

Synthesis and characterization of di-*n*-butylbis(2,4-dihydroxybenzoato)tin(IV)

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Abstract—The compound di-*n*-butylbis(2,4-dihydroxybenzoato)tin(IV), (C₄H₉)₂Sn[2,4-(OH)₂C₆H₃COO]₂ has been synthesized and characterized by elemental analysis, IR and NMR (¹H, ¹³C and ¹¹⁹Sn) spectroscopy and X-ray diffraction techniques. The compound is monomeric with the Sn atom existing in a skew-trapezoidal bipyramidal geometry, in which the asymmetrically chelating carboxylate ligands comprise the trapezoidal plane and the butyl groups occupy the axial positions with the C—Sn—C angle 139.0(3)°. Both of the oxygen atoms from the hydroxy groups residing on the ligand do not participate in bonding to the tin atom. However, in the crystal lattice, there are intermolecular hydrogen bonds of OH...O' type which bond the related molecules together. © 1997 Elsevier Science Ltd

Keywords: diorganotin dicarboxylate; di-*n*-butylbis(2,4-dihydroxybenzoato)tin(IV); x-ray diffraction determination; skew-trapezoidal bipyramidal geometry.

In industry, diorganotin dicarboxylate compounds are widely used as homogeneous catalysts for polyurethane and RTV silicone polymerizations and for transesterification reactions [1,2]. Owing to these applications, the structure and mechanisms of action of these diorganotin dicarboxylates remain a matter of speculation [2–6].

In this paper, we report the preparation, spectroscopic and crystal structural characterization of di-*n*-butylbis(2,4-dihydroxybenzoato)tin(IV), which has the usual monomeric hexa-coordinated diorganotin dicarboxylate structure. The compound was studied in order to reveal the influence of the presence of the additional donor atoms (OH groups) residing on the carboxylate ligand.

EXPERIMENTAL

Physical measurements

The IR absorption spectra of 2,4-dihydroxybenzoic acid and its sodium salt and the complex were recorded on a Perkin-Elmer FTIR 1650 spectro-

photometer in the frequency range of 4000–450 cm⁻¹ with the samples prepared as KBr discs. The ¹H, ¹³C and ¹¹⁹Sn NMR were obtained with a Bruker 300 MHz AC-P NMR spectrometer in CDCl₃ solution. Microanalysis was carried out on a Control Equipment Corporation model 240XA elemental analyser at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia.

*Synthesis of the complex di-*n*-butylbis(2,4-dihydroxybenzoato)tin(IV), (C₄H₉)₂Sn[2,4-(OH)₂C₆H₃COO]₂*

Dibutyltin oxide (3.73 g, 15 mmol) and 2,4-dihydroxybenzoic acid (4.62 g, 30 mmol) in 50 cm³ toluene were refluxed for 2 h until a clear pinkish solution was obtained and the solution was filtered while it was still hot. The solvent was gradually removed by evaporation *in vacuo* until the white solid product was obtained. The product was then recrystallized from toluene/hexane. Colourless needle-shaped crystals were formed on standing at room temperature. M.p. 154–156°C. Found: C, 49.2; H, 5.1. Calc. for C₂₂H₂₈O₈Sn: C, 49.0; H, 5.2%. IR(KBr): ν(COO_{asym}) 1635; ν(COO_{sym}) 1410; ν(OH) 3285–3400; ν(Sn—C) 540; ν(Sn—O) 492 cm⁻¹. ¹H NMR(CDCl₃): δ(C₄H₉) 0.88, 1.40, 1.76; δ(C₆H₃) 6.41–7.87; δ(OH) 10.92 ppm. ¹³C

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NMR(CDCl₃): $\delta(\text{C}_4\text{H}_9)$ 13.4, 26.2, 26.3, 26.5; $\delta(\text{C}_6\text{H}_5)$ 103.1, 105.8, 108.3, 133.6, 162.8, 163.2; $\delta(\text{COO})$ 177.1 ppm. ¹¹⁹Sn NMR(CDCl₃) δ : -128 ppm.

