# TRIORGANOTIN(IV) HALIDES – PRECURSORS FOR NEW ORGANOTIN(IV) TECTONS. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI AND [2-(O=CH)C$_6$H$_4$]$_3$SnCl

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The triorganotin(IV) iodide [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI (**1**) was prepared by treating [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_4$Sn with I$_2$. Hydrolysis of **1** occurs with an halogen exchange reaction to give [2-(O=CH)C$_6$H$_4$]$_3$SnCl (**2**) in a good yield. The solution behavior of both compounds **1** and **2** was investigated by multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR spectroscopy and mass spectrometry. The IR spectroscopy for derivative **2** confirms the presence of C=O double bonds. Single-crystal X-ray diffraction analyses revealed the presence of a hexacoordinated tin atom in **1** and **2**.
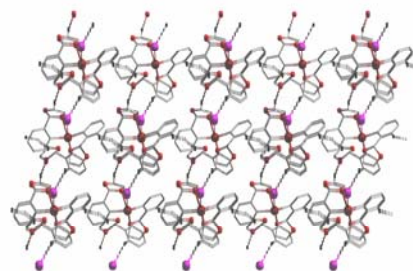
INTRODUCTION

In contrast to organic molecules and inorganic anions (*e.g. pseudo*-halides as azide,[1] cyanate,[2] thio-[1n,3] or selenocyanates,[3a,4] etc.), functionalized organometallic compounds are not very common used as spacers / linkers in crystal engineering to build either discrete heterometalic species or 1D coordination polymers and extended 2D and 3D architectures (MOFs). More often employed as organometallic ligands were functionalized ferrocenes [*e.g.* neutral 1,1′-bis(diorganophosphino)ferrocene species[5] or the dianion resulted from deprotonated ferrocene-1,1′-dicarboxylic acid[6]], but other few organometallic compounds were also used as spacers or tectons for homo- or heterometallic coordination compounds.[5a,7] For many of these organometallic ligands the presence of a pyridyl group is a common feature.[5a,7c-7l,8]

Recently we reported on the use of hypercoordinated organotin(IV) compounds to prepare molecular heterometallic species or as tectons for hybrid organometallic/inorganic polymeric architectures.[7j] As a development of this research strategy we report here on the synthesis and characterization of the halides [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI (**1**) and [2-(O=CH)C$_6$H$_4$]$_3$SnCl (**2**), the later being a useful precursor for the preparation of new triorganotin(IV) tectons after condensation with pyridyl-containing amines.

RESULTS

The triorganotin(IV) iodide [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI (**1**) was obtained from the reaction of the tetraorganotin(IV) derivative with iodine. Deprotection of the carbonyl functions in **1** was achieved by hydrolysis in a dichloromethane–water mixture, using HCl as a catalyst, to give the monochloride [2-(O=CH)C$_6$H$_4$]$_3$SnCl (**2**) in good yield (Scheme 1). The compounds were isolated as yellow (**1**) and colorless (**2**) solids which are well soluble in common solvents.

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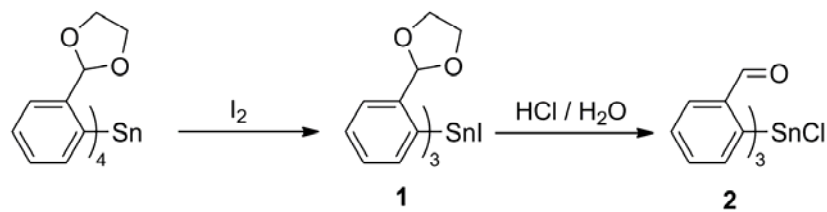
Scheme 1
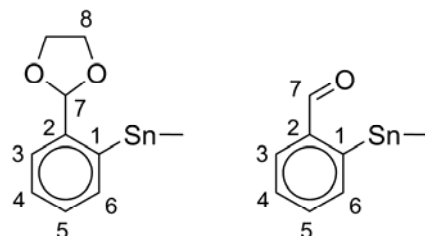
Scheme 2

The conversion of **1** into **2** was confirmed by the IR spectrum of the chloride which exhibits the expected bands assigned to the stretching vibration of the C=O double bonds. In the ESI+ mass spectra the base peak was assigned to the fragment $[\{2-[(CH_2O)_2CH]C_6H_4\}_3Sn]^+$ (*m/z* 567.08105) for **1**, and $[\{2-(O=CH)C_6H_4\}_3Sn]^+$ (*m/z* 435.00974) for **2**. Compounds **1** and **2** were investigated by multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectroscopy in solution at room temperature. The assignment of the ^1H and ^{13}C resonances was based on the 2D NMR (HSQC and COSY) correlation spectra and tin–carbon coupling constants, according to the numbering schemes depicted in Scheme 2.

