

Dedicated to Academician Cristian Silvestru
on the occasion of his 70th anniversary

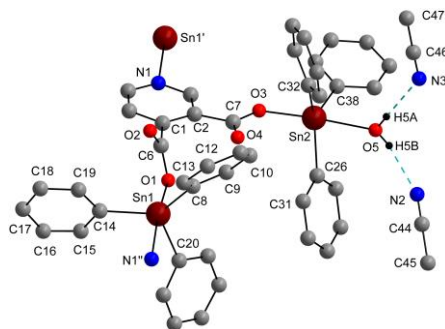
TRIBUTYL- AND TRIPHENYLTIN(IV) DICARBOXYLATES – FROM MONONUCLEAR SPECIES TO POLYMERIC STRUCTURES^{**}

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By reacting potassium pyridine 3,4-dicarboxylate (K₂PDC) with two molar equivalents of Bu₃SnCl or Ph₃SnCl, two novel triorganotin(IV) pyridine-3,4-dicarboxylates [(Bu₃Sn)₂(PDC)] (**1**), [(Ph₃Sn)₂(PDC)] (**2**) were obtained. Triphenyltin(IV) chloride was also treated with sodium 5-aminoisophtalate (AIP) to give [(Ph₃Sn)₂(AIP)] (**3**). The resulting tin complexes were characterized by standard spectroscopic techniques (NMR, IR, MS) and single-crystal X-ray diffraction analysis. The triorganotin(IV) derivatives **1** and **2** exhibit polymeric solid-state structures featuring distorted trigonal bipyramidal configurations of the tin cores. Additionally, two distinct polymorphs were found for complex **1**, both showing 2D polymeric structures with carboxylate groups acting in an asymmetric bidentate fashion. In the structure of **2**, one water molecule and two acetonitrile molecules stop the polymer from growing in more than one dimension. This results in the formation of a 1D chain-like polymer involving only one carboxylate group. The crystal structure of **3** displays a monomeric complex showing five-coordinated tin atoms with both carboxylates binding in an asymmetric bidentate mode; thus, the resulting geometry of the metal centers in **3** is better described as capped tetrahedron.



INTRODUCTION

Organotin(IV) carboxylates have long been studied for their antitumor activity as an alternative to the ubiquitous *cis*platin.^{1–7} Several examples of tin species showed higher cytotoxicity and better selectivity than the usual treatments.^{8–12} Yet, there are still some mechanisms that need to be clarified,^{13,14} but encouraging advancements in the elucidation of structure-activity relationship have

been reported in the last two decades.^{15,16} In addition to the cytotoxic activity illustrated by different organotin(IV) carboxylates, other specific features are currently gaining interest. For instance, the selective detection of Cu²⁺ was achieved by using a triphenyltin(IV) carboxylate.¹⁷ Other organotin(IV) carboxylates illustrated great potential to be employed as visualization agents of the anticancer action, based on their optical properties.¹⁸ Recent investigations on their antiparasitic,¹⁹

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antimicrobial,²⁰ antifungal,²¹ herbicidal,²² or disinfecting²³ activity lead to promising findings, even in the treatment of tropical diseases.^{19,24,25} Moreover, the geometry around the metal centre in organotin(IV) carboxylates affects their biological activity.^{26,27} The oligomerization of the target compounds is also crucial in terms of reactivity and specific properties. Thus, reports on organotin(IV) carboxylates adopting monomeric, dimeric, oligomeric ladder or even 1-D zig-zag chain polymer structures are known.^{28–30}

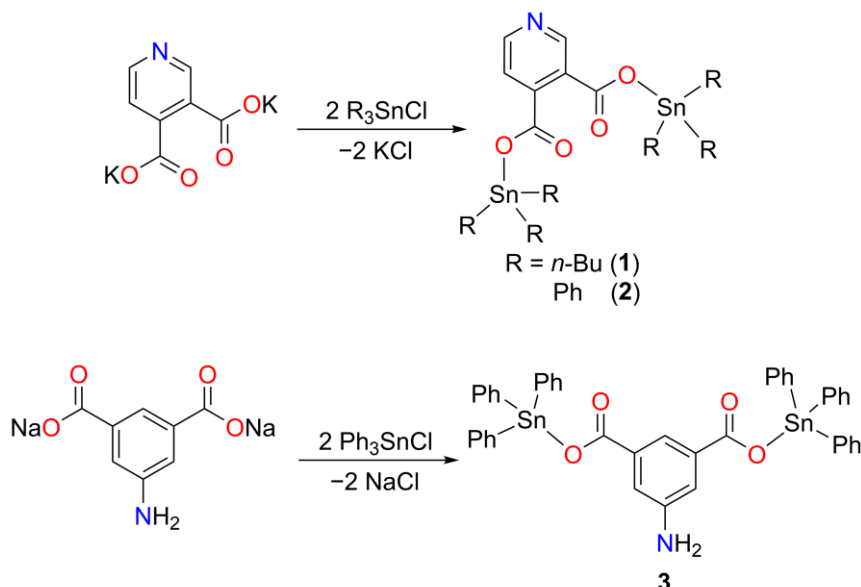
We have on our side decorated a series of organotin(IV) carboxylates with aromatic *C,O*-chelating ligands [e.g. 2-[(CH₂O)₂CR]C₆H₄, 2-(O=CR)C₆H₄, R = H,^{31,32} Me³³ and we presented their antiproliferative and anticancer activity on various cancer cell lines.

Within this study, we are reporting on the synthesis and structural characterization of three

triorganotin(IV) dicarboxylates (Bu₃Sn)₂[3,4-(OOC)₂C₅H₃N] (**1**), (Ph₃Sn)₂[3,4-(OOC)₂C₅H₃N] (**2**) and (Ph₃Sn)₂[1,3-(OOC)₂C₆H₂NH₂-5] (**3**).

