STRUCTURAL CHEMISTRY OF ORGANOTIN CARBOXYLATES. XXI. CRYSTAL STRUCTURE OF DI-TERT-BUTYLTIN BIS(PICOLINATE)

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Abstract.

The crystal structure of the title compound, $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$, shows that each picolinate anion chelates the tin atom employing the nitrogen atom and one oxygen atom only, and the t-butyl groups to be disposed such as to lie over the weaker Sn-N interactions. This arrangement leads to a skew-trapezoidal planar geometry about the tin atom. This structure contrasts those found for the Me_2Sn and Ph_2Sn analogues.

Introduction.

The structural diversity of organotin carboxylates is well documented [2,3]. Added structural variation in these systems may be found when the carboxylate residue also carries additional potential donor atoms such as pyridine-nitrogen atoms. Pertinent to the present report are the crystal structures of $[Me_2Sn(O_2CC_5H_4N\text{-}2)_2]_n$ [4] and $[Ph_2Sn(O_2CC_5H_4N\text{-}2)_2]$ [5] in which the pyridine-nitrogen atoms participate in bonding to the tin atom in addition to the oxygen atoms. In the dimethyltin compound the tin atom exists in a distorted pentagonal bipyramidal geometry owing to bridging carboxylate ligands; this arrangement results in a polymeric structure. By contrast, the structure of $[Ph_2Sn(O_2CC_5H_4N\text{-}2)_2]$ features monomeric molecules and distorted octahedral tin centres [5]. The $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$ compound has been prepared previously and infrared and NMR (^1H and ^{119}Sn) data indicated a hexacoordinate structure, both in solution and in the solid state [6]. The crystal and molecular structure

* Part XX. See ref. [1].

of $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$ has been investigated to determine the precise molecular geometry for this compound and forms a part of a systematic study of organotin carboxylate structures.

Experimental.

The $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$ compound was prepared as in the literature [6]. Intensity data for a colourless crystal (0.10 x 0.10 x 0.32 mm) were measured at room temperature on a Rigaku AFC6R four-circle diffractometer fitted with nickel-filtered CuKα radiation, λ = 1.5412 Å. A total of 1747 data were measured (ω:2θ scan technique and θ_{max} was 60.0°), of these 1443 satisfied the $I > 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis. The data were corrected for Lorentz and polarization effects and for absorption employing the DIFABS program [7] which resulted in a range of transmission coefficients of 0.886 to 1.043.

Crystal data for $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$: $C_{20}H_{26}N_2O_4Sn$, M = 477.1, monoclinic, space group Cc, (C_s^4. No. 9), a = 9.207(1), b = 14.375(1), c = 15.933(1) Å, β = 98.433(7)°, V = 2085.8(3) Å^3, Z = 4 , D_{calcd} = 1.519 g cm^{-3}, $F(000)$ = 968, μ = 99.84 cm^{-1}.

The structure was solved by direct methods [8] and refined by a full-matrix least-squares procedure based on F [9]. Non-H atoms were refined with anisotropic thermal parameters and H-atoms were included in the model at their calculated positions (C-H 0.97 Å). At convergence R = 0.046 and R_W = 0.059 (sigma weights [9]).* Refinement in the centrosymmetric $C2/c$ space group (constraining the tin atom to lie on a 2-fold axis) was attempted but this resulted in non-sensible thermal and interatomic parameters confirming the original choice of space group, i.e. Cc; this choice was also supported by the distribution of e-statistics. The absolute configuration was determined by refining the inverted structure which resulted in a larger residual. The analysis of variance showed no special features and the maximum residual in the final difference map was 0.77 e Å^{-3}. An extinction correction was applied such that the coefficient was 1.54236 x 10^{-8} [10]. The final fractional atomic coordinates are listed in Table 1 and the crystallographic numbering scheme used is shown in Figure 1, which was drawn with

* where $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}$

ORTEP [11] at 25% probability ellipsoids. Data manipulation was performed with the teXsan package [9] installed on an Iris Indigo workstation.

