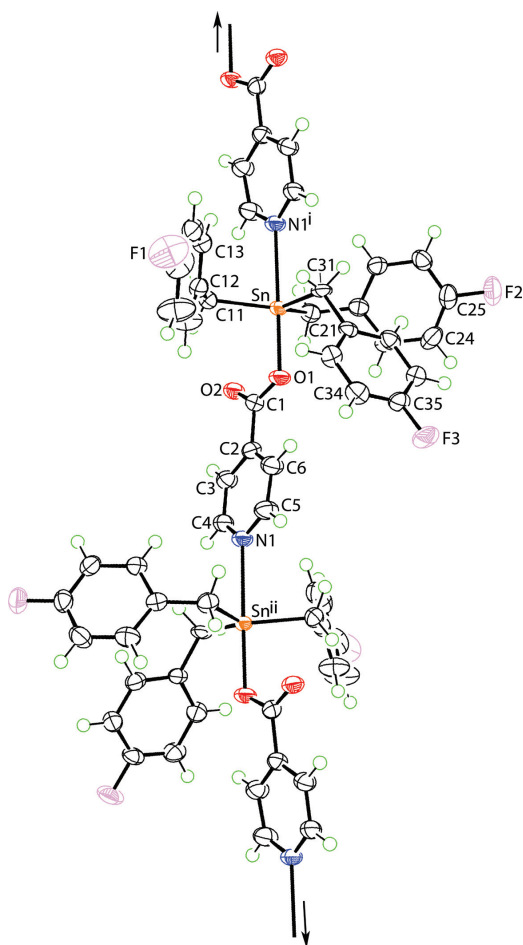


Kong Mun Lo, See Mun Lee and Edward R.T. Tiekink\*

# Low temperature redetermination of the crystal structure of *catena*-poly[[tri-4-fluorobenzyltin(IV)] $\mu_2$ -pyridine-4-carboxylato- $\kappa^2$ N:O], {C<sub>27</sub>H<sub>22</sub>F<sub>3</sub>NO<sub>2</sub>Sn}<sub>n</sub>



$V = 2338.87(11) \text{ \AA}^3$ ,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0324$ ,  $wR_{\text{ref}}(F^2) = 0.0873$ ,  $T = 100(2) \text{ K}$ .

CCDC no.: 1964838

A part of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.11 × 0.07 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
$\mu$ :	9.12 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\text{max}}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	28977, 4175, 0.056
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 3731
$N(\text{param})_{\text{refined}}$ :	307
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

## Source of material

Tri(4-fluorobenzyl)tin chloride was prepared from the direct reaction of 4-fluorobenzyl chloride (Sigma-Aldrich) and metallic tin powder (Sigma-Aldrich) in water according to a literature procedure [5]. The base hydrolysis of tri(4-fluorobenzyl)tin chloride using 10% sodium hydroxide solution (Merck) afforded tri(4-fluorobenzyl)tin hydroxide. Tri(4-fluorobenzyl)tin hydroxide (0.46 g, 1.0 mmol) and isonicotinic acid (Sigma-Aldrich, 0.12 g, 1.0 mmol) were heated in 95% ethanol (30 mL) for 1 h until the hydroxide dissolved. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. **Yield:** 0.34 g (59.8%). **M.pt** (Electrothermal digital melting point apparatus): 439–441 K. **Elem. Anal.** (Perkin-Elmer EA2400 CHN analyser): Calc. for C<sub>27</sub>H<sub>22</sub>F<sub>3</sub>NO<sub>2</sub>Sn: C 56.94; H 3.87; N 2.46%. Found: C 56.49; H 3.79; N 2.33%. **IR** (Nujol mull between KBr plates on a Perkin-Elmer RX1 spectrophotometer; cm<sup>-1</sup>): 1353(s)  $\nu_s(\text{COO})$ , 574 (m)  $\nu(\text{Sn}-\text{O})$ , 471 (w)  $\nu(\text{Sn}-\text{N})$ . **<sup>1</sup>H NMR** (Bruker AVN FT-NMR 400 MHz spectrometer, chemical shifts relative to Me<sub>4</sub>Si, CDCl<sub>3</sub> solution; ppm):  $\delta$  2.59 (s, 6H, CH<sub>2</sub>), 6.90–6.98