RESULTS

Triorganotin(IV) complexes, bis(tributyltin) pyridine-3,4-dicarboxylate [(Bu₃Sn)₂(PDC)] (**1**), bis(triphenyltin) pyridine-3,4-dicarboxylate [(Ph₃Sn)₂(PDC)] (**2**) (PDC = pyridine-3,4-dicarboxylate), and bis(triphenyltin) 5-aminoisophthalate [(Ph₃Sn)₂(AIP)] (**3**) (AIP = 5-aminoisophthalate), were prepared in ethanol upon reaction of two equivalents of the corresponding organotin halides with potassium pyridine-3,4-dicarboxylate (K₂PDC) or with sodium 5-aminoisophthalate (Na₂AIP), respectively (Scheme 1).



Scheme 1 – Synthesis of complexes **1–3**.

The compounds were isolated as colorless, air-stable solids in good yields. All the complexes show good solubility in chlorinated solvents (CH₂Cl₂, CHCl₃) and are insoluble in aliphatic hydrocarbons. They were characterized by solution NMR spectroscopy (¹H, ¹³C{¹H}, ¹¹⁹Sn{¹H}) and infrared spectroscopy, while their solid-state molecular structures were established by single crystal X-ray diffraction analysis (XRD). Satisfactory analytical results and high-resolution mass spectrometry (HRMS) data were also obtained.

The base peak in the ESI+ mass spectrum of **1** is assigned to [Bu₃Sn]⁺ fragment, whereas in the APCI+ HRMS spectrum of **2** the [Ph₃Sn]⁺ fragment

was detected. Although the molecular peak could not be observed for these complexes, a relevant fragment was found in the ESI– HRMS spectrum of **2**, with *m/z* 516.02456 corresponding to the [M–Ph₃Sn][–] fragment.

The IR spectra of **1–3** illustrate the COO[–] asymmetric stretching vibrations of the carbon–oxygen double bond as strong bands between 1679–1612 cm^{–1}. The symmetric stretching vibrations of the COO[–] fragments are also visible between 1379–1301 cm^{–1}, thus indicating an unidentate binding mode of the carboxylate moieties in all the reported triorganotin(IV) complexes (Δ*ν* values > 250, Δ*ν* = [ν_a(COO[–]) – ν_s(COO[–])]).^{9,34}

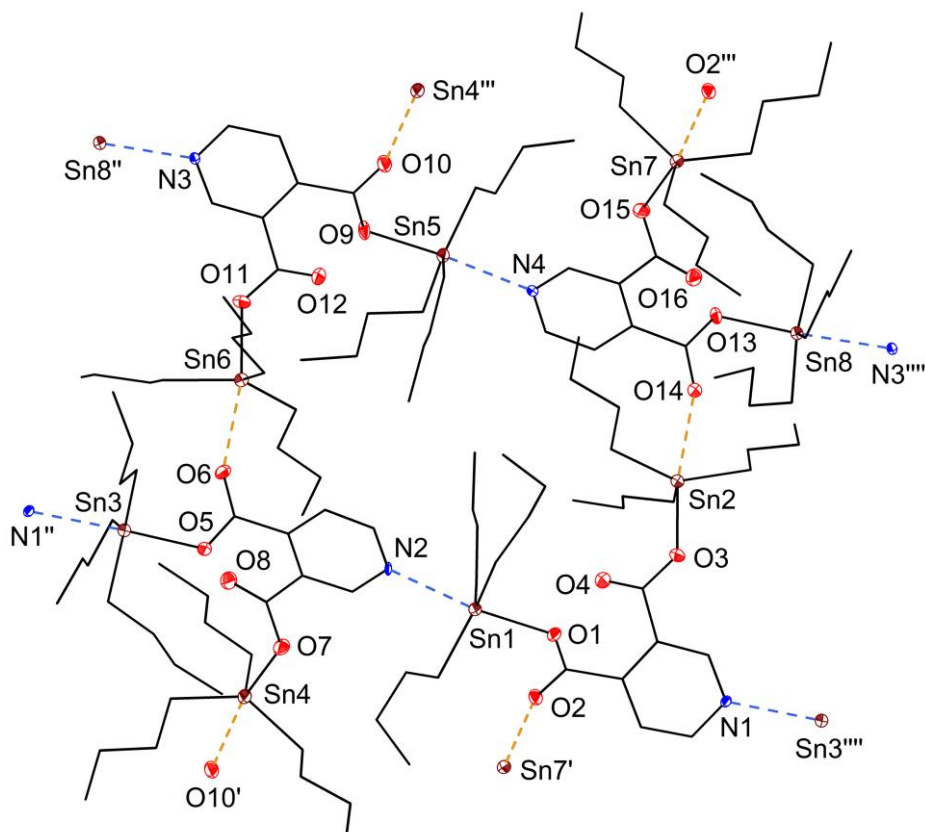


Fig. 1 – Solid-state structure representation showing ellipsoids at 50% probability level (except for the carbon atoms drawn as sticks) of **1a** polymorph. H atoms omitted for clarity. [symmetrically equivalent atoms $(1 + x, y, z)$, $(x, 1 + y, z)$, $(-1 + x, y, z)$, and $(x, -1 + y, z)$ are given by ', '', '' and '''' respectively].

Two distinct polymorphs were found for compound **1**, *i.e.* **1a** (Fig. 1) and **1b** (Fig. 2). Suitable crystals for XRD analysis of **1a** grew by slow diffusion of Et₂O into a concentrated CH₂Cl₂ solution of **1**, whereas for **1b**, hexane was used instead of Et₂O.

