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Redetermination of the crystal structure of *catena*-poly[[tribenzyltin(IV)]-(μ_2 -pyridine-4-carboxylato- $\kappa^2N:O$)], $C_{27}H_{25}NO_2Sn$

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Abstract

$C_{27}H_{25}NO_2Sn$, monoclinic, $P2_1/c$ (no. 14), $a = 9.61670(10)$ Å, $b = 16.3285(2)$ Å, $c = 14.5921(2)$ Å, $\beta = 97.6430(10)^\circ$, $V = 2270.99(5)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0221$, $wR_{ref}(F^2) = 0.0566$, $T = 296(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.26 \times 0.10 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.15 mm^{-1}
Diffractometer, scan mode:	CCD, φ and ω
$\theta_{\max}$, completeness:	30.9° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	24990, 6662, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6005
$N(\text{param})_{\text{refined}}$:	280
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

A part of the title coordination polymer 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.

Source of material

General: The melting point (uncorrected) of the compound was measured on an Electrothermal digital melting point apparatus. The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates. The ^1H NMR spectra were recorded in CDCl_3 solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to Me_4Si .

Synthesis: Tribenzyltin chloride was prepared from the direct synthesis method [6] using tin powder (Sigma-Aldrich) and benzyl chloride (Sigma-Aldrich) in water. Isonicotinic acid (Sigma-Aldrich; 0.12 g, 1.0 mmol) dissolved in ethanol

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Sn	0.46556(2)	0.34533(2)	0.62306(2)	0.01544(4)
O1	0.68633(11)	0.32862(7)	0.62347(8)	0.0224(2)
O2	0.70526(11)	0.44867(6)	0.55155(8)	0.0228(2)
N1	1.20316(13)	0.35298(7)	0.62174(9)	0.0178(2)
C1	0.75589(14)	0.38702(9)	0.59054(10)	0.0178(3)
C2	0.91246(14)	0.37383(9)	0.60328(10)	0.0167(3)
C3	0.97249(15)	0.29745(10)	0.62331(12)	0.0240(3)
H3	0.916641	0.252145	0.631098	0.029*
C4	1.11679(16)	0.29003(9)	0.63144(12)	0.0246(3)
H4	1.156095	0.238589	0.644336	0.030*
C5	1.14439(15)	0.42656(9)	0.60260(11)	0.0195(3)
H5	1.202582	0.470917	0.595311	0.023*
C6	1.00103(15)	0.43935(9)	0.59323(11)	0.0191(3)
H6	0.964331	0.491407	0.580311	0.023*
C7	0.47402(15)	0.45431(9)	0.70675(12)	0.0234(3)
H7A	0.454171	0.501081	0.666136	0.028*
H7B	0.400020	0.451221	0.745767	0.028*
C8	0.61033(15)	0.46957(9)	0.76731(11)	0.0208(3)
C9	0.6595(2)	0.41639(12)	0.83873(14)	0.0368(4)
H9	0.607963	0.369730	0.848489	0.044*
C10	0.7844(2)	0.43177(15)	0.89583(14)	0.0449(5)
H10	0.816092	0.395351	0.943004	0.054*
C11	0.86127(19)	0.50120(14)	0.88243(14)	0.0389(4)
H11	0.943911	0.512260	0.921221	0.047*
C12	0.81479(18)	0.55385(11)	0.81135(13)	0.0306(4)
H12	0.866984	0.600246	0.801644	0.037*
C13	0.69077(16)	0.53829(9)	0.75407(11)	0.0225(3)
H13	0.660908	0.574306	0.706102	0.027*
C14	0.44879(14)	0.22642(9)	0.68671(11)	0.0199(3)
H14A	0.406328	0.233803	0.742835	0.024*
H14B	0.385521	0.192858	0.645107	0.024*
C15	0.58387(15)	0.18038(9)	0.71066(12)	0.0224(3)
C16	0.63618(18)	0.12925(10)	0.64640(13)	0.0277(3)
H16	0.585333	0.122494	0.588070	0.033*
C17	0.76327(19)	0.08826(10)	0.66839(15)	0.0348(4)
H17	0.797266	0.055258	0.624416	0.042*
C18	0.83880(18)	0.09639(11)	0.75491(15)	0.0368(4)
H18	0.923968	0.069293	0.769294	0.044*
C19	0.78765(19)	0.14476(12)	0.81994(15)	0.0352(4)
H19	0.837323	0.149326	0.878911	0.042*
C20	0.66161(17)	0.18702(11)	0.79786(12)	0.0284(3)
H20	0.628948	0.220215	0.842182	0.034*
C21	0.41066(16)	0.35365(9)	0.47559(11)	0.0201(3)
H21A	0.359488	0.404155	0.460729	0.024*
H21B	0.495840	0.355694	0.446756	0.024*
C22	0.32292(16)	0.28294(9)	0.43653(10)	0.0199(3)
C23	0.18223(17)	0.29149(10)	0.40092(12)	0.0271(3)
H23	0.140865	0.343030	0.399726	0.032*
C24	0.10232(19)	0.22456(12)	0.36709(13)	0.0348(4)
H24	0.008408	0.231665	0.343494	0.042*
C25	0.1618(2)	0.14728(11)	0.36833(14)	0.0360(4)
H25	0.108228	0.102420	0.345834	0.043*
C26	0.3017(2)	0.13742(11)	0.40335(13)	0.0327(4)
H26	0.342489	0.085745	0.404332	0.039*
C27	0.38106(18)	0.20441(10)	0.43696(11)	0.0249(3)
H27	0.474993	0.196993	0.460304	0.030*