Crystal structure determination of (C₄H₉)₂Sn[2,4-(OH)₂C₆H₃COO]₂

Intensity data for a crystal with dimensions 0.4 × 0.5 × 0.6 mm was measured at 298 K on a Huber diffractometer fitted with graphite monochromator Mo-K_α radiation, $\lambda = 0.71073 \text{ \AA}$. The θ - 2θ scan technique was employed to measure a total of 11,291 reflections up to $2\theta_{\text{max}} = 52.0^\circ$. Corrections were applied for Lorentz and polarization effects but not for absorption. The 8052 out of the 10950 independent reflections ($R_{\text{int}} = 0.0282$) 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 [7]. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed in their idealized positions (C—H = 0.96 Å) and refined isotropically. A weighting scheme of the form $w = [\sigma^2(F) + 0.0007F^2]^{-1}$ was used and the refinement continued to final $R = 0.0475$ and $R_w = 0.0508$. The final difference map had peaks between -0.61 and 1.00 eÅ⁻³.

The crystal data and refinement details are given in Table 1 and selected bond lengths and angles are listed in Table 2. Lists of additional data, including fractional atomic coordinates, hydrogen atom coor-

dinates, 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.

RESULTS AND DISCUSSION

The IR spectra show that the band assignable to the asymmetrical stretching of COO ($\nu(\text{COO})_{\text{asym}}$) for 2,4-dihydroxybenzoic acid (1640 cm⁻¹) is shifted towards a lower frequency (1635 cm⁻¹) and the band for symmetrical COO stretching ($\nu(\text{COO})_{\text{sym}}$) is shifted from 1270 to 1410 cm⁻¹ upon complex formation. The shifts in the $\nu(\text{COO})_{\text{asym}}$ and $\nu(\text{COO})_{\text{sym}}$ bands indicate that the carboxylate group of the free acid is coordinated to the tin atom [8]. The presence of a new band at 492 cm⁻¹ due to Sn—O stretch [9,10] further supports the participation of carboxylate group which possesses O atom as the donating atom. The difference between $\nu(\text{COO})_{\text{asym}}$ and $\nu(\text{COO})_{\text{sym}}$ ($\Delta\nu$) of the complex is 225 cm⁻¹ and is comparable to that for the corresponding sodium salt ($\Delta\nu = 220 \text{ cm}^{-1}$) but is 135 cm⁻¹ smaller than that observed in the spectrum of the free ligand which implies the presence of bidentate, chelating carboxylate group [11].

The broad band for $\nu(\text{OH})$ of carboxylic acid group in the range 2500–3000 cm⁻¹ disappears in the IR spectrum of the complex indicating that deprotonation of the ligand occurs during coordination to the tin atom. The OH region on the IR spectrum of the complex which is caused by the stretching mode of the pendant hydroxy group of the ligand reflects the appearance of hydrogen bonds. Correlations have been found between the OH stretching frequencies and the O...O distances in hydrogen bonds [7,11]. Hydrogen bonds of the OH...O type are expected to have $\nu(\text{OH})$ values between 2600–3500 cm⁻¹ for O...O distances of 2.60–2.90 Å. Therefore $\nu(\text{OH})$ of the title compound at 3000–3400 cm⁻¹ implies the presence of hydrogen bonds with O...O distances in the range 2.73–2.86 Å and this is in close agreement with the O...O distances from crystallographic determination, 2.722–2.858 Å (Table 3). The presence of a Sn—C absorption band at 540 cm⁻¹ indicates a *trans* configuration of the butyl groups [9].

The ¹H, ¹³C and ¹¹⁹Sn NMR spectra of the complex were recorded in CDCl₃ solution. The ¹H NMR spectrum shows the expected integration and peak multiplicities. The signals observable at δ 0.88, 1.40 and 1.76 ppm are ascribable to the proton of the butyl groups with the integration ratio 3:2:4. The appearance of a singlet at δ 10.92 ppm due to the hydroxyl proton resonance of the ligand moiety in the complex suggests that the OH groups residing on the carboxylate ligand are not involved in bonding to the tin atom. The signals from the aromatic protons appear as complex multiplets in the region δ 6.41–7.87 ppm.

The ¹³C NMR spectrum displays only one set of Sn—R and ligand carbon resonances. The signals of

Table 1. Crystal data and refinement details for (C₄H₉)₂Sn[O₂CC₆H₃(OH)₂]₂

Formula	C ₂₂ H ₂₈ O ₈ Sn
Formula weight	539.1
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.773(2)
b (Å)	11.863(2)
c (Å)	19.177(4)
α (°)	80.32(3)
β (°)	82.17(3)
γ (°)	84.94(3)
V (Å ³)	2388.0(8)
Z	4
D _c (Mg m ⁻³)	1.500
μ (mm ⁻¹)	1.112
F(000)	1096
Reflections collected	11291
Independent reflections	10950 ($R_{\text{int}} = 0.0282$)
Observed reflections	8052 ($F > 4.0\sigma(F)$)
No. of parameters refined	559
R	0.0475
R _w	0.0508
w	$[\sigma^2(F) + 0.0007F^2]^{-1}$
Largest diff. peak and hole (eÅ ⁻³)	1.00 and -0.61