Complex **2** is also identified as a polymer in solid-state (Fig. 3), while the molecular structure of the mononuclear complex **3** is illustrated in Fig. 4. Selected interatomic distances and bond angles are summarized in Table 1 and Table 2.

Table 1

Selected interatomic distances (Å) and bond angles (°) for **1a**

1a		1a	
Sn1–O1	2.196(2)	O1–Sn1–N2	172.48(10)
Sn2–O3	2.130(2)	O3–Sn2–O14	169.36(10)
Sn3–O5	2.186(3)	O5–Sn3–N1''	178.24(10)
Sn4–O7	2.134(3)	O7–Sn4–O10'	168.65(10)
Sn5–O9	2.190(3)	O9–Sn5–N4	176.05(10)
Sn6–O11	2.140(3)	O11–Sn6–O6	168.67(11)
Sn7–O15	2.131(3)	O15–Sn7–O2'''	171.17(10)
Sn8–O13	2.191(2)	O13–Sn8–N3''''	177.01(10)
Sn1...N2	2.538(3)		
Sn2...O14	2.592(3)		
Sn3...N1''	2.588(3)		
Sn4...O10'	2.575(2)		
Sn5...N4	2.552(3)		
Sn6...O6	2.546(3)		
Sn7...O2'''	2.612(2)		
Sn8...N3''''	2.550(4)		

DISCUSSION

Solid state structure

Polymorph **1a** crystallizes in the triclinic space group $P\bar{1}$, with eight distinct tin atoms in the asymmetric unit. Four of the tin centers (Sn1, Sn2, Sn5 and Sn6) are connected by four PDC moieties generating the tetranuclear unit of the two-dimensional layer in the crystal of **1a**. The

polymeric structure of **1a** contains two types of five-coordinated tin atoms. The first type (Sn1, Sn3, Sn5 and Sn8) discloses a trigonal bipyramidal geometry about the tin cores, with three carbon atoms in the equatorial positions. In its axial sites, each of these tin atoms holds one oxygen atom from an asymmetric bidentate bridging carboxylate group and one nitrogen atom from an adjacent PDC ligand settled in a head-to-tail fashion.

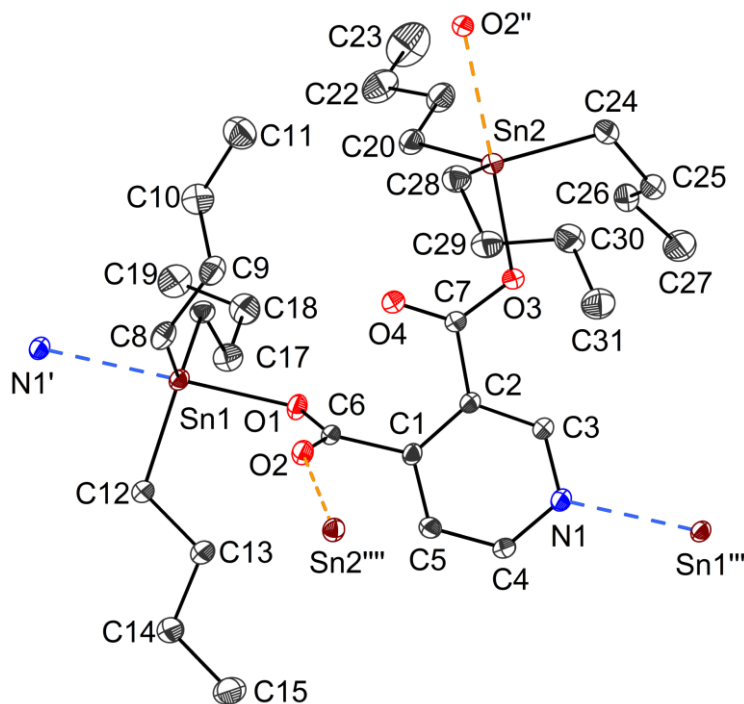


Fig. 2 – ORTEP representation at 50% probability and the atom numbering scheme for polymorph **1b**. H atoms omitted for clarity. [symmetrically equivalent atoms $(x, y, 1+z)$, $(-1/2+x, 3/2-y, -1/2+z)$, $(x, y, -1+z)$, and $(1/2+x, 3/2-y, 1/2+z)$ are given by ', '' and '''' respectively].

The N→Sn interactions established *trans* to the oxygen atoms [$\text{Sn1}\cdots\text{N2}$ 2.538(3) Å, $\text{Sn3}\cdots\text{N1}''$ 2.588(3) Å, $\text{Sn5}\cdots\text{N4}$ 2.552(3) Å, $\text{Sn8}\cdots\text{N3}''''$ 2.550(4) Å] are significantly shorter than the sum of the van der Waals radii of the constituent atoms [$\Sigma r_{\text{vdw}}(\text{Sn}, \text{N})$ 4.08 Å],³⁵ thus presenting comparable values with those observed in similar triorganotin(IV) coordination polymers with pyridine-containing linkers [e.g. $\text{R}_3\text{Sn}[\text{O}(\text{O})\text{CC}_5\text{H}_4\text{N}-4]$, R = Me, 2.572(3) Å;³⁶ *n*Bu, 2.603(16) Å;³⁷ $\text{R}_3\text{Sn}[\text{O}(\text{O})\text{CC}_5\text{H}_4\text{N}-3]$, R = Me, 2.593(3) Å;³⁶ Ph 2.568(7) Å³⁸].

