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Structural chemistry of organotin carboxylates

II *. The crystal structure of the dicarboxylato tetraorganodistannoxane: $\{[^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CC}_5\mathrm{H}_4\mathrm{N})]_2\mathrm{O}\}_2$

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Abstract

The crystal structure determination of the compound $\{[^n\mathrm{Bu}_2\mathrm{Sn}(2\text{-pic})]_2\mathrm{O}\}_2$ (2-pic = $\mathrm{O}_2\mathrm{CC}_5\mathrm{H}_4\mathrm{N}$) has revealed the presence of two distinct tin atom geometries in the dicarboxylato tetraorganostannoxane structure. The centrosymmetric dimer also features two unique carboxylate groups, one of which bridges two tin centres via one oxygen atom only (the pendant oxygen atom is not coordinated to tin) and the other carboxylate functions essentially in the monodentate mode. One tin atom is six coordinate, and the other is seven coordinate by virtue of weak but significant intramolecular interactions. The two tin atom environments are are best described as being based on distorted octahedral and pentagonal bipyramidal geometries, respectively. The 2-pyridinecarboxylate ligands introduce a major structural change in the dicarboxylato tetraorganostannoxane structure as a result of the formation of Sn–N bonds. In solution, ^{119}Sn NMR spectroscopy indicates the presence of two distinct hexacoordinate tin centres. Crystals are orthorhombic with space group *Pbca* and unit cell dimensions *a* 15.760(2), *b* 18.208(3) and *c* 22.369(2) Å. The structure was refined by a full-matrix least-squares procedure to final $R = 0.035$ for 3665 reflections with $I \geq 2.5\sigma(I)$.

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* For Part I, see ref. 22.

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Introduction

Organotin compounds have many industrial applications [1,2] and for this reason their study has attracted considerable attention. For example, organotin carboxylates may be used as biocides [3,4] and as homogeneous catalysts [5,6]. Crystallographic studies have shown that organotin carboxylates adopt structures which are dependent on both the nature of the allyl (or aryl) substituent bound to the tin atom and on the type of carboxylate ligand [7]. Relevant to this study are the various structures found for the dicarboxylato tetraorganodistannoxanes, of general formula $\{[R_2Sn(O_2CR')]_2O\}_2$, for several of which crystal structure data are available [8–13]. This communication reports the preparation, NMR (^{13}C and ^{119}Sn) characterization and crystal structure of the stannoxane derivative with R = n-butyl and R′ = 2-pyridinecarboxylic acid; hereafter $\{[^nBu_2Sn(2\text{-pic})]_2O\}_2$. It was thought of interest to determine the structure of a dicarboxylato tetraorganostannoxane derivative in which the carboxylate group possesses three potential coordination sites.

Results

The compound $\{[^nBu_2Sn(2\text{-pic})]_2O\}_2$ is formed in 70% yield from the facile 1/1 reaction of $^nBu_2SnO$ and 2-pyridinecarboxylic acid in benzene solution. The ^{119}Sn NMR spectrum ($CDCl_3$) of this compound shows two distinct resonances, at -229.8 and -269.0 ppm consistent with previous observations for similar compounds [14]. Although it is difficult to assign coordination with certainty to the tin atoms on the basis of their ^{119}Sn chemical shifts, values of $\delta(^{119}Sn)$ in the ranges -210 to -400, -90 to -190 and 200 to -60 ppm have been associated with six-, five- and four-coordinate tin centres, respectively [15]. On this basis two six coordinate tin centres are present in solution for $\{[^nBu_2Sn(2\text{-pic})]_2O\}_2$. The ^{13}C NMR spectrum of $\{[^nBu_2Sn(2\text{-pic})]_2O\}_2$ displayed two sets of ^nBu–Sn resonances (except for the terminal methyl groups which were magnetically equivalent), consistent with a dimeric dicarboxystannoxane structure. The $^1J(^{119}Sn-^{13}C)$ couplings of 719 and 755 Hz are as expected [12], and by use of the Holeček equation [16] the two unique C–Sn–C angles are calculated to be 146.6 and 150.2°. In order to determine the fine structural details for this compound a single crystal X-ray diffraction study was performed.