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for non-hydrogen atoms. (shown for molecule A)

Sn(1)—O(3A)	2.559(4)	Sn(1)—O(4A)	2.110(4)
Sn(1)—O(7A)	2.508(4)	Sn(1)—O(8A)	2.124(4)
Sn(1)—C(15A)	2.114(6)	Sn(1)—C(19A)	2.107(7)
O(1A)—C(2A)	1.363(6)	O(2A)—C(4A)	1.351(6)
O(3A)—C(7A)	1.246(6)	O(4A)—C(7A)	1.294(7)
O(5A)—C(9A)	1.356(6)	O(6A)—C(11A)	1.364(7)
O(7A)—C(14A)	1.267(6)	O(8A)—C(14A)	1.281(6)
C(1A)—C(2A)	1.403(7)	C(1A)—C(6A)	1.393(7)
C(1A)—C(7A)	1.464(7)	C(2A)—C(3A)	1.375(6)
C(3A)—C(4A)	1.379(7)	C(4A)—C(5A)	1.393(8)
C(5A)—C(6A)	1.361(7)	C(8A)—C(9A)	1.413(7)
C(8A)—C(13A)	1.391(7)	C(8A)—C(14A)	1.454(7)
C(9A)—C(10A)	1.383(8)	C(10A)—C(11A)	1.368(7)
C(11A)—C(12A)	1.372(8)	C(12A)—C(13A)	1.375(8)
C(15A)—C(16A)	1.489(11)	C(16A)—C(17A)	1.531(13)
C(17A)—C(18A)	1.336(21)	(18A)—C(20A)	1.513(10)
C(20A)—C(21A)	1.446(11)	C(21A)—C(22A)	1.522(11)
O(3A)—Sn(1)—O(4A)	54.9(1)	O(3A)—Sn(1)—O(7A)	167.0(1)
O(4A)—Sn(1)—O(7A)	138.0(1)	O(3A)—Sn(1)—O(8A)	137.7(1)
O(4A)—Sn(1)—O(8A)	82.8(1)	O(7A)—Sn(1)—O(8A)	55.3(1)
O(3A)—Sn(1)—C(15A)	90.0(2)	O(4A)—Sn(1)—C(15A)	108.9(2)
O(7A)—Sn(1)—C(15A)	86.4(2)	O(8A)—Sn(1)—C(15A)	105.3(2)
O(3A)—Sn(1)—C(19A)	84.8(2)	O(4A)—Sn(1)—C(19A)	101.0(2)
O(7A)—Sn(1)—C(19A)	89.8(2)	O(8A)—Sn(1)—C(19A)	105.7(2)
C(15A)—Sn(1)—C(19A)	139.0(3)	Sn(1)—O(3A)—C(7A)	83.2(3)
Sn(1)—O(4A)—C(7A)	102.9(3)	Sn(1)—O(7A)—C(14A)	84.7(3)
Sn(1)—O(8A)—C(14A)	102.3(3)	C(2A)—C(1A)—C(6A)	117.6(4)
C(2A)—C(1A)—C(7A)	119.6(4)	C(6A)—C(1A)—C(7A)	122.7(5)
O(1A)—C(2A)—C(1A)	121.4(4)	O(1A)—C(2A)—C(3A)	117.7(4)
C(1A)—C(2A)—C(3A)	120.8(4)	C(2A)—C(3A)—C(4A)	120.0(5)
O(2A)—C(4A)—C(3A)	116.5(5)	O(2A)—C(4A)—C(5A)	123.4(5)
C(3A)—C(4A)—C(5A)	120.0(4)	C(4A)—C(5A)—C(6A)	119.6(5)
C(1A)—C(6A)—C(5A)	121.9(5)	O(3A)—C(7A)—O(4A)	119.0(4)
O(3A)—C(7A)—C(1A)	121.9(5)	O(4A)—C(7A)—C(1A)	119.1(4)
C(9A)—C(8A)—C(13A)	118.7(5)	C(9A)—C(8A)—C(14A)	118.9(4)
C(13A)—C(8A)—C(14A)	122.4(4)	O(5A)—C(9A)—C(8A)	121.6(5)
O(5A)—C(9A)—C(10A)	118.2(4)	C(8A)—C(9A)—C(10A)	120.2(4)
C(9A)—C(10A)—C(11A)	119.3(5)	O(6A)—C(11A)—C(10A)	121.7(5)
O(6A)—C(11A)—C(12A)	116.9(5)	C(10A)—C(11A)—C(12A)	121.4(5)
C(11A)—C(12A)—C(13A)	120.1(5)	C(8A)—C(13A)—C(12A)	120.2(5)
O(7A)—C(14A)—O(8A)	117.3(5)	O(7A)—C(14A)—C(8A)	121.5(4)
O(8A)—C(14A)—C(8A)	121.1(4)	Sn(1)—C(15A)—C(16A)	118.7(4)
C(15A)—C(16A)—C(17A)	111.2(7)	C(16A)—C(17A)—C(18A)	118.0(9)
Sn(1)—C(19A)—C(20A)	119.5(4)	C(19A)—C(20A)—C(21A)	113.3(7)
C(20A)—C(21A)—C(22A)	113.7(8)		