The second type of tin atoms in the crystal of **1a** (Sn2, Sn4, Sn6 and Sn7) is also pentacoordinated, yet they resemble those found in the polymeric structures of *trans*- R_3SnO_2 type, as described by Tiekink.²⁹ Each of these tin atoms adopts a trigonal

bipyramidal structure with two oxygen atoms to rest in the axial positions. The covalently bonded oxygen atom belongs to a monodentate carboxylate group, whereas the coordinated oxygen is part of a bridging carboxylate fragment from an adjacent PDC unit. The O–Sn–O angles lie in the range 168.65(10)–171.17(10)°. The Sn atoms are slightly displaced from the equatorial plane defined by the three carbon atoms of the butyl substituents by *ca.* 0.23 Å towards the covalently bonded oxygen atom. Parallel 2D-layers are further connected via several C–H \cdots π interactions to give a 3D supramolecular arrangement in the crystal of **1a** (Figs. S10–S11) (*i.e.* H \cdots Py_{centroid} 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 Ph_{centroid} smaller than 30°).³⁹

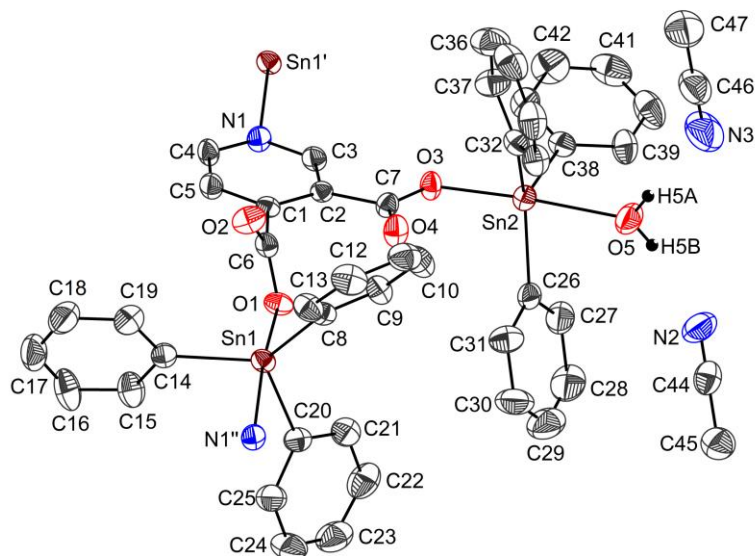


Fig. 3 – ORTEP representation at 30% probability and the atom numbering scheme for compound **2** · 2 MeCN · H₂O. H atoms omitted for clarity except for the water hydrogen atoms H5A and H5B. [symmetrically equivalent atoms $(-1 + x, y, z)$, and $(1 + x, y, z)$ are given by ' and '' respectively].

Table 2
Selected interatomic distances (Å) and bond angles (°) for **1b**, **2** and **3**

	1b	2	3
Sn1–C ^a	2.149(3)	2.144(8)	2.141(7)
Sn1–C ^b	2.147(3)	2.130(9)	2.131(9)
Sn1–C ^c	2.140(3)	2.146(9)	2.118(9)
Sn1–O1	2.174(2)	2.150(5)	2.061(6)
Sn1···N1'	2.596(3)	2.581(7)	
O1–Sn1–N1'	174.10(8)	173.9(2)	
C ^a –Sn1–C ^b	117.73(14)	125.5(3)	111.6(4)
C ^b –Sn1–C ^c	117.02(11)	112.2(3)	118.8(4)
C ^c –Sn1–C ^a	123.39(13)	119.9(3)	108.5(4)
Sn2–C ^d	2.145(3)	2.119(8)	2.114(9)
Sn2–C ^e	2.159(3)	2.131(8)	2.125(11)
Sn2–C ^f	2.145(3)	2.131(8)	2.141(10)
Sn2–O3	2.145(2)	2.139(5)	2.075(6)
Sn2···O ^x	2.595(3)	2.430(8)	
O3–Sn2–O ^x	177.62(10)	176.3(3)	
C ^d –Sn2–C ^e	117.19(14)	131.8(3)	117.5(4)
C ^e –Sn2–C ^f	119.48(14)	110.9(3)	113.0(5)
C ^f –Sn2–C ^d	119.94(14)	114.1(3)	108.3(3)

C^a = C8 for **1b**, C8 for **2**, and C9 for **3**; C^b = C12 for **1b**, C14 for **2**, and C15 for **3**; C^c = C12 for **1b**, C20 for **2**, and C21 for **3**; C^d = C20 for **1b**, C26 for **2**, and C27 for **3**; C^e = C24 for **1b**, C32 for **2**, and C33 for **3**; C^f = C28 for **1b**, C38 for **2**, and C39 for **3**; O^x = O2'' for **1b** and O5 for **2**.

The second polymorph, **1b**, reveals a polymer that crystallizes in the monoclinic space group Cc and shows only one 3,4-pyridine dicarboxylate fragment binding two distinct tin atoms constituting the elementary unit. The Sn1 atom contributes to the formation of a one-dimensional chain-like polymer with neighboring PDC moieties in a head-to-tail arrangement, thus giving a strong N→Sn interaction [2.596(3) Å]. The O1–Sn1–N1' angle [174.10(8)°]

is lightly deviated from the ideal linearity, while the C_i–Sn1–C_j angles are close to 120°, the regular value between the equatorial sites of a trigonal bipyramidal tin core. These polymers are further connected through O2''→Sn2 interactions between parallel chains. Therefore, Sn2 is rendered five-coordinate featuring a distorted trigonal bipyramidal geometry with an almost linear O3–Sn2–O2'' angle [177.62(10)°]. The 2D wave-like

layers in the crystal of **1b** are no further connected (for details, see Figs. S12–S13).