The crystal structure determination confirmed the dicarboxylato tetraorganostannoxane formulation of the compound. The structure consists of discrete molecules of $\{[^nBu_2Sn(2\text{-pic})]_2O\}_2$ there being no significant intermolecular contacts in the crystal lattice. The molecular structure is illustrated in Fig. 1, which shows the numbering scheme employed. Selected interatomic parameters are listed in Table 1. As observed for related structures [8–13], the core geometry of the molecule consists of a centrosymmetric (crystallographically imposed in this case) planar four-membered Sn_2O_2 ring with two additional $^nBu_2Sn(2\text{-pic})$ units attached at each bridging oxygen atom, with the result that these oxygen atoms are three-coordinate. The two crystallographically unique 2-pic ligands coordinate in different ways.

The 2-pic ligand containing the O(2) and O(3) atoms bridges two tin atoms via the O(2) atom only; Sn(1)–O(2) 2.303(4) and Sn(2)–O(2) 2.471(4) Å. Although the pendant O(3) oxygen atom is 3.353(4) Å from the Sn(1) atom, a distance less than the sum of the Van der Waals radii for Sn and O of 3.7 Å [17], we argue that this is

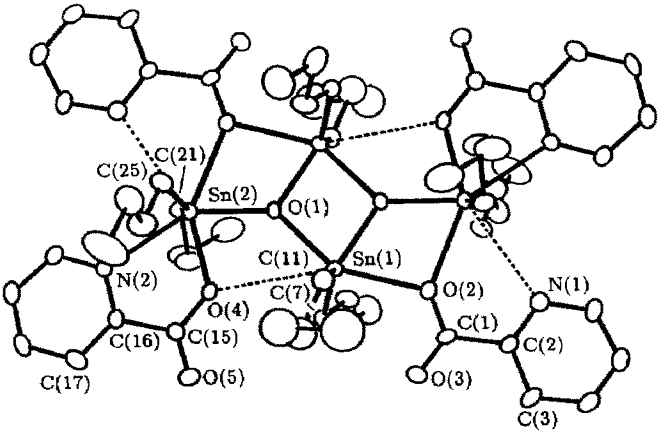

Fig. 1. Molecular structure and numbering scheme for $\{[^{n}Bu_2Sn(2\text{-pic})]_2O\}_2$.

not indicative of a significant bonding interaction when due account is taken of the bond distances within the CO_2 moiety of the carboxylato ligand. The C–O bond distance associated with the oxygen atom bridging the two tin atoms of 1.282(8) Å is significantly longer than the other C–O bond distance of 1.223(8) Å which suggests a partial localization of π-electron density in the C(1)–O(3) bond consistent with the non-coordination of the O(3) atom to Sn(1). The nitrogen atom from the pyridine ring of this 2-pic ligand makes a close contact with Sn(2′) at 3.150(5) Å,

Table 1

Selected bond distances (Å) and angles (°) for $\{[^{n}Bu_2Sn(2\text{-pic})]_2O\}_2$