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## Abstract

C<sub>27</sub>H<sub>22</sub>F<sub>3</sub>NO<sub>2</sub>Sn, monoclinic,  $P2_1/n$  (no. 14),  $a = 8.7913(2) \text{ \AA}$ ,  $b = 19.0856(5) \text{ \AA}$ ,  $c = 13.9417(4) \text{ \AA}$ ,  $\beta = 91.017(2)^\circ$ ,

**Corresponding author:** Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. <https://orcid.org/0000-0003-1401-1520>

**Kong Mun Lo and See Mun Lee:** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	U <sub>iso</sub> <sup>*</sup> /U <sub>eq</sub>
Sn	0.32442(2)	0.39712(2)	0.24950(2)	0.01849(10)
O1	0.3225(3)	0.28454(13)	0.24758(18)	0.0264(6)
O2	0.1171(3)	0.28680(12)	0.15110(18)	0.0246(5)
F1	0.1640(4)	0.40268(15)	0.7203(2)	0.0577(8)
F2	1.0138(2)	0.43234(13)	0.06022(19)	0.0408(6)
F3	0.8615(3)	0.15044(11)	0.36698(18)	0.0367(5)
N1	0.1716(3)	0.03271(15)	0.2340(2)	0.0239(6)
C1	0.2118(4)	0.25583(18)	0.2005(3)	0.0219(7)
C2	0.2019(4)	0.17703(18)	0.2121(3)	0.0222(7)
C3	0.0898(4)	0.14029(19)	0.1623(3)	0.0256(8)
H3	0.021121	0.164068	0.120233	0.031*
C4	0.0794(4)	0.06883(19)	0.1746(3)	0.0249(7)
H4	0.003269	0.044035	0.139265	0.030*
C5	0.2788(4)	0.0685(2)	0.2824(3)	0.0289(8)
H5	0.344258	0.043662	0.325350	0.035*
C6	0.2989(4)	0.1401(2)	0.2729(3)	0.0279(8)
H6	0.378018	0.163502	0.307403	0.033*
C11	0.1061(4)	0.40747(18)	0.3177(3)	0.0239(7)
H11A	0.058095	0.452236	0.297937	0.029*
H11B	0.038495	0.368761	0.296563	0.029*
C12	0.1245(4)	0.40577(19)	0.4246(3)	0.0257(8)
C13	0.1631(4)	0.4662(2)	0.4760(3)	0.0283(8)
H13	0.179573	0.508742	0.442477	0.034*
C14	0.1779(4)	0.4651(2)	0.5758(3)	0.0335(9)
H14	0.203947	0.506423	0.610291	0.040*
C15	0.1543(5)	0.4034(2)	0.6230(3)	0.0398(10)
C16	0.1175(7)	0.3424(2)	0.5756(3)	0.0496(12)
H16	0.101932	0.300038	0.609873	0.059*
C17	0.1037(5)	0.3444(2)	0.4763(3)	0.0384(10)
H17	0.079376	0.302441	0.442664	0.046*
C21	0.3778(4)	0.41445(19)	0.1016(3)	0.0241(7)
H21A	0.336681	0.375365	0.062317	0.029*
H21B	0.328550	0.458275	0.079192	0.029*
C22	0.5468(4)	0.41968(18)	0.0877(2)	0.0220(7)
C23	0.6296(5)	0.3637(2)	0.0506(3)	0.0303(8)
H23	0.577435	0.322248	0.031332	0.036*
C24	0.7867(5)	0.3672(2)	0.0412(3)	0.0334(9)
H24	0.842096	0.328629	0.016680	0.040*
C25	0.8597(4)	0.4278(2)	0.0681(3)	0.0286(8)
C26	0.7836(4)	0.48477(19)	0.1038(3)	0.0270(8)
H26	0.836969	0.526114	0.121953	0.032*
C27	0.6267(4)	0.48041(18)	0.1127(3)	0.0248(7)
H27	0.572550	0.519673	0.136389	0.030*
C31	0.5169(4)	0.39896(16)	0.3470(3)	0.0225(7)
H31A	0.585923	0.437149	0.327366	0.027*
H31B	0.480332	0.410442	0.411888	0.027*
C32	0.6067(4)	0.33213(17)	0.3530(2)	0.0192(7)
C33	0.5725(4)	0.27942(19)	0.4183(3)	0.0247(7)
H33	0.489468	0.285587	0.460208	0.030*
C34	0.6574(4)	0.21788(19)	0.4235(3)	0.0273(8)
H34	0.634027	0.182369	0.468617	0.033*
C35	0.7752(4)	0.21000(18)	0.3618(3)	0.0254(8)
C36	0.8122(4)	0.26001(19)	0.2944(3)	0.0259(8)
H36	0.893297	0.252723	0.251376	0.031*
C37	0.7271(4)	0.32122(18)	0.2917(3)	0.0238(7)
H37	0.751898	0.356600	0.246671	0.029*