The crystal of **2** contains a 1D linear coordination polymer based on head-to-tail strong N→Sn contacts [Sn1–N1' 2.581(7) Å, *cf.*: $\Sigma r_{\text{cov}}(\text{Sn},\text{N})$ 2.10 Å⁴⁰ and $\Sigma r_{\text{vdw}}(\text{Sn},\text{N})$ 4.08 Å]. The second tin atom, Sn2, in **2** has one oxygen atom from a water molecule occupying an axial position of the distorted trigonal bipyramidal coordination geometry ($\tau_5 = 0.74$)⁴¹ [Sn2–O5 2.430(8) Å]. Furthermore, water's hydrogen atoms gathered two acetonitrile molecules *via* two strong O–H⋯N bonds [H5A⋯N3 2.05 Å, H5B⋯N2 2.04 Å, $\Sigma r_{\text{vdw}}(\text{H},\text{N})$ 2.86 Å], to define the complex's solid-state formula to $\{(\text{Ph}_3\text{Sn})_2[3,4\text{-(OOC)}_2\text{C}_5\text{H}_3\text{N}]\cdot(\text{OH}_2)\cdot(\text{NCMe})_2\}$. The magnitude of O5→Sn2 contact is well correlated with those reported for analog triphenyltin(IV) carboxylates [*i.e.* [Ph₃SnO₂CR(OH₂)], R = benzo-18-crown-6, 2.471(6) Å,⁴² [Ph₃Sn{O₂CC₆H₃-*p*-OH[N=N(C₆H₄-2-CH₃)]}(OH₂):(2,2'-bipy)] 2.369(2) Å,⁴³

$\{[\text{Ph}_3\text{Sn}(2,3\text{-pdz})\text{SnPh}_3]_2(\text{OH}_2)\}$, pdz = pyrazinedicarboxylate, 2.518(10) Å,⁴⁴ {Ph₃Sn[O₂C(C₆H₄)-CH₂O-2](OH₂)} 2.380(1) Å⁴⁵]. The coordination geometry around Sn1 atom could also be described as a distorted trigonal bipyramidal one ($\tau_5 = 0.81$) with three *ipso*-carbon atoms of the phenyl rings in the equatorial sites [$\Sigma \theta_{\text{equatorial}}(\text{Sn1}) = 357.6^\circ$]. The angle between the axial positions O1–Sn1–N1' [173.9(2)°] is slightly altered from linearity and the Sn1 atom is displaced from the equatorial plane towards O1 by only 0.19 Å. Moreover, the C–O interatomic distances in **2** [C6–O2 1.219(9) Å, C7–O4 1.218(9) Å] are shorter than those of the C–O bonds in **1a** [C6–O2 1.237(4) Å, C13–O6 1.241(5) Å, C14–O7 1.298(4) Å, C20–O10 1.236(4) Å, C1C–O14 1.237(5) Å] or **1b** [C6–O2 1.241(4) Å] emphasizing a small elongation of the C–O bonds if the carboxylate acts as a bidentate ligand. No additional contacts between parallel 1D polymers in the crystal of **2** were noticed (Figs. S14–S15).

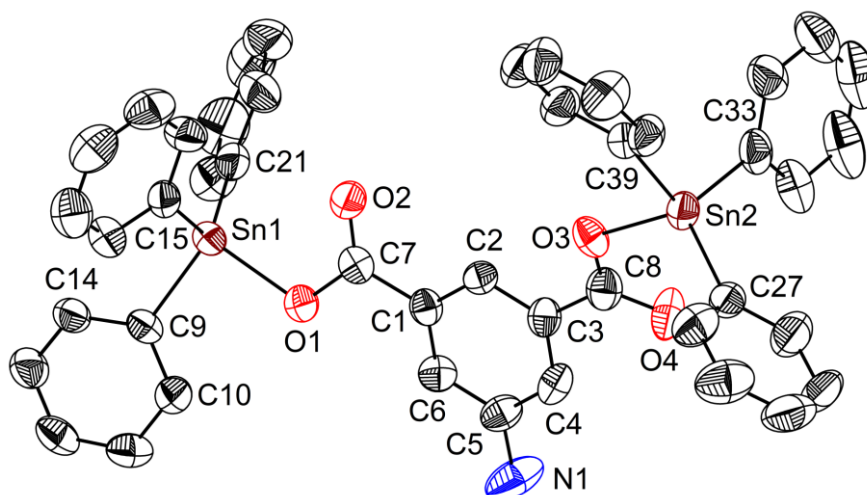


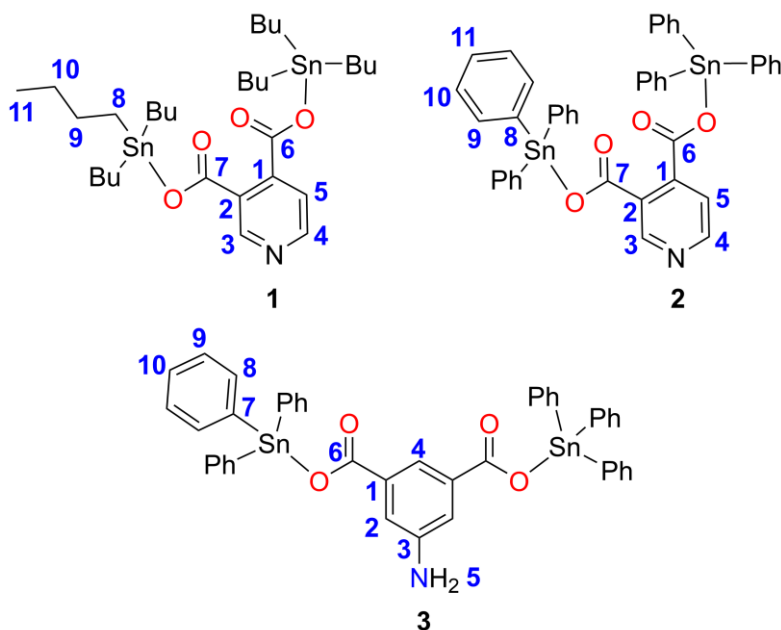
Fig. 4 – ORTEP representation at 30% probability and the atom numbering scheme for compound **3**. H atoms omitted for clarity.