Sn(1)–O(1)	2.110(4)	Sn(2)–O(1)	2.055(4)
Sn(1)–O(2)	2.303(4)	Sn(2)–O(4)	2.134(4)
Sn(1)–O(1′)	2.047(4)	Sn(2)–N(2)	2.550(5)
Sn(1)–C(7)	2.122(7)	Sn(2)–C(21)	2.116(6)
Sn(1)–C(11)	2.129(8)	Sn(2)–C(25)	2.144(7)
Sn(1)–O(4)	3.066(5)	Sn(2)–O(2′)	2.474(4)
		Sn(2)–N(1′)	3.150(5)
O(1)–Sn(1)–O(1′)	75.3(1)	O(1)–Sn–O(2)	146.8(1)
O(1)–Sn(1)–O(4)	57.3(1)	O(1)–Sn(1)–C(7)	101.3(2)
O(1)–Sn(1)–C(11)	99.6(1)	O(1′)–Sn(1)–O(2)	71.7(1)
O(1′)–Sn(1)–O(4)	132.5(1)	O(1′)–Sn(1)–C(7)	116.0(2)
O(1′)–Sn(1)–C(11)	109.4(2)	O(2)–Sn(1)–O(4)	81.7(1)
O(2)–Sn(1)–C(7)	90.5(2)	O(2)–Sn(1)–C(11)	94.3(2)
O(4)–Sn(1)–C(7)	75.4(2)	O(4)–Sn(1)–C(11)	81.8(2)
C(7)–Sn(1)–C(11)	133.4(3)	O(1)–Sn(2)–O(2)	68.0(1)
O(1)–Sn(2)–O(4)	77.3(1)	O(1)–Sn(2)–N(1′)	123.5(2)
O(1)–Sn(2)–N(2)	145.6(2)	O(1)–Sn(2)–C(21)	101.3(2)
O(1)–Sn(2)–C(25)	103.0(2)	O(2)–Sn(2)–O(4)	145.2(1)
O(2)–Sn(2)–N(1′)	55.6(2)	O(2)–Sn(2)–N(2)	145.9(2)
O(2)–Sn(2)–C(21)	84.0(2)	O(2)–Sn(2)–C(25)	86.7(2)
O(4)–Sn(2)–N(1′)	158.9(2)	O(4)–Sn(2)–N(2)	68.8(2)
O(4)–Sn(2)–C(21)	105.0(2)	O(4)–Sn(2)–C(25)	99.8(2)
N(1′)–Sn(2)–N(2)	90.7(2)	N(1′)–Sn(2)–C(21)	76.1(2)
N(1′)–Sn(2)–C(25)	73.8(2)	N(2)–Sn(2)–C(21)	82.4(2)
N(2)–Sn(2)–C(25)	88.8(2)	C(21)–Sn(2)–C(25)	148.4(3)

which is significantly less than the sum of the Van der Waals radii for Sn and N of 3.75 Å [17] and should be considered as a bonding interaction. In this connection it is relevant to note the Sn–N bond distances found in two other crystal structures of organotin complexes containing the 2-pyridinecarboxylate ligand. In polymeric $[Me_2SnCl(2\text{-pic})]_n$ [18] the two unique Sn–N bond distances are 2.50(3) and 2.47(2) Å and in polymeric $[Me_2Sn(2\text{-pic})_2]_n$ [19] the two Sn–N bond distances are 2.507(4) and 2.477(4) Å.

The second 2-pic ligand in $\{[{}^nBu_2Sn(2\text{-pic})]_2O\}_2$ forms a strong bond to Sn(2), 2.134(4) Å, and is 3.066(4) Å from Sn(1). The O(5) atom does not make any significant contacts with the tin atoms and as for the first 2-pic ligand, the C(15)–O(5) bond is shorter than the C(15)–O(4) bond; 1.217(7) vs. 1.288(7) Å. The N(2) atom of this ligand is also coordinated to the Sn(2) atom, at 2.550(5) Å, thereby forming a chelate with a five-membered ring. The result of the disparate coordination modes for the two 2-pic ligands is the presence of two distinct tin atom environments in $\{[{}^nBu_2Sn(2\text{-pic})]_2O\}_2$.

The endocyclic tin atom, Sn(1), is five-coordinate to a first approximation, and exists in a distorted trigonal bipyramidal environment, with the two n-butyl groups and the centrosymmetrically related bridging oxygen atom defining an approximate trigonal plane. The axial positions are occupied by the bridging oxygen atom, O(1), and the O(2) atom from the 2-pic ligand. The axial bond angle, O(1)–Sn–O(2), of 146.8(1)° deviates significantly from linearity owing to (i) the close approach of O(4) from the second 2-pic ligand (see above), and (ii) the tendency of O(2) to bridge the Sn(2′) atom, which pivots the carboxylato ligand about the Sn(1)–O(2) bond towards the Sn(2) atom. If the weakly bonded O(4) atom is included in the coordination polyhedron, the geometry about the tin atom can be considered as being distorted octahedral.

The exocyclic tin atom, Sn(2), forms four short bonds, two intermediate bonds (to the O(2) and N(2) atoms), and a longer bond to N(1); Table 1. The geometry is highly distorted, but if only the six shorter interactions are considered the coordination sphere can be thought of as distorted octahedral, as for the Sn(1) atom. The inclusion of the N(1′) atom in the coordination polyhedron results in a distorted pentagonal bipyramidal geometry, with the pentagonal plane defined by the O(1), O(4), O(2′), N(2) and N(1′) atoms as shown in Fig. 1. These atoms deviate by −0.035(5), 0.108(5), −0.041(4), −0.098(5), and 0.125(6) Å, respectively, from the least-squares plane, and the Sn(2) atom lies 0.0254(4) Å out of this plane in the direction of the C(25) atom. The axial positions are occupied by the n-butyl groups, which subtend an angle of 148.4(3)° at the tin atom.