Table 3. Intermolecular hydrogen bonds distances (Å) and their related symmetry operation

		Symmetry Operation
O(1A)···O(2B)	2.738(5)	x, y, z
O(2A)···O(5B)	2.772(4)	$x-1, y, z+1$
O(5A)···O(6B)	2.722(4)	$-x+1, -y, -z-1$
O(6A)···O(2B)	2.858(5)	$x+1, y+1, z$

butyl carbons resonances appear at δ 26.5, 26.3, 25.6 and 13.4 ppm, while signals from aromatic carbons appear at δ 103.1, 105.8, 108.3, 133.6, 162.8 and 163.2 ppm. The last two chemical shifts belong to the C-2 and C-4 atoms which are bearing the OH substituents in the aromatic ring. This is suggested as the OH group is electronegative and thus causes the deshielding effect and will shift the peak downfield. The carbonyl carbon absorbs further downfield (δ 177.1 ppm)

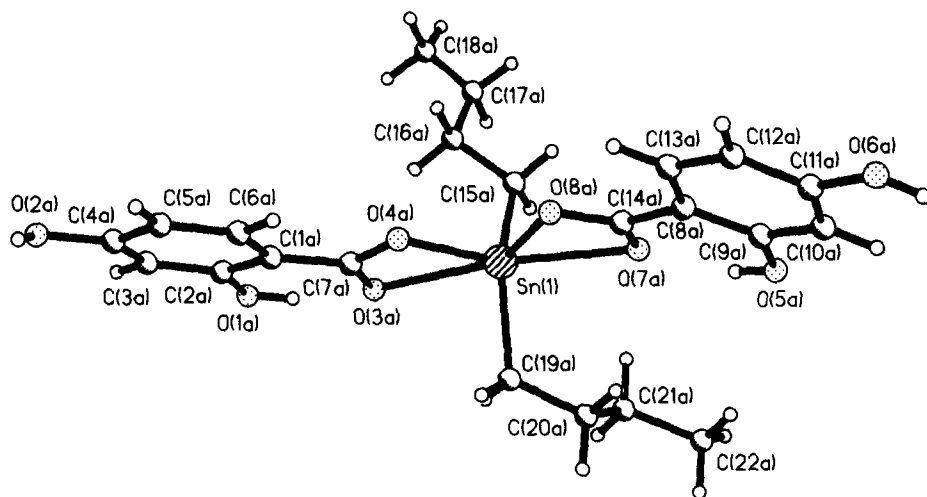


Fig. 1. Molecular structure with atom labelling for $(C_4H_9)_2Sn[O_2CC_6H_3(OH)_2]_2$ (illustrated for molecule A).

in the spectrum. The ^{119}Sn NMR spectrum exhibits a broad singlet at -128 ppm and this is consistent with those reported for the diorganotin dicarboxylates [10,13–15]. The ^{13}C and ^{119}Sn NMR data can be best interpreted in terms of the common diorganotin dicar-

boxylate structure, i.e. the tin atom is six-coordinated with two bis-chelated carboxylate ligands [10].