The molecular structure of **3** was confirmed by XRD analysis of single crystals grown by slow diffusion of hexane into a concentrated solution of the title compound in dichloromethane. The complex exists as a molecular species in the solid state, with both metal centers to rest in a four-coordinate environment featuring a distorted tetrahedral geometry [$\tau_4(\text{Sn1}) = 0.91$; $\tau_4(\text{Sn2}) = 0.91$]. The second oxygen atom of the carboxylate groups is weakly coordinated to the tin atoms [O2→Sn1 2.820(6) Å and O4→Sn2 2.718(9) Å], thus capping one of the tetrahedron's faces. This asymmetric bidentate behavior of the carboxylates is quite common when binding triphenyltin(IV)

moieties.^{45–48} Within the crystal, there are no C–H⋯π or π⋯π interactions observed and only a few weak (C–H⋯O) hydrogen bond type contacts [H⋯O > 2.62 Å, $\Sigma r_{\text{cov}}(\text{O},\text{H})$ 0.97 Å and $\Sigma r_{\text{vdw}}(\text{O},\text{H})$ 2.70 Å] are gathering the molecules in the crystal packing.

Solution behavior

The assignment of the resonances in the ¹H and ¹³C NMR spectra was based on 2D NMR (HSQC, HMBIC and COSY) correlation spectra and tin-carbon coupling constants according to the numbering shown in Fig. 5.

Fig. 5 – NMR numbering scheme for compounds **1-3**.

The room-temperature NMR (^1H , ^{13}C) spectra for compounds **1-3** display one set of characteristic resonance signals corresponding to the Sn-bound organic moieties with the expected patterns. This behavior is consistent with the equivalence of the organic substituents attached to tin on the NMR time scale. The $^1J_{^{119}\text{Sn},^{13}\text{C}}$ coupling constant (353 Hz) observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** indicates a tetrahedral arrangement of the Bu_3SnO cores with four-coordinate tin atoms in CDCl_3 solution.⁴⁹ This is also corroborated by the C–Sn–C (carbon atoms from the two butyl substituents) calculated angle based on the relationship between

$^1J_{^{119}\text{Sn},^{13}\text{C}}$ coupling constants and the C–Sn–C angle in Bu_3SnX derivatives (Table 3).⁵⁰ Additionally, the two tin atoms in **1** have slightly different chemical environments, as indicated by the $^{119}\text{Sn}\{^1\text{H}\}$ NMR chemical shifts ($\delta_{^{119}\text{Sn}}$ 127.9, 123.5 ppm), yet both are within the usual range of four-coordinate tin atoms employing a tetrahedral geometry in solution [e.g., $\delta_{^{119}\text{Sn}}$ (ppm): Bu_3SnCl : 152.8;⁵¹ $(\text{Bu}_3\text{Sn})_2\text{O}$: 92.7;⁵¹ $\text{Bu}_3\text{Sn}(\text{IBF})$: 110.9, IBF = ibuprofen,⁴⁸ $\text{Bu}_3\text{Sn}(\text{nic})$ 117.5, nic = nicotinate],⁵² thus suggesting that the polymeric solid-state structure with five-coordinate tin centers (*vide supra*) is not preserved in solution.

Table 3

Correlations between ^{13}C – ^{119}Sn coupling constants (Hz) and C–Sn–C angles (θ , °) in compounds **1-3**

Compound	^{13}C		XRD
	$^1J_{^{119}\text{Sn},^{13}\text{C}}$	θ C–Sn–C	$(\text{C–Sn–C})_{\text{av}}$
1	353	110.0 ^a	119.3
2	648	116.2 ^b	119.1
3	649	116.3 ^b	113.0

$$^a |^1J_{^{119}\text{Sn},^{13}\text{C}}| = 9.99\theta - 746; \quad ^b |^1J_{^{119}\text{Sn},^{13}\text{C}}| = 15.56\theta - 1160;$$

The same pattern was noticed for the triphenyltin(IV) complexes **2** and **3**. Therefore, the $^1J_{^{119}\text{Sn},^{13}\text{C}}$ coupling constants found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** and **3** are well correlated to those of analogue triphenyltin compounds adopting a tetrahedral arrangement in solution ($^1J_{^{119}\text{Sn},^{13}\text{C}}$ between 550 and 660 Hz).⁵³ Additionally, the $^{119}\text{Sn}\{^1\text{H}\}$ NMR resonances for **2** ($\delta_{^{119}\text{Sn}}$ –95.8, –98.1 ppm) and **3** ($\delta_{^{119}\text{Sn}}$ –108.0 ppm) are consistent with those usually observed for tetrahedral tin

compounds in solution [$\delta_{^{119}\text{Sn}}$ –82.5 ppm for Ph_3SnOH ,⁵¹ –109.9 ppm for $\text{Ph}_3\text{SnOOCPh}$ or –122.6 for $\text{Ph}_3\text{Sn}(\text{OOC})\text{C}_6\text{H}_4\text{NH}_2\text{-4}$].⁵³ The magnitude of the calculated $\text{C}_{\text{Ph}}\text{–Sn–C}_{\text{Ph}}$ angles (Table 3) based on the $^1J_{^{119}\text{Sn},^{13}\text{C}}$ coupling constants formula,⁵⁴ are rather indicating a borderline geometry between tetrahedral and trigonal bipyramid in solution for both compounds. However, complexes **2** and **3** display distinct coordination geometries in solid-state (*vide supra*).

