

Synthesis and crystal structure of di-*n*-butylbis(2-amino-5-chlorobenzoato)tin(IV)

Siang-Guan Teoh ^{a,*}, Show-Hing Ang ^a, Eng-Seng Looi ^a, Chye-Aun Keok ^a,
Soon-Beng Teo ^a, Jean-Paul Declercq ^b

^a School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

^b Laboratoire de Chimie Physique et de Cristallographie, Université Catholique de Louvain, Place L. Pasteur, 1, B-1384, Louvain-la-Neuve, Belgium

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Abstract

Reaction of di-*n*-butyltin oxide with 2-amino-5-chlorobenzoic acid in 1 : 2 stoichiometry yields the title compound which crystallizes as the six-coordinate diorganotin dicarboxylate monomer. The crystal structure of the compound reveals the tin atom situated on a crystallographic two-fold axis in a skew-trapezoidal bipyramid geometry. The trapezoidal plane is defined by two asymmetrically chelating carboxylate groups; Sn–O bonds are 2.123(4) and 2.484(5) Å and the C–Sn–C angle is 141.7(6)°. The nitrogen atom of the amino group of the carboxylate ligand does not participate in any significant interactions with the tin atom.

Keywords: Diorganotin dicarboxylate; Di-*n*-butyltin oxide; 2-Amino-5-chlorobenzoic acid; X-ray diffraction; Skew trapezoidal bipyramid; Carboxylate

1. Introduction

The study of organotin(IV) carboxylates is of current interest owing to their wide range of applications such as biocides and as homogenous catalysts in industry [1–9]. More recently, the pharmaceutical properties of organotin(IV) carboxylates have been investigated for their antitumour activity [9,10]. Crystallographic studies have revealed 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 [11,12]. Relevant to this paper are diorganotin dicarboxylates, of general formula $R_2Sn(O_2CR')_2$, for several of which crystal structure data are available [9,13–19]. We report here the synthesis, spectroscopic and crystal structure characterization of di-*n*-butylbis(2-amino-5-chlorobenzoato)tin(IV), ${}^nBu_2Sn[O_2CC_6H_3(NH_2)Cl]_2$ as it is of interest to determine whether the presence of the nitrogen atom, an additional potential donor atom residing on the R' group of the uninegative carboxylate ligand, has any influence on the structure adopted by this compound.

2. Experimental details

2.1. General and instrumental

Dibutyltin oxide and 2-amino-5-chlorobenzoic acid were purchased from Fluka Chemie AG.

Microanalyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. The IR absorption spectra were recorded using a Perkin–Elmer FTIR 1650 spectrophotometer in the frequency range 4000–450 cm^{-1} . Samples were prepared as KBr discs. The 1H and ${}^{13}C$ NMR spectra of the samples dissolved in $CDCl_3-d_1$ were recorded on a Bruker 300 MHz AC-P NMR spectrometer.

2.2. Synthesis of di-*n*-butylbis(2-amino-5-chlorobenzoato)tin(IV)

Dibutyltin oxide (4.00 g, 16 mmol), 2-amino-5-chlorobenzoic acid (5.52 g, 32 mmol) and 70 ml toluene were refluxed for 1 h until a clear yellow solution was formed. The solution was filtered while it was still hot. Solvent was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from toluene–hexane. Colourless

* Corresponding author.

needle-shaped crystals were formed. M.p. 130–132°C. Analysis: Found: C, 46.09; H, 4.51; N, 4.49. $C_{22}H_{28}Cl_2N_2O_4Sn$. Calc.: C, 46.03; H, 4.92; N, 4.88%. IR (KBr): $\nu(COO_{asym})$ 1622; $\nu(COO_{sym})$ 1353; $\nu(Sn-C)$ 525; $\nu(Sn-O)$ 491 cm^{-1} . 1H NMR ($CDCl_3-d_1$) for $(H_3C^4H_2C^3H_2C^2H_2C^1)_2Sn[OC(O)-C_6H_3-2-NH_2-5-Cl]_2$: $\delta(t, 6H, 2C^4H_3)$ 0.89; $\delta(m, 4H, 2C^3H_2)$ 1.40; $\delta(m, 8H, 2C^2H_2C^1H_2)$ 1.77; $\delta(s, 4H, 2NH_2)$ 5.71; $\delta(m, 6H, 2C_6H_3)$ 6.59–7.99 ppm. ^{13}C NMR ($CDCl_3-d_1$) δ : C^1 25.6; C^2 26.6; C^3 26.2; C^4 13.4; $C(O)O$ 176.1; C_6H_3 111.7, 117.9, 120.7, 131.8, 149.0 ppm.