Table 1. Fractional atomic coordinates for [$tBu_2Sn(O_2CC_5H_4N\text{-}2)_2$]

Atom	x	y	z
Sn	0.2941(-)	0.20494(6)	-0.1518(-)
O(1)	0.3711(13)	0.1911(9)	-0.2677(7)
O(2)	0.4302(17)	0.2421(10)	-0.3899(9)
O(3)	0.3886(15)	0.0720(8)	-0.1424(7)
O(4)	0.4796(21)	-0.0521(10)	-0.0708(9)
N(1)	0.2382(20)	0.3529(13)	-0.2408(13)
N(2)	0.2639(17)	0.1302(11)	-0.0069(9)
C(1)	0.3717(20)	0.2541(13)	-0.3260(11)
C(2)	0.3007(20)	0.3456(15)	-0.3170(10)
C(3)	0.2870(23)	0.4136(14)	-0.3750(11)
C(4)	0.2095(25)	0.4947(16)	-0.3590(16)
C(5)	0.1469(21)	0.5024(14)	-0.2863(13)
C(6)	0.1687(21)	0.4304(15)	-0.2286(13)
C(7)	0.4070(22)	0.0200(13)	-0.0764(13)
C(8)	0.3319(19)	0.0495(12)	-0.0037(12)
C(9)	0.3405(34)	-0.0060(21)	0.0669(22)
C(10)	0.2767(33)	0.0270(22)	0.1365(20)
C(11)	0.2075(26)	0.1104(19)	0.1310(13)
C(12)	0.2043(24)	0.1603(18)	0.0572(14)
C(13)	0.0563(20)	0.1701(13)	-0.1896(15)
C(14)	0.0158(40)	0.1853(25)	-0.2821(24)
C(15)	-0.0323(24)	0.2279(18)	-0.1384(20)
C(16)	0.0394(25)	0.0683(17)	-0.1724(15)
C(17)	0.4730(19)	0.2851(13)	-0.0795(13)
C(18)	0.5685(38)	0.2236(18)	-0.0153(23)
C(19)	0.5690(23)	0.3260(15)	-0.1439(14)
C(20)	0.4027(31)	0.3621(18)	-0.0290(16)

Results and Discussion.

The molecular structure of [$tBu_2Sn(O_2CC_5H_4N\text{-}2)_2$] is shown in Figure 1 and selected interatomic parameters are listed in Table 2. The structure is molecular there being no significant intermolecular interactions; the closest non-hydrogen contact of 3.11(3) Å occurs between the O(2) and C(12)′ atoms (symmetry operation: $0.5+x$, $0.5-y$, $-0.5+z$). Each of the two picolinate ligands chelates the tin atom via one of the carboxylate oxygen atoms and the nitrogen atom. The Sn-N bond distances of 2.56(2) and

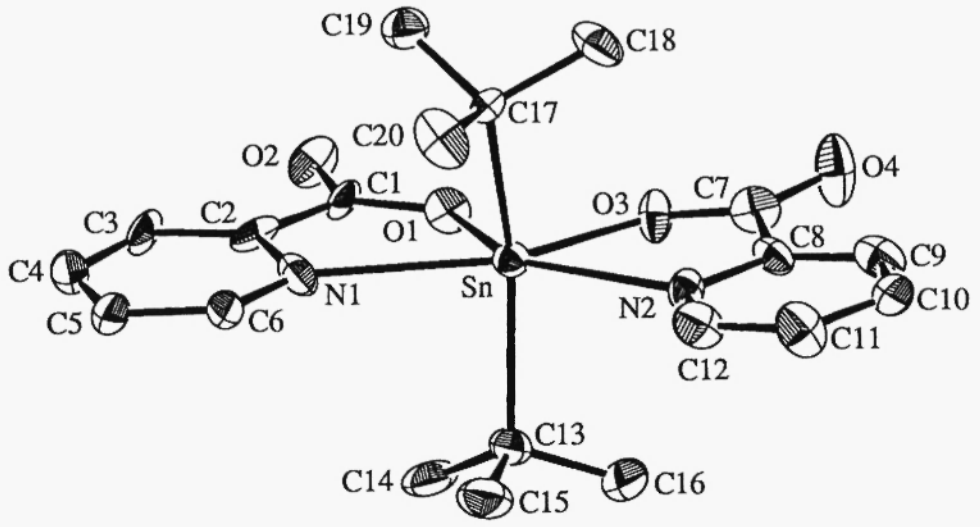

Figure 1. Molecular structure of $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$.