(30 mL) and tribenzyltin chloride (0.41 g, 1 mmol) in chloroform (15 mL) were heated for 1 h. After filtration, the filtrate was evaporated slowly to obtain a white crystalline solid. Yield: 0.41 g (80%). M. pt: 433–435 K. Calcd for C₂₇H₂₅NO₂Sn: C 63.07; H 4.90; N 2.72%. Found: C 62.91; H 4.85; N 2.71%. IR (cm⁻¹): 452 (*m*) ν(Sn–N), 571 (*m*) ν(Sn–O), 1645 (*s*) ν_{asym}(COO), 1354 (*s*) ν_{sym}(COO), 1559 (*s*) ν(C=N). ¹H NMR (CDCl₃, p.p.m.): δ 7.48–8.61 (4*H*, pyridine-*H*), 6.92–7.12 (15*H*, Ph-*H*), 2.60 (6*H*, Ph-CH₂).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. Owing to poor agreement, the (2 0 0) and (9 16 2) reflections were omitted from the final cycles of refinement.

Discussion

The structural chemistry of organotin carboxylates is well established to present a fascinating array of structural motifs [7]. Of relevance to the present study, triorganotin carboxylates, R₃Sn(O₂CR') are usually zero-dimensional, whereby the tin atom is distorted tetrahedral within a C₃O donor set, or one-dimensional, owing to the presence of μ₂-bridging carboxylate ligands with the resulting five-coordinate tin atoms having a *trans*-C₃O₂ donor set [7]. The adoption of one motif over the other is often ascribed to steric effects so that polymeric species with tin-bound (bulky) R = cyclohexyl are rarely observed for mono-functional carboxylates and, conversely, the overwhelming majority of structures with, e.g. (small) R = methyl, are polymeric [7]. Variations to the above occur when the R' substituent of the carboxylate ligands carry additional groups capable of coordination, e.g. a pyridyl-nitrogen atom, as in the title compound. Additional interest in metal complexes of pyridyl-derived carboxylic acids is encouraged by the reports on the potential biological activities of these compounds [8, 9]. Following a recent report on the enhanced anti-cancer potential of tribenzyltin carboxylates [10], the title compound, [(benzyl)₃Sn(O₂CC₅H₄N-4)]_n, was investigated crystallographically.

The polymeric structure of [(benzyl)₃Sn(O₂CC₅H₄N-4)]_n has been determined previously but the three-dimensional atomic coordinates are not available [11]. The structure is a linear, one-dimensional coordination polymer as illustrated in the figure (70% displacement ellipsoids; symmetry operations i: –1 + *x*, *y*, *z* and ii: 1 + *x*, *y*, *z*). The chain is propagated by translational symmetry along the *a* axis. The tin atom exists within a *trans*-C₃NO donor set defined by the carbon atoms derived from the three benzyl substituents, an oxygen atom from the carboxylate group and a pyridyl-nitrogen atom

from a symmetry-related pyridine-4-carboxylate ligand. The $O1-Sn-N1^i$ angle is $175.49(4)^\circ$. This, coupled with the $C-Sn-C$ angles lying in the narrow range of $117.58(6)^\circ$, for $C7-Sn-C21$, to $120.06(6)^\circ$, for $C14-Sn-C21$, is consistent with a trigonal bipyramidal geometry. The non-coordinating $Sn \cdots O2$ separation is $3.1448(11)$ Å and consistent with this is the significant disparity in the associated $C1-O1$, $O2$ bond lengths, *i.e.* $1.2936(17)$ and $1.2249(17)$ Å, respectively.

In the crystal, the only prominent directional intermolecular interaction is a methylene- $C-H \cdots O$ (carbonyl) contact [$C21-H21a \cdots O2^{iii}$: $H21a \cdots O2^{iii} = 2.48$ Å, $C21 \cdots O2^{iii} = 3.4207(18)$ Å with angle at $H21a = 163^\circ$ for symmetry operation $iii: 1-x, 1-y, 1-z$]. These contacts serve to link centrosymmetrically chains into double chains.

The title compound has also been characterized as a hydrate with one water molecule per repeat unit [12]. This, too, is a linear coordination polymer. The difference in the structures relates to the $Sn-O$ bond lengths which are each slightly longer in the hydrate, *i.e.* $Sn-O1$, $O2 = 2.189(4)$ and $3.170(5)$ Å. Despite crystallizing as a hydrate, no apparent role is evident for the water molecule in the molecular packing. There are eight other structures of the general formula $R_3Sn(O_2CC_5H_4N)_4$ in the crystallographic literature [13] and each follow the trends established herein. It is noteworthy that the $R =$ cyclohexyl compound [14] adopts the common motif but that the $Sn-N$ bond length is long at $2.662(3)$ Å *cf.* $2.5240(12)$ Å in the title structure, as is the $Sn \cdots O2$ separation of $3.345(3)$ Å, reflecting the influence of the bulky tin-bound substituents.

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