The NMR spectra of the obtained compounds, recorded in CDCl$_3$, are consistent with the molecular structures determined by single crystal X-ray diffraction. The ^1H and ^{13}C NMR spectra showed the expected resonances in the alkyl as well as in the aryl regions for the organic groups attached to tin atom. Most of the ^{13}C resonances are surrounded by the satellites corresponding to tin-carbon couplings. Single crystals of **1** and **2** were grown from a CH$_2$Cl$_2$/n-hexane solvent mixture using the slow diffusion technique. Selected bond distances and angles are listed in Tables 1 and 2. Fig. 1 shows the ORTEP-like view of the molecular structure of **1** and **2**, respectively, with the atom numbering scheme.

Table 1

Selected interatomic distances (Å) and angles (°) in [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI (**1**)

Sn(1)–C(1)	2.138(8)	Sn(1)–O(1)	2.598(4)
Sn(1)–C(10)	2.146(8)	Sn(1)–O(3)	2.849(5)
Sn(1)–C(19)	2.176(8)		
Sn(1)–I(1)	2.7901(9)		
C(1)–Sn(1)–C(10)	129.2(3)	I(1)–Sn(1)–C(1)	101.0(2)
C(1)–Sn(1)–C(19)	107.0(3)	I(1)–Sn(1)–C(10)	103.6(2)
C(10)–Sn(1)–C(19)	110.1(3)	I(1)–Sn(1)–C(19)	102.3(2)
O(1)–Sn(1)–I(1)	170.2(9)	O(3)–Sn(1)–C(19)	177.7(2)
O(1)–Sn(1)–C(1)	70.8(2)	O(3)–Sn(1)–C(1)	73.9(2)
O(1)−Sn(1)−C(10)	78.7(2)	O(3)–Sn(1)–C(10)	68.0(2)
O(1)−Sn(1)−C(19)	85.6(2)	O(3)–Sn(1)–I(1)	79.5(1)
		O(3)–Sn(1)–O(1)	92.8(1)

Table 2

Selected interatomic distances (Å) and angles (°) in $[2\text{-}(O=CH)C_6H_4]_3SnCl$ (**2**)

	2a		**2b**
Sn(1)–C(1)	2.126(7)	Sn(2)–C(22)	2.170(8)
Sn(1)–C(8)	2.142(8)	Sn(2)–C(29)	2.127(7)
Sn(1)–C(15)	2.140(8)	Sn(2)–C(36)	2.145(8)
Sn(1)–Cl(1)	2.422(2)	Sn(2)–Cl(2)	2.484(2)
Sn(1)–O(1)	2.586(7)	Sn(2)–O(4)	2.571(7)
Sn(1)–O(2)	2.848(7)	Sn(2)–O(5)	2.863(7)
C(1)–Sn(1)–C(8)	109.5(3)	C(22)–Sn(2)–C(29)	109.0(3)
C(1)–Sn(1)–C(15)	133.5(3)	C(22)–Sn(2)–C(36)	108.1(3)
C(8)–Sn(1)–C(15)	107.6(3)	C(29)–Sn(2)–C(36)	135.7(3)
Cl(1)–Sn(1)–C(1)	101.7(2)	Cl(2)–Sn(2)–C(22)	95.0(2)
Cl(1)–Sn(1)–C(8)	97.1(2)	Cl(2)–Sn(2)–C(29)	100.5(2)
Cl(1)–Sn(1)–C(15)	100.6(2)	Cl(2)–Sn(2)–C(36)	99.5(2)
O(1)–Sn(1)–Cl(1)	168.8(2)	O(4)–Sn(2)–Cl(2)	167.1(2)
O(1)−Sn(1)–C(1)	83.5(2)	O(4)–Sn(2)–C(22)	72.1(2)
O(1)–Sn(1)–C(8)	71.8(3)	O(4)−Sn(2)−C(29)	84.3(2)
O(1)–Sn(1)–C(15)	82.3(3)	O(4)–Sn(2)–C(36)	84.8(2)
O(2)–Sn(1)–C(8)	172.9(2)	O(5)–Sn(2)–C(22)	170.9(2)
O(2)–Sn(1)–C(1)	68.7(2)	O(5)–Sn(2)–C(29)	68.3(2)
O(2)–Sn(1)–C(15)	77.5(3)	O(5)–Sn(2)–C(36)	78.3(2)
O(2)–Sn(1)–Cl(1)	76.9(1)	O(5)–Sn(2)–Cl(2)	77.3(1)
O(2)–Sn(1)–O(1)	114.3(2)	O(5)–Sn(2)–O(4)	115.5(2)
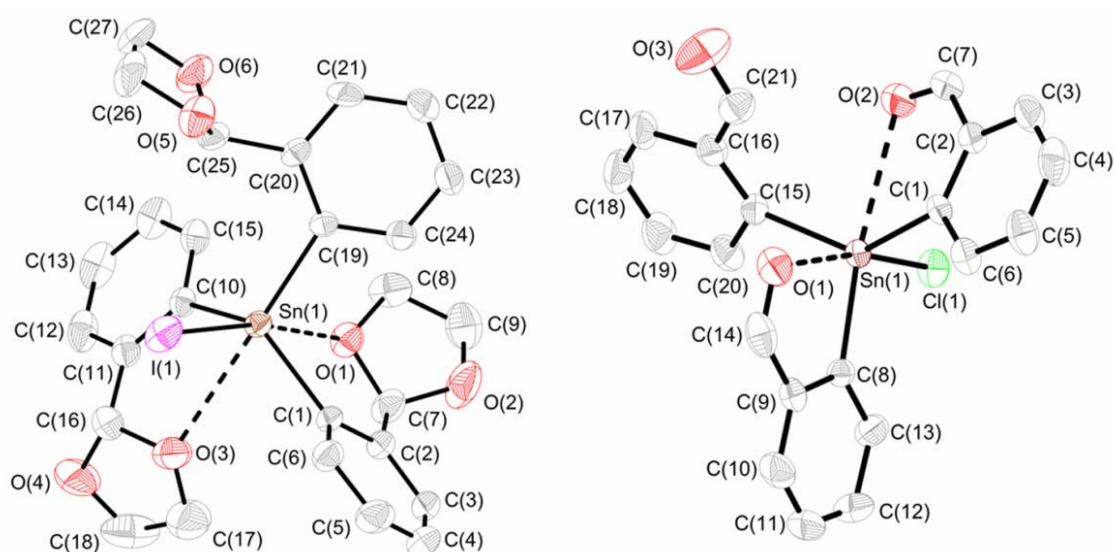
Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for
$\Delta\text{-}[pS_{O(1)}pS_{O(3)}]\text{-}[S_{C(7)}R_{C(16)}]$-**1** (left) and Δ-**2a** (right) (hydrogen atoms are removed for clarity).