Table 2. Selected bond distances (Å) and angles (°) for $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$

Sn-O(1)	2.08(1)	Sn-O(3)	2.10(1)
Sn-N(1)	2.56(2)	Sn-N(2)	2.60(2)
Sn-C(13)	2.24(2)	Sn-C(17)	2.19(2)
O(1)-Sn-O(3)	77.5(5)	O(1)-Sn-N(1)	69.8(6)
O(1)-Sn-N(2)	147.5(5)	O(1)-Sn-C(13)	100.8(7)
O(1)-Sn-C(17)	100.9(6)	O(3)-Sn-N(1)	147.4(6)
O(3)-Sn-N(2)	69.9(5)	O(3)-Sn-C(13)	101.2(6)
O(3)-Sn-C(17)	99.8(6)	N(1)-Sn-N(2)	142.7(6)
N(1)-Sn-C(13)	85.8(6)	N(1)-Sn-C(17)	86.0(6)
N(2)-Sn-C(13)	85.3(7)	N(2)-Sn-C(17)	85.5(6)
C(13)-Sn-C(17)	152.6(8)	Sn-O(1)-C(1)	127(1)
Sn-O(3)-C(7)	126(1)	Sn-N(1)-C(2)	110(1)
Sn-N(1)-C(6)	133(2)	Sn-N(2)-C(8)	107(1)
Sn-N(2)-C(12)	132(1)		

2.60(2) Å are significantly longer than the two Sn-O distances of 2.08(1) and 2.10(1) Å and the two t-butyl groups are disposed so as to lie over the weaker Sn-N interactions. Thus, the tin atom exists in a skew-trapezoidal bipyramidal geometry with a N_2O_2 donor set defining the basal plane; the mean deviation of the SnN_2O_2 atoms from their least-squares plane is 0.029 Å. The pendent O(2) and O(4) atoms do not form significant interactions to tin. The first picolinate anion is strictly planar as seen in the O(1)/C(1)/C(2)/N(1) torsion angle of 1(2)° but there appears to be a small twist about the C(7)-C(8) bond in the second as the O(3)/C(7)/C(8)/N(2) angle is -7(3)°.

The structure reported here for $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$ resembles the most common motif found for compounds of the general formula $[R_2Sn(O_2CR')_2]$ [2,3], i.e. based on a skew-trapezoidal bipyramid. The difference arises as a result of the coordination of the nitrogen atom, rather than the second carboxylate oxygen atom, of each ligand. The structure of $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$ is different, however, from those found for each of $[Me_2Sn(O_2CC_5H_4N\text{-}2)_2]_n$ [4] and $[Ph_2Sn(O_2CC_5H_4N\text{-}2)_2]$ [5].

A monomeric structure is found in $[Ph_2Sn(O_2CC_5H_4N\text{-}2)_2]$ in which the tin atom is situated on a crystallographic 2-fold axis [5]. The tin atom in this compound exists in a distorted octahedral geometry with Sn-O, Sn-N and Sn-C distances of 2.095(4), 2.284(5) and 2.128(5) Å, respectively. About the tin atom, the oxygen atoms are *trans*, the phenyl groups *cis* and, as for $[tBu_2Sn(O_2CC_5H_4N\text{-}2)_2]$, the pendent oxygen atoms do not form significant contacts to tin. The structure found for $[Me_2Sn(O_2CC_5H_4N\text{-}2)_2]_n$ [4] does not conform to either of the analogues described above. In this structure one of the picolinate ligands chelates the tin atom via one oxygen atom and the nitrogen atom (the second oxygen atom does not coordinate to tin) whereas the second picolinate utilizes these atoms as well as coordinating a symmetry related tin atom via the second carboxylate oxygen atom leading to a polymeric structure with the result that each tin atom is seven coordinate; the Sn-N distances of 2.393(4) and 2.507(4) Å are intermediate between those found in the R = Ph and R = tBu analogues. The geometry about the tin atom is distorted pentagonal bipyramidal with the two methyl groups occupying the axial positions. Thus, for the three structurally characterized $[R_2Sn(O_2CC_6H_4N\text{-}2)_2]$ compounds, three different coordination geometries are found and even a different coordination number is evident. Reasons for such structural diversity for these systems and indeed related organotin systems are not clear and further, systematic studies are required on this subject.

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