Therefore in $\{[{}^nBu_2Sn(2\text{-pic})]_2O\}_2$ the Sn(1) atom can be considered as being six coordinated distorted octahedral, and the Sn(2) atom as being seven coordinated distorted pentagonal bipyramidal. This compared well with that predicted from the ^{119}Sn study, which suggested two six coordinate tin centres on the basis of $\delta(^{119}Sn)$ [15]. The C–Sn–C angles in the structure were found to be 133.3(3) and 148.4(3)°. While the later value agrees with that predicted from the Holeček equation [16] the former does not, but, we note the high thermal motion associated with the C(11)–C(14) n-butyl chain which may account for this disparity. Other bond distances lie in the expected ranges for their respective connectivities.

The structure reported here for $\{[{}^nBu_2Sn(2\text{-pic})]_2O\}_2$ represents a new structural type for dicarboxyl tetraorganostannoxanes in that two carboxylate groups function as bridging ligands via one oxygen atom only, and the other two carboxylate groups coordinate essentially in a monodentate mode, as found in previous examples [8–13]. These changes in the structure are influenced undoubtedly by the presence of the N-donor sites on the substituted pyridine rings which coordinate the Sn(2) atoms. The structure found for $\{[^n\mathrm{Bu}_2\mathrm{Sn(2\text{-}pic)}]_2\mathrm{O}\}_2$ differs from the major structural type [8–11,13] in that in the latter two carboxylate groups bridge two tin atoms via both oxygen atoms and two carboxylate groups function essentially as monodentate ligands. A third structural type was found for $\{[\mathrm{Me_2Sn(OAc)}]_2\mathrm{O}\}_2$ [12], in which there are three bidentate acetate groups, each bridging two tin atoms, and a fourth carboxylate which coordinates in a monodentate mode.

Experimental

Synthesis

The reagents 2-pyridinecarboxylic acid and n-$\mathrm{Bu_2SnO}$ were obtained from Fluka. To a benzene suspension of $^n\mathrm{Bu_2SnO}$ (2.06 g; 8.28 mmole) was added a benzene solution (60 cm^3) of 2-pyridine carboxylic acid (1.02 g; 8.29 mmole). The mixture was heated under reflux with stirring for 2 h, water formed during the reaction being removed azeotropically through a Dean and Stark apparatus. The clear solution thus obtained was evaporated under vacuum to leave a white solid, which was recrystallized from benzene/hexane solution in 70% yield; m.p. 215 ° C. (Found: C, 46.31; H, 6.06; N, 3.84; Sn 32.70. $C_{56}H_{88}N_4O_{10}Sn_4$ calc: C, 46.32; H, 6.11; N, 3.86; Sn, 32.70%). The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded in $CDCl_3$ solution on a Varian FT-80A spectrometer operating at 79.5, 20.0 and 29.6 MHz

Table 2

Crystal and refinement details for $\{[^n\mathrm{Bu}_2\mathrm{Sn(2\text{-}pic)}]_2\mathrm{O}\}_2$

Formula	$C_{56}H_{88}N_4O_{10}Sn_{14}$
MW	1452.1
Crystal system	orthorhombic
Space group	*Pbca*
a, Å	15.760(2)
b, Å	18.208(3)
c, Å	22.369(2)
Vol. (Å^3)	6419(2)
Z	4 (tetramers)
D_c (g cm^{-3})	1.503
F(000)	2928
μ, cm^{-1}	14.59
Transmission factors (max/min)	0.575; 0.482
θ limits (°)	1.0–25.0
No. of data collected	8958
No. of unique data	5637
No. of unique reflections used with $I \geq 2.5\sigma(I)$	3665
R	0.035
k	1.34
g	0.001
R_w	0.041
residual ρ_{max} (e Å^{-3})	0.62

