 one apical position is occupied by one oxygen atom of SeO₄²⁻ [Sn1–O2 = 2.213(3) Å], and the
61 second by the oxygen atom of a coordinated CH₃OH molecule [Sn1–O1 = 2.320(3) Å]. The
62 Sn–O(Se) distances of **1** are in the range of those already reported for triphenyltin(IV) selenates
63 [2.15–2.31 Å] (Plasseraud, 2018). Regarding the Ph₃Sn–O(H)CH₃ distance [Sn1–O1 = 2.320(3)
64 Å], a comparable value was recorded for [(Ph₃Sn)₂CrO₄].CH₃OH [2.361(3) Å] which is
65 structurally similar to **1**. [(Ph₃Sn)₂CrO₄].CH₃OH was previously characterized as polymer

66 chains resulting from the association of Ph₃Sn moieties linked to tridentate CrO₄ groups, and
67 bearing also pendant Ph₃Sn–O(H)CH₃ units (Diallo et al., 2007).

68 In the crystal lattice, [(Ph₃Sn)₂SeO₄]·CH₃OH]_n (**1**) is organized in infinite zig-zag
69 chains, propagating along the *a*-axis and whose structure is based on alternating Ph₃Sn⁺ and
70 SeO₄²⁻ building-blocks (Figure 2). In addition, non-coordinated oxygen atoms of selenate
71 anions are involved in intermolecular hydrogen bonding interactions with hydroxyl groups of
72 methanol molecule of neighboring chains [O···H–O = 2.663 Å]. This results in the propagation
73 of a grid-shaped three-dimensional network depicted in Figure 3.

74

75 Infrared spectroscopy analysis of **1** mainly shows the absorption bands corresponding
76 to νSeO₄ at 818, 727, and 693 cm⁻¹ (Baran et al., 1997; Soukrata et al., 2014; Ben Hassen et al.,
77 2014). In solution, despite the difficulties of solubilization in usual solvents, we were able to
78 obtain the ¹¹⁹Sn NMR fingerprint of **1** in CD₃OD showing two broad resonances at δ –193.6
79 and δ –215.1 ppm. The synthetic precursor, [(Ph₃Sn)₂SeO₄]·1.5H₂O, exhibited only one
80 resonance at δ –213.0 ppm (Diop et al., 2017). These values of chemical shift, are consistent
81 with five-coordinated tin(IV) atoms in a *trans* trigonal bipyramidal geometry environment
82 (Holeček et al., 1983) and support for **1** the preservation of the structure in solution. For
83 comparison, the chromato structural analogue of **1**, [(Ph₃Sn)₂CrO₄]·CH₃OH, exhibits in CDCl₃
84 only one resonance at δ –44 pm, which was explained by the disruption of the polymeric chains
85 and reflecting the four-coordination environment of tin atoms in solution (Diallo et al., 2007).
86 Regarding the ¹³C{¹H} NMR spectrum of **1**, carbon atoms of the phenyl groups exhibit
87 chemical shifts comparable to [(Ph₃Sn)₂SeO₄]·1.5H₂O (Diop et al., 2007), however the
88 resonance corresponding to the *ipso* carbon is not visible.

89

90 In summary, the complex of $[\{(Ph_3Sn)_2SeO_4\} \cdot CH_3OH]_n$ (**1**) constitutes a new specimen
 91 of triorganotin(IV) selenate and thus extends this class of compounds predisposed to lead to the
 92 development of inorganic polymer networks.

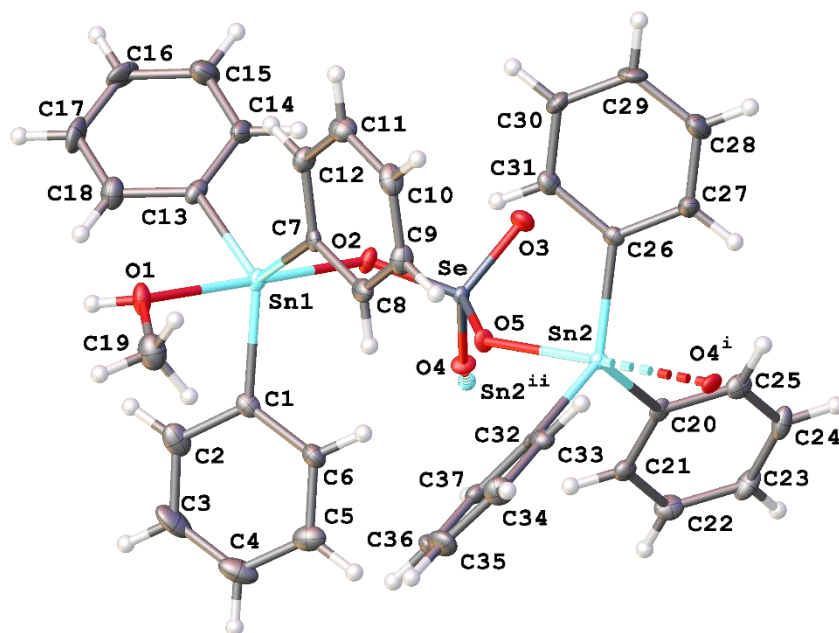
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94 **Table 1.** Crystal data and structure refinement of **1**.