2.3. Crystal structure determination

Intensity data for a crystal with dimensions $0.3 \times 0.3 \times 0.3$ mm³ were measured at 298 K on a Huber diffractometer fitted with graphite monochromator Mo K α radiation, $\lambda = 0.71073$ Å. The θ - 2θ scan technique was employed to measure a total of 2728 reflections up to $2\theta_{max} = 52.0^\circ$. Corrections were applied for Lorentz and polarization effects but not for absorption. The 1402 out of the 2444 independent reflections ($R_{int} = 0.025$) satisfying the $F > 4.0\sigma(F)$ criterion of observability were used for the solution and refinement. The structure was solved by using direct methods and refined by a full-matrix least squares procedure based on F using Siemens SHELXTL (PC version) system [20]. Hydrogen atoms were placed in their calculated positions ($C-H = 0.96$ Å; $N-H = 0.90$ Å) and refined isotropically. A weighting scheme of the form $w = (\sigma^2(F) + 0.0004F^2)^{-1}$ was used and the refinement continued to final $R = 0.0596$ and $R_w = 0.0578$. The

Table 1
Crystal data and refinement details for $(C_4H_9)_2Sn(O_2CC_6H_3(NH_2)Cl)_2$

Formula	$C_{22}H_{28}Cl_2N_2O_4Sn$
Formula weight	574.1
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	16.504(11)
b (Å)	7.144(3)
c (Å)	23.307(12)
β (deg)	115.25(6)
V (Å ³)	2486(2)
Z	4
D_c (Mg m ⁻³)	1.534
μ (mm ⁻¹)	1.272
$F(000)$	1160
Reflections collected	2728
Independent reflections	2444 ($R_{int} = 0.025$)
Observed reflections	1402 ($F > 4.0\sigma(F)$)
No. of parameters refined	141
R	0.0596
R_w	0.0578
w	$[\sigma^2(F) + 0.0004F^2]^{-1}$
Largest diff. peak and hole (e Å ⁻³)	0.73 and -0.58

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}^a
Sn(1)	0	3451.0(11)	2500	76.1(4)
Cl(1)	-4504.1(14)	3183(4)	-376.7(11)	96.0(12)
O(1)	-802(3)	1274(6)	1910(2)	65(2)
O(2)	-1369(4)	3993(7)	1504(3)	90(3)
C(1)	-2200(4)	1302(9)	973(3)	52(3)
C(5)	-3646(5)	1716(12)	110(3)	64(4)
C(7)	-1426(5)	2245(11)	1473(3)	62(4)
N(1)	-1624(5)	-1848(8)	1263(3)	91(4)
C(6)	-2884(5)	2426(11)	568(3)	59(4)
C(3)	-3071(5)	-1334(12)	417(4)	77(4)
C(2)	-2277(5)	-655(10)	898(3)	60(4)
C(4)	-3734(5)	-206(13)	33(4)	75(4)
C(8)	733(7)	4412(14)	2016(5)	123(6)
C(9)	859(10)	6495(20)	2046(7)	178(11)
C(10)	1247(11)	7393(24)	1768(7)	187(11)
C(11)	1389(8)	9372(18)	1777(6)	150(10)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

final difference map had peaks between -0.58 and 0.73 e Å⁻³ only.

The crystal data and refinement details are given in Table 1. Fractional atomic coordinates and their equivalent isotropic displacement parameters are listed in Table 2 and bond lengths and angles in Table 3. Lists of additional data, including hydrogen atom coordinates, anisotropic temperature factors and observed and calculated structure factors have been deposited as supplementary material with the editor from whom copies are available on request.

3. Results and discussion

As depicted in Fig. 1, di-*n*-butylbis(2-amino-5-chlorobenzoato)tin(IV) is present as discrete molecules, there being no significant intermolecular interactions in the crystal lattice. The tin atom lies on a crystallographic two-fold rotation axis of symmetry implying the presence of one unique type of carboxylate ligand in the structure. The carboxylate groups coordinate in an asymmetric mode forming both short Sn-O bonds ($2 \times 2.123(4)$ Å) and long Sn-O bonds ($2 \times 2.484(5)$ Å). The anisobidentate mode of coordination of the carboxylate groups is reflected in the disparity of the associated C-O bonds; as expected, the longer C-O bond distances are associated with the shorter Sn-O bonds. That is, the C-O bond lengths for the strongly coordinating oxygen atoms (O(1), O(1A)) of 1.297(8) Å are longer than the C-O bond lengths associated with the weakly coordinating oxygen atoms (O(2) and O(2A)) of 1.253(9) Å. However, the longer Sn-O distances are within the sum of the van der Waals radii for these