(m, 12H, Ph-H), 7.90–8.63 (4H, pyridine-H). <sup>13</sup>C{<sup>1</sup>H} NMR (as for <sup>1</sup>H NMR): δ 27.0 (CH<sub>2</sub>), 115.0, 130.0, 137.1, 158.8 (Ph-C), 123.4, 142.5, 150.4 (pyridine-C). 168.6 (C=O).

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The maximum and minimum electron density peaks of 1.45 and 0.61 e Å<sup>-3</sup>, respectively, were located 1.01 and 0.81 Å, respectively, from the Sn atom. Owing to poor agreement, the (4 15 0) reflection was omitted from the final cycles of refinement.

### Comment

Steric bulk associated with heavy element- and/or ligand-bound organic substituents are well-documented to moderate the formation of secondary M···O/S bonding interactions [6, 7] in crystals of the zinc-triad [8], tin [9], arsenic-triad [10] and tellurium [11] carboxylates/1,1-dithiolates. This effect is nicely illustrated in the series of solvent-free crystal structures of triorganotin(pyridine-4-carboxylato) molecules, i.e. molecules of the general formula R<sub>3</sub>Sn(O<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N-4). The common feature of these structures is the presence of five-coordinate tin-atom geometries defined by *trans*-C<sub>3</sub>NO donor sets owing to the presence of μ<sub>2</sub>-pyridine-4-carboxylato bridges. Thus, derivatives with R = methyl [12, 13], *n*-butyl [14], cyclohexyl [15], benzyl [16], 2-chlorobenzyl [17], 2-fluorobenzyl [18], 4-fluorobenzyl [19], phenyl [20] and the mixed species R<sub>3</sub> = phenyl<sub>2</sub>(ethyl) [21] are known. The title compound, i.e. the species with R = 4-fluorobenzyl, (I), was isolated as part of continuing interest in this area [9, 16]; over and above structural considerations, recent work has indicated both nicotinic and isonicotinic acid derivatives of organotins [12], including benzyltin compounds, display potential as anti-cancer agents [22]. During characterisation of the previously described R = 4-fluorobenzyl derivative [19] by X-ray crystallography at 100(2) K, significant differences in some tin-bound parameters were noted between the new data and the literature analysis, conducted at 298(2) K [19]. Hence, herein the crystal and molecular structures of the R = 4-fluorobenzyl compound, redetermined at 100(2) K. are described and compared with literature structures and more specifically with the room temperature structure [19].