DISCUSSION

Solution behavior

The ^{1}H NMR spectra of both compounds show all the expected resonance signals of the organic groups bonded to tin. The aliphatic region of the ^{1}H NMR spectrum for compound **1** contains two different resonance signals, a AA′XX′ multiplet corresponding to the protons H-8 from the 1,3-dioxolane ring and a singlet resonance signal which can be assigned to the H-7 protons. Both the ^{1}H and ^{13}C spectra show one set of resonances, respectively, a behavior which is consistent with equivalence of the organic groups attached to tin on the NMR time scale. Such a dynamic behavior is supported by the ^{119}Sn chemical shifts observed at room temperature for compound **1** ($\delta = -186.5$ ppm, in CDCl$_3$) and for compound **2** ($\delta = -159.72$ ppm, in CDCl$_3$), which magnitude is typical for hexacoordinated organotin(IV) species in solution (cf. [2-(O=CH)C$_6$H$_4$]$_2$SnCl$_2$: $\delta = -201.1$ ppm, in CDCl$_3$).[7j]

Solid state structure

For compound **2** there are two independent molecules (**2a** and **2b**) in the unit cell, with very similar molecular parameters (Table 2) and in the subsequent discussion we will refer only to molecule **2a**. For both compounds **1** and **2** the crystals contain similar molecular units in which the metal centers are coordinated by two oxygen atoms from the pendant arms. The third aryl ligand is twisted to bring the potential oxygen donor atom far from the metal centre. The interatomic O→Sn distances in both compounds (Tables 1 and 2) exceed the sum of the covalent radii [Σr_{cov}(Sn,O) 2.06 Å] but are shorter than the sum of the van der Waals radii [Σr_{vdW}(Sn,O) 3.6 Å] of the corresponding atoms.[9] The Sn–O distances in a molecular unit are different [Sn(1)–O(1) 2.598(4) Å, Sn(1)–O(3) 2.849(5) Å in **1**; Sn(1)–O(1) 2.586(7) Å, Sn(1)–O(2) 2.848(7) Å in **2a**], with the shorter one placed *trans* to the tin-halogen bond. These short tin-oxygen bonds in **1** and **2a** are however longer than those found in [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_2$SnCl$_2$ [Sn–O 2.475(5) / 2.500(5) Å] and [2-(O=CH)C$_6$H$_4$]$_2$SnCl$_2$ [Sn–O 2.431(7) / 2.480(7) Å],[7j] respectively, a behavior consistent with a lower Lewis acidity at the metal centre in the monohalides **1** and **2a** with respect to the related dichlorides. On the other hand, the longer tin-oxygen bonds in **1** and **2a** are of the same magnitude as observed in the related

tetraaryltin(IV) [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_4$Sn [Sn–O 2.825(6) / 2.853(10) Å], but shorter than in [2-(O=CH)C$_6$H$_4$]$_4$Sn [Sn–O 2.989(8) / 3.006(7) Å].[10] Taking into account both intramolecular O→Sn interactions per molecular unit, the coordination geometry around the tin centre can be described as distorted octahedral, with the longer tin-oxygen bond bisecting the opened equatorial C-Sn-C angle [C(1)–Sn(1)–C(10) 129.2(3)° in **1**; C(1)–Sn(1)–C(15) 133.5(3)° in **2a**].