Table 3
Bond lengths (Å) and angles (deg) with e.s.d.s in parentheses for non-hydrogen atoms

Sn(1)–O(1)	2.123(4)	Sn(1)–O(2)	2.484(5)
Sn(1)–C(8)	2.090(13)	Sn(1)–O(1A)	2.123(4)
Sn(1)–O(2A)	2.484(5)	Sn(1)–C(8A)	2.090(13)
C(1)–C(5)	1.738(8)	O(1)–C(7)	1.297(8)
O(2)–C(7)	1.253(9)	C(1)–C(7)	1.475(9)
C(1)–C(6)	1.379(9)	C(1)–C(2)	1.408(10)
C(5)–C(6)	1.354(9)	C(5)–C(4)	1.385(13)
N(1)–C(2)	1.352(9)	C(3)–C(2)	1.399(9)
C(3)–C(4)	1.347(11)	C(8)–C(9)	1.500(17)
C(9)–C(10)	1.264(27)	C(10)–C(11)	1.432(21)
O(1)–Sn(1)–O(2)	56.1(2)	O(1)–Sn(1)–C(8)	103.6(3)
O(2)–Sn(1)–C(8)	87.1(3)	O(1)–Sn(1)–O(1A)	85.8(2)
O(2)–Sn(1)–O(1A)	141.9(2)	C(8)–Sn(1)–O(1A)	104.2(3)
O(1)–Sn(1)–O(2A)	141.9(2)	O(2)–Sn(1)–O(2A)	162.1(2)
C(8)–Sn(1)–O(2A)	87.0(3)	O(1A)–Sn(1)–O(2A)	56.1(2)
O(1)–Sn(1)–C(8A)	104.2(3)	O(2)–Sn(1)–C(8A)	87.0(3)
C(8)–Sn(1)–C(8A)	141.7(6)	O(1A)–Sn(1)–C(8A)	103.6(3)
O(2A)–Sn(1)–C(8A)	87.1(3)	Sn(1)–O(1)–C(7)	100.6(4)
Sn(1)–O(2)–C(7)	85.0(4)	C(7)–C(1)–C(6)	117.1(6)
C(7)–C(1)–C(2)	123.6(6)	C(6)–C(1)–C(2)	119.3(6)
C(1)–C(5)–C(6)	120.9(7)	C(1)–C(5)–C(4)	120.1(5)
C(6)–C(5)–C(4)	119.0(7)	O(1)–C(7)–O(2)	118.3(6)
O(1)–C(7)–C(1)	120.4(6)	O(2)–C(7)–C(1)	121.3(6)
C(1)–C(6)–C(5)	122.3(7)	C(2)–C(3)–C(4)	122.9(8)
C(1)–C(2)–N(1)	122.9(6)	C(1)–C(2)–C(3)	116.6(6)
N(1)–C(2)–C(3)	120.5(7)	C(5)–C(4)–C(3)	119.7(7)
Sn(1)–C(8)–C(9)	113.7(10)	C(8)–C(9)–C(10)	124.8(16)
C(9)–C(10)–C(11)	127.5(17)		

atoms (3.68 Å) [21] and as a result they must be considered as bonding.

From Fig. 1, it can be seen that the tin atom has a coordination number of six. In the idealized case of a

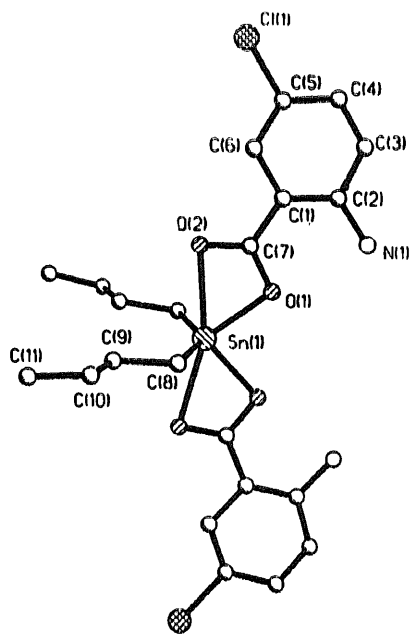


Fig. 1. Molecular structure with atom labelling for $(C_4H_9)_2Sn(O_2CC_6H_3(NH_2)Cl)_2$.