The crystal structure analysis reveals that there are two molecules of $(C_4H_9)_2Sn[2,4-(OH)_2C_6H_3COO]_2$ in the triclinic unit cell, and they are related to each other

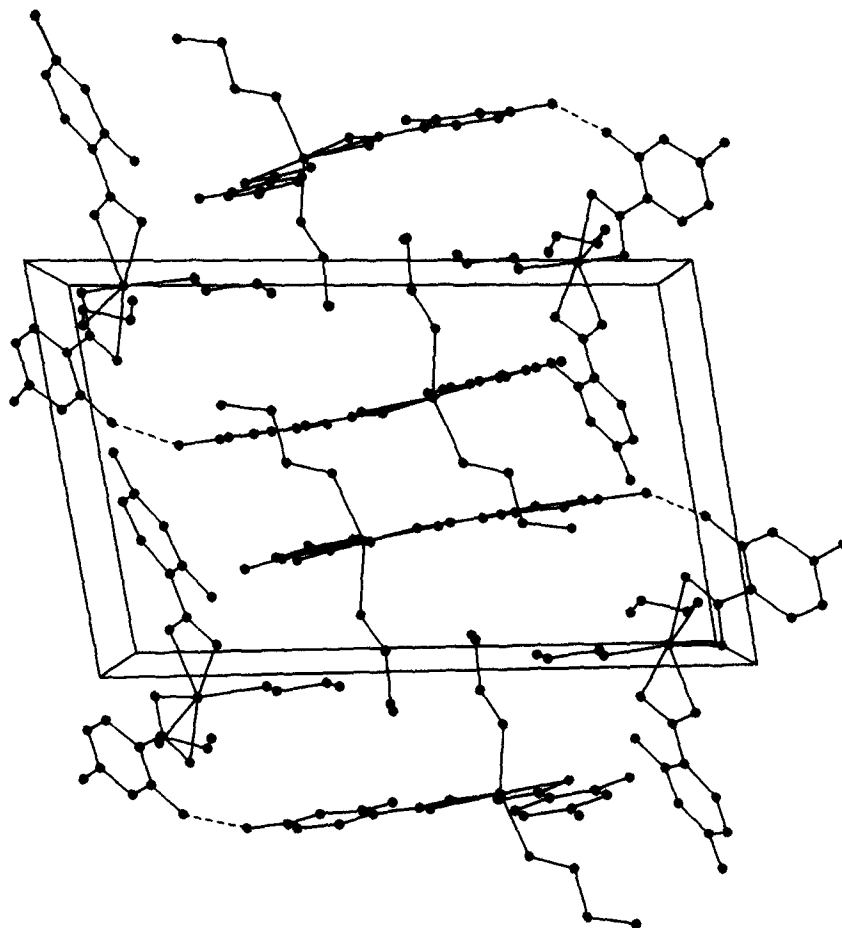


Fig. 2. Packing of unit cell viewed down α axis showing the hydrogen bond linkages.

through the crystallographic inversion centre about the positions (0, 0, 0) and (1/2, 1/2, 1/2). Since both independent molecules have similar molecular structure, only one molecule is shown in Fig. 1, i.e. molecule A and only its interatomic parameters are listed in Table 2.

From Fig. 1, it can be seen that the tin atom exists in a skew-trapezoidal bipyramidal geometry, in which the basal plane is occupied by four O atoms derived from the two chelating carboxylate ligands. The carboxylate ligands coordinate the centre tin atom with asymmetric Sn—O distances. The degree of asymmetry in the Sn—O bond lengths is not equal however, with the differences between Sn—O bond lengths for the two carboxylate ligands being 0.449 and 0.384 Å, respectively. The anisobidentate mode of coordination of the two carboxylate groups is reflected in the disparity of associated C—O bond distances; as expected the C—O bond distance associated with the weaker or longer Sn—O bond is shorter than the C—O bond distance associated with the strongly bound oxygen atom (shorter Sn—O bond). The two butyl groups occupy positions approximately *trans* to each other, the distortion being such that these groups lie over the weaker Sn—O interactions [Sn(1)—O(3a) and Sn(1)—O(7a)] with the C(15a)—Sn(1)—C(19a) angle 139.0(3)° a value which is close to the average of the two extreme angles, 90 and 180°. It is noteworthy that although the geometry of the title compound is skew-trapezoidal bipyramidal, the tin atom does not lie on a two-fold crystallographic axis such as found in most of the diorganotin dicarboxylate structures [6,16–19].

The oxygen atoms of the two hydroxy groups of the ligand are not involved in coordination to the tin atom. As can be seen from Fig. 1, both of the ortho and para hydroxy groups are directed away from the tin atom. Furthermore, the oxygen atoms do not make close intermolecular interactions to tin atom in the crystal lattice and it could be explained on the basis of intermolecular hydrogen bonds between the oxygen atom to OH group of the other molecules (OH...O) in the crystal lattice. The H-bonded distances and related symmetry operations are shown in Table 3.

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