EXPERIMENTAL

General procedures

Multinuclear NMR spectra (^1H , ^{13}C , ^{119}Sn and 2D) were recorded at room temperature on Bruker Avance III 400 and 600 spectrometers. The ^1H chemical shifts are reported in δ units (ppm) relative to the residual resonance of the deuterated solvent (ref. CDCl_3 : ^1H 7.26 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the signal of the solvent (ref. CDCl_3 : ^{13}C 77.16 ppm). For the ^{119}Sn NMR spectra the chemical shifts are reported in ppm relative to SnMe_4 . ^1H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HMQC and HMBC). The NMR spectra were processed using the *MestReNova* software.⁵⁵ Mass spectra were recorded on a Thermo Scientific LTQ Orbitrap XL mass spectrometer equipped with a standard ESI/APCI source. Infrared spectra were recorded on a JASCO FT/IR-615 instrument. Melting points were established on an Electrothermal 9200 apparatus and are not corrected. Elemental analyses were carried out on a VarioEl analyzer. Solvents were dried and freshly distilled prior to use. Starting materials such as Bu_3SnCl , Ph_3SnCl , pyridine-3,4-dicarboxylic acid and 5-aminoisophtalic acid were obtained from Sigma or Merck and used as received. The alkali salts K_2PDC and sodium 5-aminoisophtalate were prepared according to literature methods.⁵⁶

Synthesis of $(\text{Bu}_3\text{Sn})_2[3,4-(\text{OOC})_2\text{C}_5\text{H}_3\text{N}]$ (1). $[3,4-(\text{KOOC})_2\text{C}_5\text{H}_3\text{N}]$ (0.245 g, 1.01 mmol) and Bu_3SnCl (0.656 g, 2.01 mmol) were stirred in ethanol (30 mL), then heated to reflux for 3 h. After cooling, the solvent was removed *in vacuo* and the title compound was dissolved in dichloromethane (30 mL). The resulting mixture was filtered and the solvent removed to give the title compound as a colorless solid (0.688 g, 92%). M.p. 106–109°C. Elemental analysis: calcd for $\text{C}_{31}\text{H}_{57}\text{NO}_4\text{Sn}_2$ (745.22 g/mol): C, 49.96; H, 7.71; N, 1.88%. Found: C, 49.59; H, 7.96; N, 1.53%. ^1H NMR (400.1 MHz, CDCl_3 , 22 °C): δ 0.92t (18H, H-11, $^2J_{\text{H,H}} = 7.3$ Hz), 1.36m (24H, H-8, H-10), 1.66m (12H, H-9), 7.36d (1H, H-5, $^3J_{\text{H,H}} = 5.0$ Hz), 8.65d (1H, H-4, $^3J_{\text{H,H}} = 5.0$ Hz), 8.98s (1H, H-3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 22°C): δ 13.80s (C-11), 16.84s (C-8, $^1J_{\text{Sn,C}} = 338/353$ Hz), 27.21s (C-10, $^3J_{\text{Sn,C}} = 66$ Hz), 27.24s (C-10', $^3J_{\text{Sn,C}} = 66$ Hz), 27.95s (C-9, $^2J_{\text{Sn,C}} = 19$ Hz), 121.61s (C-5), 127.14s (C-2), 143.50s (C-1), 150.84s (C-3), 151.56s (C-4), 170.14s (C-7), 171.96s (C-6). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.2 MHz,

CDCl_3 , 22°C): δ 127.9s, 123.5s. HRMS (ESI+, MeOH) m/z (relative intensity, %): $[\text{Bu}_3\text{Sn}]^+$, calcd. for $\text{C}_{12}\text{H}_{27}\text{Sn}$: 291.11292. Found 291.11413 (24). IR (KBr pellet, ν , cm^{-1}): 3650 (w), 2959 (vs) 2924 (vs), 2854 (s), 1659 (vs), 1612 (vs), 1543 (m), 1459 (m), 1379 (vs), 1333 (vs), 1280 (m), 1182 (m), 11159 (m), 1117 (m), 1078 (m), 1055 (m), 1024 (m), 961 (w), 881 (m), 866 (m), 814 (m), 773 (w), 673 (vs), 610 (m), 570 (w).