As a result of the intramolecular O→Sn interactions two five membered SnC$_3$O rings are formed in **1**. Both rings are folded along the Sn(1)⋯C(7) and Sn(1)⋯C(16) axes, with SnC$_3$/SnCO dihedral angle of 9.1(3)° and 30.9(3)°, respectively. The oxygen atoms are out from the mean plane of the rest of the ring atoms by 0.159 Å and 0.563 Å, respectively. The non-planarity of these two five-membered SnC$_3$O rings induces planar chirality (with the aromatic ring and the oxygen atom as chiral plane and pilot atom, respectively; isomers given as pR_O and pS_O)[11,12] (alternatively, the chirality due to the conformers of a chelate ring can also be described in terms of δ and λ isomers).[13] On the other hand, in a 1,3-dioxolan-2-yl ring the oxygen atoms are nonequivalent (only one is coordinated to tin atom) and thus the methyne carbon atom of this heterocycle becomes chiral. Moreover, the two (*C,O*)-chelating ligands in the octahedral molecule of **1** results in helical chirality for the whole (*C,O*)$_2$CSnI core designated by the symbols Δ and Λ.[13] As a consequence, the crystal of the iodide **1** contains a 1:1 mixture of Δ-[$pS_{O(1)}pR_{O(3)}$]-[$R_{C(7)}S_{C(16)}$]-**1** and Λ-[$pR_{O(1)}pS_{O(3)}$]-[$S_{C(7)}R_{C(16)}$]-**1** isomers. By contrast, in the molecule of **2** the five-membered SnC$_3$O rings are planar due to the –HC=O double bond and therefore the crystal contains a 1:1 mixture of Δ and Λ isomers.

No intermolecular interactions between heavy atoms were observed in compounds **1** and **2**. A closer check of the crystal packing revealed intermolecular contacts which involve hydrogen atoms, including π interactions between hydrogen atoms and the aromatic rings present in the molecule (*i.e.* H⋯Cg contacts shorter than 3.1 Å, with an angle γ between the normal to the aromatic ring and the line defined by the H atom and Cg smaller than 30°).[14] Thus, Δ-[$pS_{O(1)}pR_{O(3)}$]-[$R_{C(7)}S_{C(16)}$]-**1** and Λ-[$pR_{O(1)}pS_{O(3)}$]-[$S_{C(7)}R_{C(16)}$]-**1** isomers are connected through C–H⋯π contacts [C(3a)–H(3a)$_{aryl}$⋯Cg(1) 2.71 Å, γ = 12.3°; C(26b)–H(26Ab)$_{methylene}$⋯Cg(1) 2.85 Å; γ = 3.9°; Cg(1) is the Ph$_{centroid}${C(10)-C(15)}; symmetry equivalent atoms (*−0.5+x, −0.5+y, z*) and (*x, 1+y, z*) are given by "a" and "b", respectively] in a layer along the

ab plane. Parallel layers are further associated through I···H [I(1)···H(21e)$_{aryl}$ 3.27 Å; cf. Σr_{vdW}(I,H) 3.35 Å[9]; symmetry equivalent atom (*x, 1–y, –0.5+z*) given by "e"] and O···H [O(6)···H(18Bg)$_{methylene}$ 2.36 Å; cf. Σr_{vdW}(O,H) 2.60 Å[9]; symmetry equivalent atom (*x, 1–y, –0.5+z*) given by "e"] hydrogen bond type interactions to produce a 3D supramolecular architecture (Fig. 2).
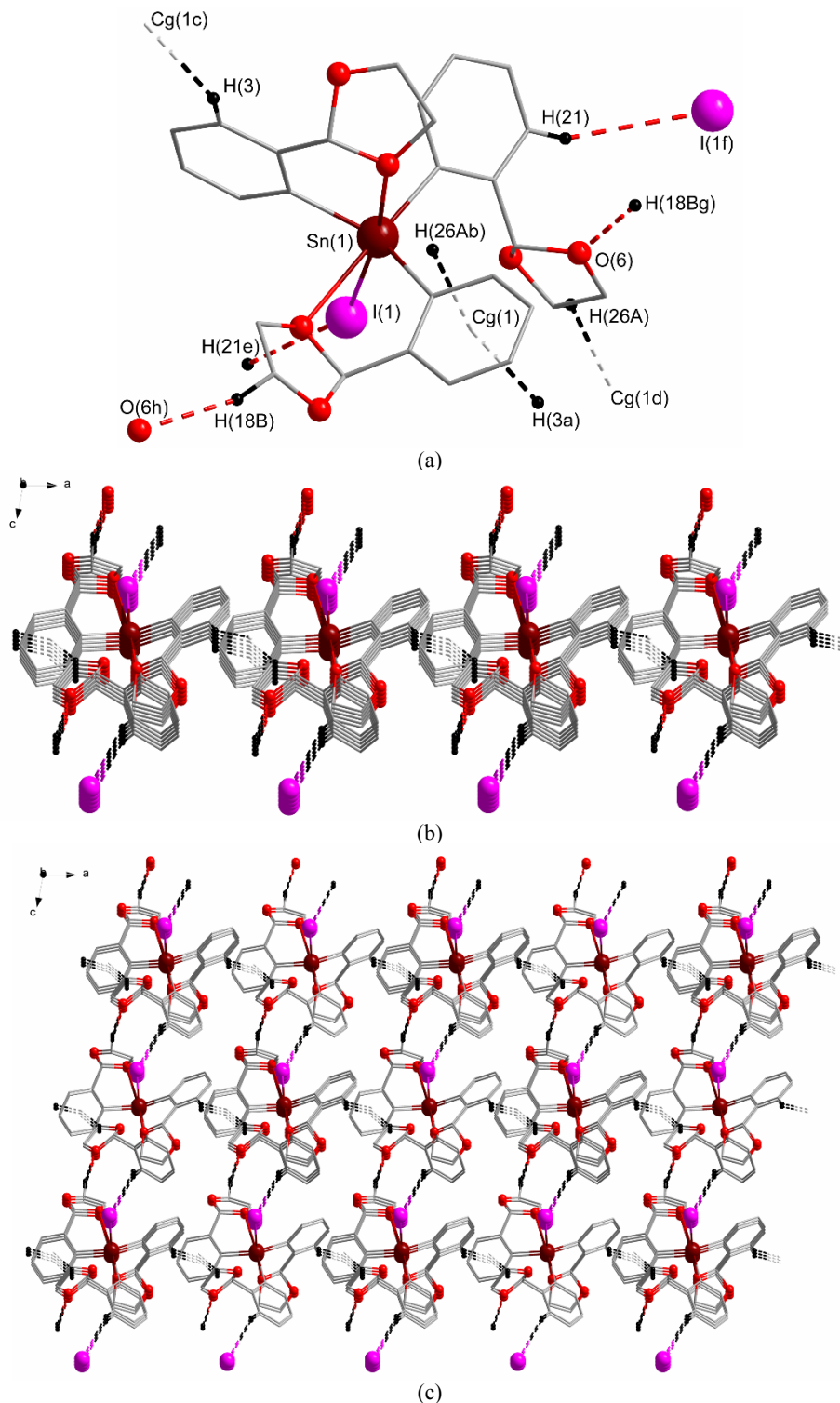