respectively. Chemical shifts are reported in ppm from internal chloroform peaks at 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C and external 33% Me_4Sn in C_6D_6 for ^{119}Sn. ^{1}H NMR: δ (CH_3) 0.45(br); δ (CH_2) 1.05(br); δ (H5) 7.29(br); δ (H4) 7.67; δ (H3) 8.0(br); and δ (H6) 8.70(br) ppm. ^{13}C NMR: δ ($CH_2\alpha$) 29.3, 28.4 $^1J(^{13}C-^{119}Sn)$ 719 and 755 Hz; δ ($CH_2\beta$) 27.3, 27.1; δ ($CH_2\gamma$) 26.5, 26.3; δ (CH_3) 13.1; δ (C5) 124.6; δ (C3) 126.2; δ (C4) 137.5; δ (C6) 147.1; δ (C2) 149.6; and δ (CO_2) 166.6 ppm. ^{119}Sn NMR δ -229.8 and -269.0 ppm.

Crystallography

Intensity data for 8958 reflections were measured on an Enraf–Nonius CAD4F diffractometer by use of graphite monochromatized Mo-K_α radiation and the $\omega/2\theta$

Table 3

Fractional atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for remaining atoms) for $\{[^nBu_2Sn(2\text{-pic})]_2O\}_2$

Atom	x	y	z
Sn(1)	−8667(3)	2178(2)	3696(2)
Sn(2)	12670(3)	2096(2)	11752(2)
O(1)	456(3)	85(2)	463(2)
O(2)	−2011(3)	233(2)	−270(2)
O(3)	−2976(3)	443(4)	431(2)
O(4)	68(3)	500(3)	1549(2)
O(5)	−794(3)	858(3)	2274(2)
N(1)	−3214(4)	176(3)	−1121(3)
N(2)	1431(3)	686(3)	2241(2)
C(1)	−2774(4)	338(4)	−90(3)
C(2)	−3449(4)	333(3)	−577(3)
C(3)	−4277(4)	523(5)	−416(4)
C(4)	−4879(5)	531(5)	−849(4)
C(5)	−4646(6)	390(5)	−1419(5)
C(6)	−3817(6)	201(5)	−1531(4)
C(7)	−1001(4)	1363(4)	519(3)
C(8)	−787(5)	1837(4)	2(4)
C(9)	−845(6)	2675(4)	116(5)
C(10)	−662(7)	3106(6)	−447(5)
C(11)	−1288(5)	−729(5)	843(4)
C(12)	−1806(10)	−692(10)	1431(5)
C(13)	−1868(12)	−1398(10)	1817(8)
C(14)	−2404(14)	−1871(13)	1384(10)
C(15)	−85(4)	741(4)	2080(3)
C(16)	689(4)	869(3)	2474(3)
C(17)	610(5)	1162(4)	3047(3)
C(18)	1336(6)	1247(5)	3384(3)
C(19)	2101(5)	1068(5)	3139(3)
C(20)	2117(4)	781(4)	2565(3)
C(21)	1854(4)	1223(3)	965(3)
C(22)	1321(6)	1911(5)	1122(4)
C(23)	1769(9)	2619(5)	953(6)
C(24)	1756(8)	2701(7)	283(7)
C(25)	1386(5)	−888(4)	1513(3)
C(26)	875(6)	−1098(5)	2029(4)
C(27)	934(7)	−1906(5)	2197(4)
C(28)	376(12)	−2122(6)	2745(6)

scan technique. The data were corrected for Lorentz and polarization effects and for absorption [20]. Of the reflections measured (θ_{max} 25°) 5637 were unique (R_{amal} 0.023) and of these 3665 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. Relevant crystal data and refinement details are given in Table 2.

The structure was solved from the interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure based on F [20]. The n-butyl group C(11)–C(14) was refined with constrained bond distances (1.55 Å) and isotropic thermal parameters owing to high thermal motion associated with these atoms. The remaining non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model (except for the C(11)–C(14) atoms) at their calculated positions. Refinement with a weighting scheme of the form $w = k/[\sigma^2(F + g(F)^2]$ converged with final R 0.035, R_w 0.041, k 1.34 and g 0.001.

Fractional atomic coordinates are listed in Table 3 and the numbering scheme used is shown in Fig. 1 (diagram drawn at 15% probability ellipsoids with the ORTEP [21] program). Scattering factors for all atoms were those incorporated in the SHELX76 program system [20]. Other crystallographic data are available from the authors (E.R.T.T.).

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