95		
96	Formula	$C_{37}H_{34}O_5SeSn_2$
97	Formula weight, $g \cdot mol^{-1}$	874.98
98	Crystal system	Orthorhombic
99	Space group	$P2_12_12_1$
100	a , Å	12.6189(3) Å
101	b , Å	15.4979(4) Å
102	c , Å	17.1412(4) Å
103	α , °	90
104	β , °	90
105	γ , °	90
106	V , Å ³	3352.24(14)
107	Z	4
108	ρ_{calcd} , $g \cdot cm^{-3}$	1.734
109	T, K	115
110	μ (Mo $K\alpha$), mm^{-1}	2.618 mm^{-1}
111	$F(000)$	1720
112	θ range, °	2.40-27.49
113	Index ranges	$-12 \leq h \leq 16$
114		$-20 \leq k \leq 20$,
115		$-22 \leq l \leq 22$

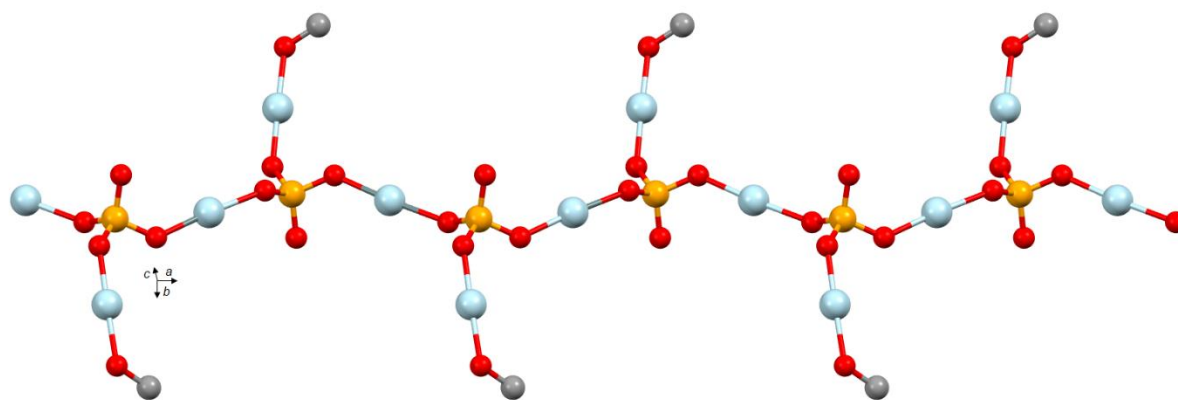
116	No. of reflections collected	22656
117	Completeness to θ_{\max}	99.00%
118	No. of independent reflections	7638
119	No. of observed reflections with $[I > 2 \sigma(I)]$	6939
120	No. of refined parameters	410
121	Goodness of fit on (F^2)	0.967
122	$R1(F) [I > 2\sigma(I)]$	0.0238
123	$wR2(F2)$ (all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