(a)

(b)

(c)

Fig. 2 – View of the (a) intermolecular interactions, (b) layer based on intermolecular C–H···π interactions and (c) 3D supramolecular architecture in the crystal of 1 based on intermolecular C–H···π , I···H and O···H interactions [only hydrogens involved in interactions are shown; symmetry equivalent positions given by "a", "b", "b", "d", "e", "f", "g" and "h": (*–0.5+x, –0.5+y, z*), (*x, 1+y, z*), (*0.5+x, 0.5+y, z*), (*x, –1+y, z*), (*x, 1–y, –0.5+z*), (*x, 1–y, 0.5+z*), (*x, 2–y, 0.5+z*) and (*x, 2–y, –0.5+z*)].

In the crystal of **2** dimer associations of Δ-**2a** and Λ-**2a** isomers are formed through C–H···π contacts [C(10a)–H(10a)$_{aryl}$···Cg(1) 2.69 Å, γ = 7.3°; Cg(1) is the Ph$_{centroid}${C(15)-C(20)}; symmetry equivalent atoms (*1–x, –y, 1–z*) given by "a"] while alternating Δ-**2b** and Λ-**2b** isomers are connected through C–H···π interactions [C(39c)–H(39c)$_{aryl}$···Cg(2) 2.94 Å, γ = 6.6°; Cg(2) is the Ph$_{centroid}${C(29)-C(34)}; symmetry equivalent atoms (*1/2+x, y, 3/2–z*) given by "c"] in a 1D polymer like structure (Fig. 3). This structural units are