A portion of the polymeric structure of (I) is shown in the figure with the crystallographic asymmetric unit, corresponding to a repeat unit, labelled (70% displacement ellipsoids; symmetry operations i: 1/2 - x, 1/2 + y, 1/2 - z and ii: 1/2 - x, -1/2 + y, 1/2 - z). The structure is a one-dimensional coordination polymer and being propagated by a 2<sub>1</sub> screw symmetry along the *b*-axis direction, has a helical topology. A *trans*-C<sub>3</sub>NO donor set coordinates the tin atom: the donor atoms

are derived from the carbon atoms of the three benzyl substituents, an oxygen atom from the carboxylato group and a pyridyl-nitrogen atom from a symmetry-related pyridine-4-carboxylato ligand. The carboxylato ligand coordinates in a monodentate mode with Sn–O1 of 2.149(2) Å being significantly shorter than Sn···O2 of 3.090(2) Å. The disparity in the Sn–O separations is also reflected in the large difference in the C1–O1, O2 bond lengths of 1.287(4) and 1.223(4) Å, respectively, i.e. following the anticipated trends. The Sn–N<sup>i</sup> bond length is 2.598(3) Å, and the Sn–C bonds are experimentally equivalent, ranging from 2.149(4) Å, for Sn–C21, to 2.166(4) Å, for Sn–C11. The *trans* O1–Sn–N<sup>i</sup> angle is 175.62(10)°, and the C–Sn–C angles lie in a range from narrow 114.89(14)°, for C21–Sn–C31, to a wide 128.15(14)°, for C11–Sn–C21. This disparity in the C–Sn–C angles is traced to the close approach of the loosely associated O2 atom which serves to widen the C11–Sn–C21 angle. Overall, the coordination geometry is based on a trigonal-bipyramid.

In the crystal, the only prominent directional intermolecular interaction occurring between chains is a phenyl-C–H···O(carbonyl) contact [C36–H36···O2<sup>iii</sup>; H36···O2<sup>iii</sup> = 2.52 Å, C36···O2<sup>iii</sup> = 3.410(5) Å with angle at H36 = 156° for symmetry operation iii: 1 + x, y, z]. These lead to the formation of supramolecular layers that stack along the *c*-axis direction without directional interactions between them.

Across the series of R<sub>3</sub>Sn(O<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N-4) structures, the most symmetrically coordinating carboxylato ligand is found in the R = phenyl derivative where Sn–O1, O2 = 2.158(3) and 2.952(4) Å [20]. The closest Sn···N interaction of 2.480(3) Å is found in the structure of the R = 2-fluorobenzyl derivative [18]. By contrast, the maximum difference in the Sn–O1, O2 bond lengths, i.e. 2.160(3) and 3.343(3) Å, and the longest Sn···N separation of 2.662(3) Å is found in the R = cyclohexyl structure [15], pointing to the steric influence of the tin-bound cyclohexyl substituents in this compound.

A comment on the topologies of the formed one-dimensional coordination polymers of R<sub>3</sub>Sn(O<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>N-4) is appropriate. Only two other of the literature precedents form a helical chain in its crystals, namely in the R = 2-chlorobenzyl [17] and 2-fluorobenzyl [18] structures. The chain in the R = phenyl derivative adopts a zig-zag topology (glide symmetry) [20] whereas the remaining coordination polymers have linear topologies.

Finally, a comparison of the new data with previously described room temperature determination of the R = 4-fluorobenzyl [19] compound is made. While the majority of the interatomic parameters about the tin atoms in both structures are equal within experimental error, a considerable shortening of the Sn···N interaction is evident. Thus, Sn···N of 2.639(4) Å in the 298(2) K structure contracts to 2.598(3) K at

100(2) K which is also reflected in the intra-chain Sn···Sn separations of 2.671(8) and 2.63261(6) Å, respectively. The contraction of the Sn···N interaction with reducing temperature is entirely consistent with this contact being primarily a secondary bonding interaction [6, 7].

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