126



128

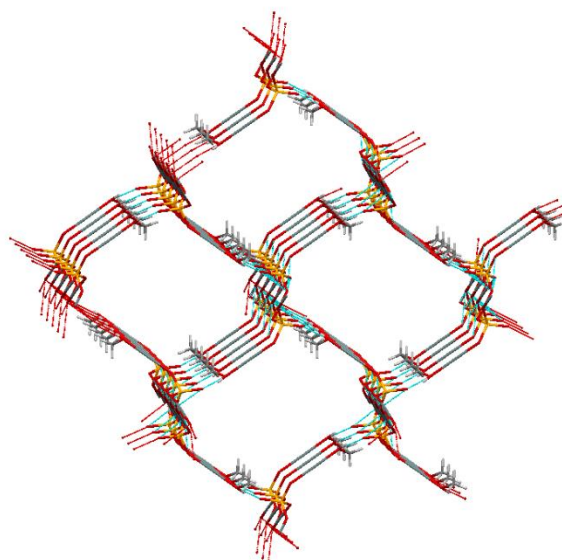
129 **Figure 1.** Crystal structure of **1** showing 50% probability ellipsoids and the crystallographic
 130 numbering scheme (OLEX2 view). Selected bond lengths and angles [\AA , $^\circ$]: Sn1–O1 2.320(3),
 131 Sn1–O2 2.213(3), Sn1–C1 2.119(4), Sn1–C7 2.123(4), Sn1–C13 2.119(4), Sn2–O5 2.230(2),
 132 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),
 133 Se–O3 1.616(3), Se–O4 1.636(3), Se–O5 1.651(2), C19–O1 1.464(5); C13–Sn1–C7
 134 117.07(16), C1–Sn1–C7 120.93(14), C1–Sn1–C13 121.54(14), C26–Sn2–C32 121.34(15),
 135 C26–Sn2–C20 119.84(15), C20–Sn2–C32 118.59(16), Se–O2–Sn1 139.91(14), Se–O5–Sn2
 136 133.94(14), O4–Se–O5 107.04(13), O4–Se–O2 108.48(13), O2–Se–O5 107.71(13),
 137 O3–Se–O5 110.65(12), O3–Se–O4 113.23(13), O3–Se–O2 109.55(14), C19–O1–Sn1
 138 115.4(2), [Symmetry operation: ⁱ = $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; ⁱⁱ = $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$].



139

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

142



143

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

147

148 **Experimental**

149 **General**

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

159

160 **Isolation of [(Ph₃Sn)₂SeO₄].CH₃OH]_n (1)**

161 An amount of [(Ph₃Sn)₂SeO₄].1.5H₂O (0.3 g) was dissolved at room temperature in methanol
162 (20 mL). Suitable colorless prism-shape crystals were obtained after few days of evaporation
163 (37 % yield) and characterized by single-crystal X-ray diffraction as [(Ph₃Sn)₂SeO₄].CH₃OH]_n
164 (**1**). Compound **1** is relatively stable over time and in ambient air (no significant degradation
165 observed), which facilitated its handling and characterization.

166 ¹H-NMR (ppm): δ = 7.75 [br, 12H, phenyl protons, $J(^{117,119}\text{Sn-H}) = 63$ Hz]; δ = 7.42 [br, 18H,
167 phenyl protons], δ = 3.34 [s, 3H, CH₃OH]. ¹³C{¹H}-NMR (ppm): δ = 137.6, C(o)
168 [$J(^{117,119}\text{Sn-C}) = 46$ Hz]; δ = 130.9, C(p), δ = 129.9, C(m) [$J(^{117,119}\text{Sn-C}) = 70$ Hz]. ¹¹⁹Sn{¹H}-
169 NMR (ppm): -193.6; -215.1. IR (ATR, cm⁻¹): 3046 (w), 1622 (w), 1578 (w), 1480 (w), 1430
170 (m), 1075 (w), 1023 (w), 998 (w), 818 (s), 727 (s), 693 (s). Anal. Calc. for C₃₇H₃₄O₅SeSn₂
171 (804.04 g·mol⁻¹): Calc: C 50.79, H 3.92. Found: C 50.49, H 4.00.

172

173 **X-ray crystallography**

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

175 data collection was recorded with a Bruker Kappa Apex II diffractometer. The crystal ($0.33 \times$
176 $0.25 \times 0.12 \text{ mm}^3$) was kept at $T = 115 \text{ K}$ during data collection. Using OLEX2 (Dolomanov et
177 al., 2009), the structure was solved with the XT (Sheldrick, 2015) structure solution program,
178 using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of XL
179 (Sheldrick, 2008) using Least Squares minimisation. All non-hydrogen atoms were refined
180 anisotropically. Hydrogen atom positions were calculated geometrically and refined using the
181 riding model. Programs used for the representation of the molecular and crystal structures:
182 OLEX2 (Dolomanov et al., 2009), and MERCURY (Macrae et al., 2008).

183

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

188

189 **Research funding:** This work was supported by the Cheikh Anta Diop University of Dakar
190 (Senegal), the Centre National de la Recherche Scientifique (CNRS, France) and the University
191 of Bourgogne Franche-Comté (Dijon, France).

192

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

196

197 **Conflict of interest:** Authors state no conflict of interest.

198

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