further associated through weak Cl···H interactions [Cl(1)···H(40b)$_{aryl}$ 2.95 Å; Cl(2)···H(28e)$_{methine}$ 2.92 Å; cf. Σr$_{vdW}$(Cl,H) 3.01 Å;[9] symmetry equivalent atoms (*1/2+x, 1/2–y, 1–z*) and (*1/2–x, 1/2+y, z*) given by "b" and "e", respectively] in a 3D supramolecular architecture (Fig. 4).
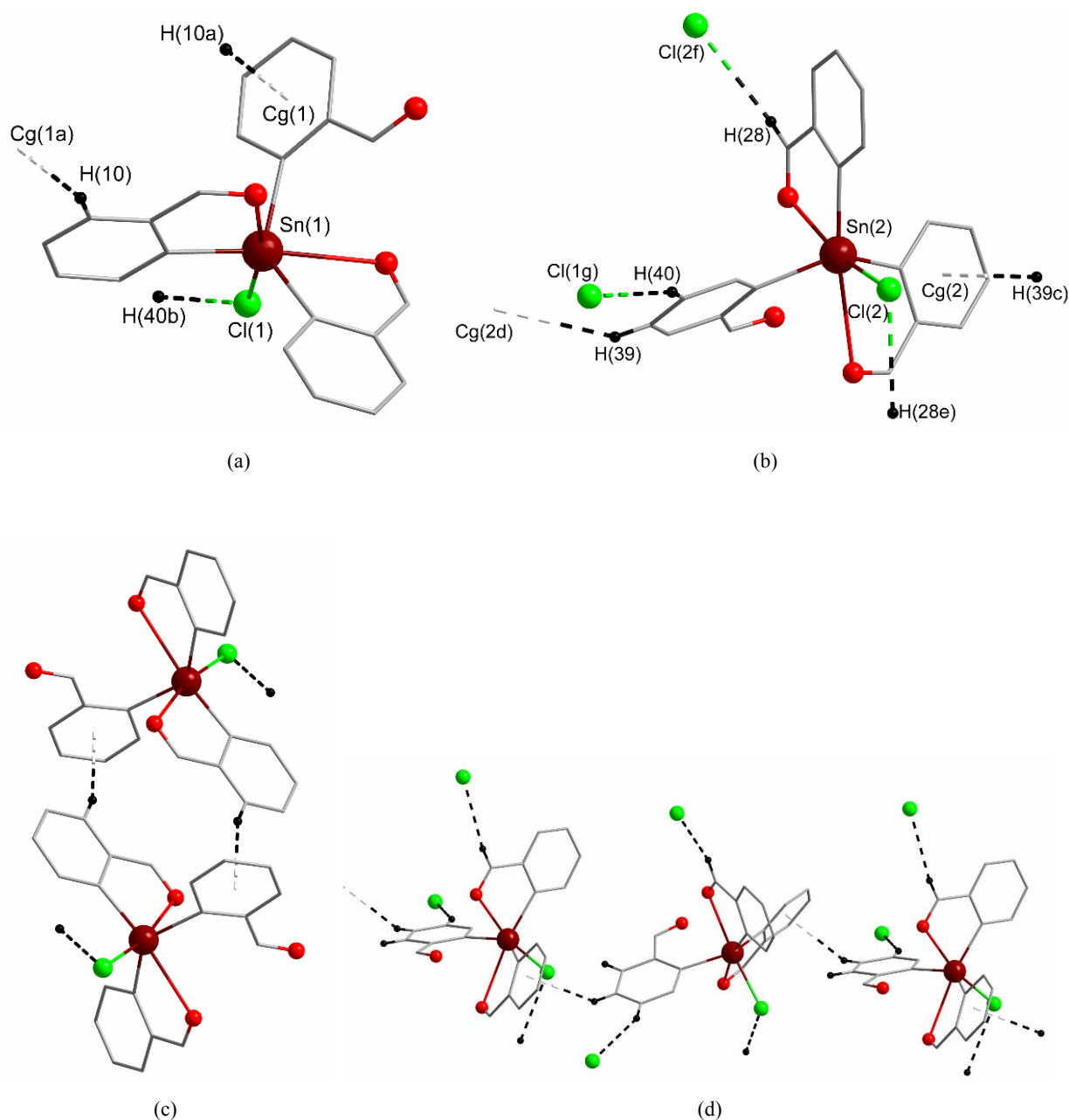

(a)

(b)

(c)

(d)

Fig. 3 – View of the intermolecular interaction in (a) Δ-2a and (b) Δ-2b, (c) the Δ-2a - Λ-2a dimer and (d) the polymer of alternating Δ-2b and Λ-2b isomers based on intermolecular C–H···π interactions [only hydrogens involved in interactions are shown; symmetry equivalent positions given by "a", "b", "b", "d", "e", "f" and "g": (*1–x, –y, 1–z*), (*1/2+x, 1/2–y, 1–z*), (*1/2+x, y, 3/2–z*), (*–1/2+x, y, 3/2–z*), (*1/2–x, 1/2+y, z*), (*1/2–x, –1/2+y, z*) and (*–1/2+x, 1/2–y, 1–z*)].
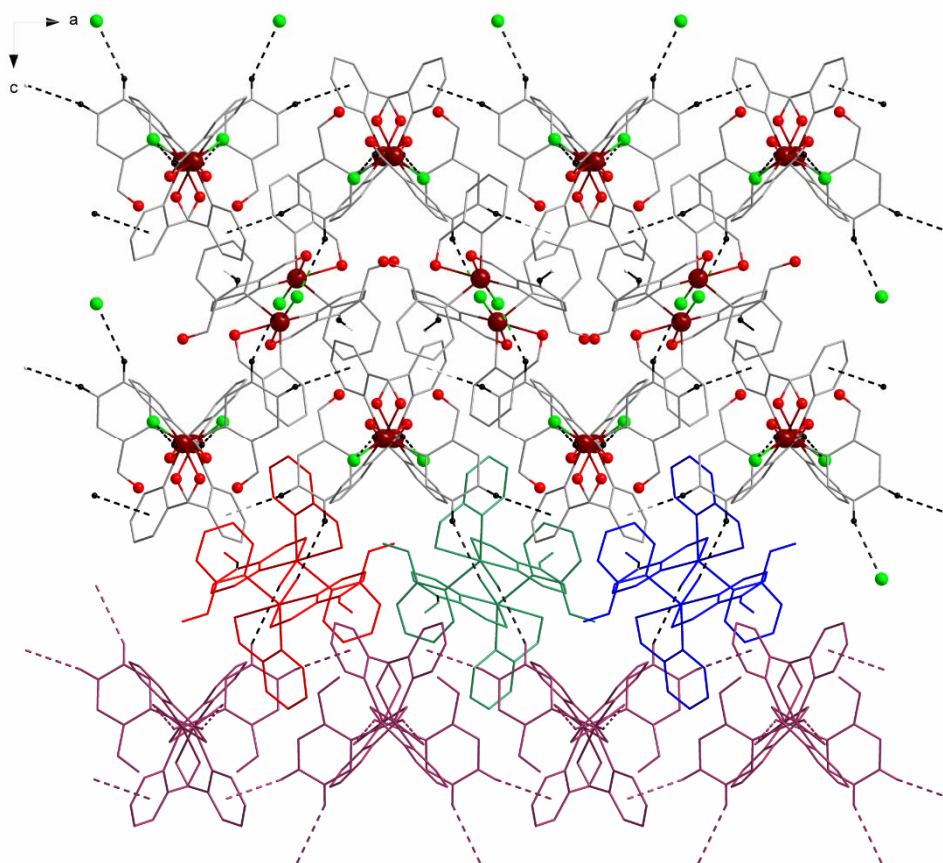
Fig. 4 – View of the 3D supramolecular architecture (highlighting the structural units)
based on intermolecular C–H···π and Cl···H interactions in the crystal of **2** (only hydrogens involved in interactions are shown).