six-coordinated diorganotin bischelate, the carbon–tin–carbon angle is 90° for the cis- and 180° for the trans-isomers. The angle of Bu–Sn–Bu ($141.7(6)^\circ$) found for the title compound is close to the average of these two extremes and lies in the range of C–Sn–C angles of 122.6 – 156.9° found for diorganotin chelates in which the organo substituents do not adopt cis- or trans-geometries about the tin atom [22]. This coordination geometry is best described as skew-trapezoidal bipyramidal. The skew-trapezoidal bipyramid can be envisaged as a distortion of a regular trans octahedron and it is especially favoured if the chelate bite angle is small [23,24]. Therefore, the bite angle (O(1)–Sn–O(2)) of the title compound, $56.1(2)^\circ$, is not reconcilable with an octahedral geometry but with a skew-trapezoidal bipyramid geometry. As a result, the Sn atom in ${}^nBu_2Sn(O_2CC_6H_3(NH_2)Cl)_2$ exists in a skew-trapezoidal planar geometry in which the basal plane is defined by the four O atoms derived from two chelating carboxylate ligands and the axial positions are occupied by the two organo substituents (Bu) which lie over the weaker Sn–O bonds (Sn–O(2) and Sn–O(2A)).

The most interesting aspect of the structure concerns the non-coordination of the nitrogen atom of amino group of the carboxylate ligand. As can be seen from Fig. 1, the nitrogen atom is directed away from the tin atom. Furthermore, the nitrogen atom does not make

close intermolecular contacts to the tin atom in the crystal lattice.

There are now several crystal structures in the literature of compounds of the general formula $[R_2Sn(O_2CR')_2]$, and the interatomic parameters determined for the title compound agree well with those reported for these related compounds [9,13–19]. Nevertheless, meaningful comparison of the interatomic parameters between the compounds is not possible owing to the lack of consistency in the R and R' groups across the series.

The assignment of IR bands of these complex has been made by comparison with the IR spectra of the complex, the free acid and its sodium salt. The free acid shows a broad O–H adsorption at 2500–3100 cm^{-1} which is absent in the spectrum of the complex, showing the deprotonation and coordination of the carboxylate ligands. IR spectral data of the title compound also imply the presence of bidentate, chelating carboxylate groups, with $\Delta\nu$ ($\nu(COO)_{asym} - \nu(COO)_{sym}$) of 269 cm^{-1} ; this is comparable with that of the sodium salt of the ligand ($\Delta\nu = 268$ cm^{-1}) whereas this is 90 cm^{-1} lower than that observed in the spectrum of the free ligand ($\Delta\nu = 359$ cm^{-1}) [25]. The presence of a Sn–C adsorption band at 525 cm^{-1} indicates a trans configuration of the R–Sn moiety [18]. The band at 491 cm^{-1} is assigned to the stretching mode of the Sn–O linkage [18,19].

The 1H NMR spectrum shows the expected integration and peak multiplicities. The dibutyltin compounds exhibit resonance in the 0.87–1.89 ppm region. Signals for the other groups, such as phenyl H appear at the same positions as in the ligand.

The monomeric structure found for this title compound is contrasted with the polymeric structure for $[(CH_3)_2Sn(picolate)]_n$ [13] which also has the same general formula, $[R_2Sn(O_2CR')_2]$. In the latter compound, the Sn atom is seven-coordinated because of the multidentate nature of the picolate ligands, where both of its carboxylate O and heterocyclic N atoms are participating in coordination to the tin atom. There are two distinct carboxylate groups in the $[(CH_3)_2Sn(picolate)]_n$, one is bidentate, chelating the Sn atom through one carboxylate O atom and the pyridyl N atom, and the other is tridentate, coordinating to one Sn atom through the N atom and one O atom and bridging a neighbouring Sn atom via the second O atom. For the title compound, there is no intra- and inter-molecular coordination of the amino-type N atom which is present in the carboxylate group to the Sn atom. This can be explained by electronic and steric factors of the R and R' groups. The O atom which is more electronegative, and hence is a stronger donating group, is preferable to stabilize the discrete form of the title compound rather than the N atom [26]. Therefore, the two O atoms from the carboxylate ligands prefer to coordinate to the Sn

atom. The presence of the bulky phenyl group at the carboxylate ligand precludes the N atom and the O atom from close contact with the neighbouring tin atom, and hence there are no intermolecular contacts and no bridging to the tin atom by these atoms.

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