Synthesis of $(\text{Ph}_3\text{Sn})_2[3,4-(\text{OOC})_2\text{C}_5\text{H}_3\text{N}]$ (2). In a similar manner, $[3,4-(\text{KOOC})_2\text{C}_5\text{H}_3\text{N}]$ (0.245 g, 1.01 mmol) and Ph_3SnCl (0.656 g, 2.01 mmol) were stirred in ethanol (30 mL), then heated to reflux for 3 h. The resulting precipitate was filtered and then the title compound was dissolved in dichloromethane (70 mL). The resulting suspension was filtered, and the solvent was removed *in vacuo* to obtain the compound as a colorless solid (0.728 g, 79%). Recrystallization from MeCN afforded colorless crystals, m.p. : >250°C dec. Elemental analysis: calcd for $\text{C}_{43}\text{H}_{33}\text{NO}_4\text{Sn}_2$ (865.16 g/mol): C, 59.70; H, 3.84; N, 1.62%. Found: C, 60.25; H, 4.46; N, 1.42%. ^1H NMR (600.1 MHz, CDCl_3 , 21°C): δ 7.37m (18H, H-10, H-11), 7.43m (1H, H-5), 7.68m (12H, H-9), 8.66d (1H, H-4, $^3J_{\text{H,H}} = 5.0$ Hz), 9.10s (1H, H-3). ^{13}C NMR (150.9 MHz, CDCl_3 , 22 °C): δ 121.94s (C-5), 125.53s (C-2), 129.03s (C-10, $^3J_{\text{Sn,C}} = 64$ Hz), 130.30s (C-11), 137.02s (C-9, $^2J_{\text{Sn,C}} = 49$ Hz), 137.88s (C-8, $^1J_{\text{Sn,C}} = 619/648$ Hz), 142.67s (C-1), 151.38s (C-3), 152.32s (C-4), 170.67s (C-7), 172.60s (C-6). ^{119}Sn NMR (149.2 MHz, CDCl_3 , 21°C): δ -95.8s, -98.1s. HRMS (APCI+, $\text{CH}_2\text{Cl}_2+\text{MeOH}$), m/z (relative intensity, %): $[\text{Ph}_3\text{Sn}]^+$, calcd. for $\text{C}_{15}\text{H}_{18}\text{Sn}$: 351.01902. Found 351.01891 (100). HRMS (ESI-, $\text{CH}_2\text{Cl}_2+\text{MeOH}$), m/z (relative intensity, %): $[\text{M}-\text{Ph}_3\text{Sn}]^-$, calcd. for $\text{C}_{25}\text{H}_{18}\text{O}_4\text{NSn}$: 516.02523. Found 516.02456 (100). IR (KBr pellet, ν , cm^{-1}): 3069 (w), 3046 (w), 1679 (s), 1660 (s), 1550 (m), 1481 (m), 1430 (m), 1409 (w), 1337 (vs), 1316 (s), 1284 (w), 1189 (w), 1158 (w), 1112 (w), 1076 (m), 1023 (m), 997 (w), 861 (w), 833 (w), 809 (w) 774 (vs), 729 (s), 697 (m), 677 (w), 618 (w).

Synthesis of $(\text{Ph}_3\text{Sn})_2[1,3-(\text{OOC})_2\text{C}_6\text{H}_3\text{NH}_2-5]$ (3). Triphenyltin chloride (0.685 g, 1.78 mmol) was added to a suspension of sodium 5-aminoisophtalate (0.220 g, 0.98 mmol) in ethanol (30 mL) and heated to reflux for 3 h. The solvent was then removed, and the title compound was dissolved in CH_2Cl_2 (40 mL). The suspension was filtered and the solvent removed using a rotary evaporator resulting in 0.564 g, 72%, of compound **3** as a colorless solid. m.p. 197–199 °C. Elemental analysis: calcd for

$C_{44}H_{35}NO_4Sn_2$ (879.19 g/mol): C, 60.11; H, 4.01; N, 1.59%. Found: C, 60.92; H, 4.50; N, 1.39%. 1H NMR (400.13 MHz, $CDCl_3$, 21°C): δ 3.80s (2H, H-5), 7.46m (18H, H-9, H-10), 7.58d (2H, H-2, $^4J_{H,H} = 1.5$ Hz), 7.80m (12H, H-8), 8.27t (1H, H-4, $^3J_{H,H} = 1.5$ Hz). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 21 °C): δ 120.86s (C-2), 123.09s (C-4), 129.07s (C-9, $^3J_{Sn,C} = 63$ Hz), 130.30s (C-10, $^4J_{Sn,C} = 13$ Hz), 131.93s (C-1), 137.06s (C-8, $^2J_{Sn,C} = 48$ Hz), 138.36s (C-7, $^1J_{Sn,C} = 649$ Hz), 146.43s (C-3), 172.36s (C-6). $^{119}Sn\{^1H\}$ NMR (149.20 MHz, $CDCl_3$, 21°C): δ -108.0s. IR (KBr pellet, ν , cm^{-1}): 3067 (w), 3046 (w), 1643 (s), 1619 (s), 1596 (s), 1566 (s), 1480 (m), 1430 (s), 1379 (m), 1301 (vs), 1257 (m), 1190 (w), 1130 (w), 1076 (m), 1022 (w), 997 (w), 813 (w), 772 (m), 746 (vs), 729 (vs), 696 (vs).

Crystal structures

The details of the crystal structure determination and refinement are given in Table S1. The crystals of **1a** and **1b** were collected on a Bruker D8 VENTURE diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) from a I μ S 3.0 microfocus source with multilayer optics, at low temperature (100 K). The structures were refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the Bruker APEX5 Software Package was used.⁵⁷ The crystals of **2** and **3** were mounted on cryoloops and data were collected with a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature (297 K). 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-2019 was used. The drawings were created with the Diamond program.⁵⁸ CCDC reference numbers: 2426304 (**1a**), 2426303 (**1b**), 2426301 (**2**), and 2426302 (**3**).

CONCLUSIONS

This study focuses on the preparation and structural characterization of a series of novel triorganotin(IV) dicarboxylates with pyridine-3,4-dicarboxylic and 5-aminoisophthalic acids. Single-

crystal X-Ray diffraction analysis revealed their solid-state structures, whereas their identity and purity was confirmed by various spectroscopic and analytical methods. $^{119}Sn\{^1H\}$ NMR spectroscopic investigations indicated that all the isolated species have tetracoordinated tin atoms in $CDCl_3$, thus the coordination geometries observed in solid-state are not maintained. The crystal of the polymer **1a** evidenced a 3D supramolecular architecture as result of multiple C-H $\cdots\pi$ intermolecular interactions, while the parallel layers in **1b** or the mono-dimensional chains in **2** are not further connected in the crystal. The solid-state structure of **3** revealed a molecular complex, contrasting the polymers observed in **1** and **2**. Both tin centers in **3** featured a capped distorted tetrahedral coordination geometry with no additional intermolecular interactions detected in the crystal.

Supplementary material. The data supporting the work presented in the manuscript is available as ESI. The crystallographic data for the four compounds discussed herein are available from the CCDC as references: 2426301–2426304.

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