EXPERIMENTAL

Multinuclear NMR spectra (^{1}H, ^{13}C, ^{119}Sn and 2D) were recorded at room temperature on a Bruker Avance III 400 instrument. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. CDCl$_3$: ^{1}H 7.26 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the solvent (ref. CDCl$_3$: ^{13}C 77.16 ppm).[15] For the ^{119}Sn NMR spectra the chemical shifts are reported in ppm relative to SnMe$_4$. The NMR spectra were processed using the *MestReNova* software.[16] Mass spectra were recorded with an Applied Biosystems (Type Mariner) (ESI/APCI-TOF) instrument. The infrared spectrum of **2** was obtained in the range 4000–400 cm^{-1} on a Jasco FT/IR-615 spectrometer. Melting points were measured with an Electrothermal 9200 apparatus and are not corrected. The starting material [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_4$Sn was prepared according to the literature method.[10]

Synthesis of [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI (**1**)

Elemental iodine (0.666 g, 2.63 mmol) was added to a solution of [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_4$Sn (1.878 g, 2.63 mmol) in 50 mL CH$_2$Cl$_2$ and the reaction mixture was left under stirring for 24h. The solvent was removed under vacuo and the resulting solid was washed with Et$_2$O to give **1** as a yellow solid (1.47 g, 81%). Mp 200-202 °C. Yellow crystals of **1** were obtained from CH$_2$Cl$_2$/*n*-hexane. ^{1}H NMR (CDCl$_3$, 400.1 MHz, 20 ºC): δ 3.60-3.78 (m, 12H, OC*H*$_2$), 5.88 (s, 3H, H-7, $^3J_{SnH}$ 7.1 Hz), 7.37-7.46 (m, 6H, H-4, H-5), 7.59 (dd, 3H, H-3, $^3J_{HH}$ 7.1 Hz, $^4J_{HH}$ 1.9 Hz, $^4J_{SnH}$ 26.2 Hz), 7.84 (dd, 3H, H-6, $^3J_{HH}$ 7.1 Hz, $^4J_{HH}$ 1.7 Hz, $^3J_{SnH}$ 73.0 Hz). ^{13}C NMR (CDCl$_3$ 100.6 MHz, 20 ºC): δ 64.85 (C-8), 103.33 (C-7, $^3J_{SnC}$ 23.5 Hz), 126.96 (C-3, $^3J_{SnC}$ 56.1 Hz), 129.04 (C-5, $^3J_{SnC}$ 69.3 Hz), 129.50 (C-4, $^4J_{SnC}$ 13.8 Hz), 137.02 (C-6, $^2J_{SnC}$ 49.1 Hz), 139.76 (C-1), 142.17 (C-2, $^2J_{SnC}$ 36.9 Hz). ^{119}Sn NMR (CDCl$_3$ 149.2 MHz, 20 ºC): δ −186.1 (s). MS (ESI+): *m/z* (%) 567.08121 (100) [R$_3$Sn]$^+$, R = 2-{(CH$_2$O)$_2$CH}C$_6$H$_4$.

Synthesis of [2-(O=CH)C$_6$H$_4$]$_3$SnCl (**2**)

Water (10 mL) and hydrochloric acid (0.35 mL, 37%) were added to a solution of [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI (**1**) (0.555 g, 0.8 mmol) in CH$_2$Cl$_2$ and then the reaction mixture was refluxed for 24h. After the solvent was removed under vacuo, the compound was extracted with acetone to give **2** as a solid (0.30 g, 80% based on **1**). Mp 202-204 °C. Colorless crystals were obtained by slow diffusion of *n*-hexane in a CH$_2$Cl$_2$ solution of **2**. IR (KBr, cm^{-1}): 1698(s), 1667(s), 1642(s) [ν(CH=O)]. ^{1}H NMR (CDCl$_3$, 400.1 MHz, 20 ºC): δ 7.60 (ddd, 3H, H-4, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.3 Hz), 7.68 (ddd, 3H, H-5, $^3J_{HH}$ 7.3 Hz, $^4J_{HH}$ 1.5 Hz, $^4J_{SnH}$ 18.4 Hz), 7.82-8.01 (m, 6H, H-6, H-3, $^3J_{SnH}$ 72.4 Hz, $^4J_{SnH}$ 24.4 Hz), 9.93 (s, 3H, H-7, $^4J_{SnH}$ 6.9 Hz). ^{13}C NMR (CDCl$_3$ 100.6 MHz, 20 ºC): δ 129.93 (C-4, $^4J_{SnC}$ 13.6 Hz), 134.10 (C-3, $^3J_{SnC}$ 57.7 Hz), 135.36 (C-5, $^3J_{SnC}$ 71.6 Hz), 136.88 (C-6, $^2J_{SnC}$ 44.1 Hz), 139.34 (C-2, $^2J_{SnC}$ 42.2 Hz), 144.38 (C-1, $^1J_{117/119SnC}$ 769.8 Hz/805.6 Hz), 193.75 (C-7, $^3J_{SnC}$ 20.5 Hz). ^{119}Sn NMR (CDCl$_3$ 149.2 MHz, 20 ºC): δ −159.7 (s). MS (ESI+): *m/z* (%) 435.00262 (100) [R$_3$Sn]$^+$, R = 2-(O=CH)C$_6$H$_4$.

Table 3

Crystallographic data for [2-{(CH$_2$O)$_2$CH}C$_6$H$_4$]$_3$SnI (**1**) and [2-(O=CH)C$_6$H$_4$]$_3$SnCl (**2**)

Compound	**1**	**2**
Molecular formula	C$_{27}$H$_{27}$IO$_6$Sn	C$_{21}$H$_{15}$ClO$_3$Sn$_2$
M	693.07	469.47
Crystal system	Monoclinic	Orthorhombic
Space group	*Cc*	*Pbca*
Temperature (K)	297(2)	297(2)
a/Å	16.700(3)	18.0735(14)
b/Å	9.4178(15)	16.7817(13)
c/ Å	16.846(3)	25.370(2)
α/º	90	90
β/º	100.802(3)	90
γ/º	90	90
V/Å^3	2602.5(7)	7694.7(10)
Z	4	16
D_{calc}/gcm^{-3}	1.769	1.621
$F(000)$	1360	3712
μ(Mo-Kα)/mm^{-1}	2.207	1.484
Crystal size (mm^3)	0.21 x 0.20 x 0.18	0.30 x 0.25 x 0.23
θ range for data collection (º)	2.46 to 25.00	1.84 to 25.00
Reflections collected	11976	70438
Independent reflections	4564 [R_{int} = 0.0463]	6772 [R_{int} = 0.0990]
Absorption correction	Multi-Scan[17]	Multi-Scan[17]
Maximum and minimum transmissions	0.6921 and 0.6543	0.713 and 0.645
Data / restraints / parameters	4564 / 2 / 316	6772 / 4 / 487
Goodness-of-fit on F^2	0.990	1.220
Final R indices [$I>2\sigma(I)$][a]	R_1 = 0.0331	R_1 = 0.0736
	wR_2 = 0.0632	wR_2 = 0.1440
R indices (all data)[a]	R_1 = 0.0362	R_1 = 0.0863
	wR_2 = 0.0652	wR_2 = 0.1498
Largest difference peak and hole (e Å^{-3})	0.486 and -0.426	2.551 and -0.754

[a] Definition of the R values: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$.

Crystal structure determination

Crystallographic data for the structural analysis of compounds **1** and **2** have been collected on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell constants are given in Table 3, along with other experimental parameters and relevant information pertaining to structure solution and refinement.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-2014 was used.[18] The drawings were created with the Diamond program.[19] One molecule from the asymmetric unit of compound **2** contains a –CH=O fragment disordered over two positions and was refined with a site occupancy of 60:40; only the major part was represented in the figures.

Supplementary material

CCDC-1413230 (**1**) and -1413229 (**2**) 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.

CONCLUSIONS

Two new triorganotin(IV) derivatives containing ligands with oxygen donor atoms were prepared and characterized both in solution and in solid state. The tin atom in **1** and **2** is hexacoordinated with a distorted octahedral geometry. Single-crystal X-ray diffraction reveals the formation of 3D supramolecular architectures through C–H⋯π and hydrogen bond-type intermolecular interactions. Hydrolysis of **1** occurs with an halogen exchange to give the deprotected compound, [2-(O=CH)C$_6$H$_4$]$_3$SnCl (**2**). Infrared spectroscopy confirms formation of the C=O double bounds.

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