CRYSTAL STRUCTURE OF BIS[AQUADIBUTYL(2,6-PYRIDINE-DICARBOXYLATO)TIN] *N*-METHYLANILINE SOLVATE AT 158 K

Seik Weng Ng

Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia

Abstract

The crystal structure of bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] *N*-methylaniline solvate, determined at 158 K, consists of a centrosymmetric bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] molecule whose coordinated water [Sn-O = 2.331(7) Å] forms an intramolecular hydrogen bond with a carbonyl oxygen atom [O_{water}...O = 2.646(9) Å] and an intermolecular hydrogen bond with the carbonyl oxygen atom belonging to an adjacent molecule [O_{water}...O = 2.729(9) Å] to link the dimeric molecules into undulated layers; the *N*-methylaniline molecules occupy the space between the layers, which are 8.61 Å apart. The tin atom shows *trans*-C₂SnNO₄ pentagonal bipyramidal [C-Sn-C = 164.7(4)°] coordination.

Introduction

Bis(dicyclohexylammonium) bis(2,6-pyridinedicarboxylato)dibutylstannate has been assigned a seven-coordinate geometry at tin on the basis of spectroscopic measurements, and the assignment has been corroborated by X-ray diffraction analysis on the monohydrate. The lattice water molecule is only weakly hydrogen-bonded in the crystal structure, which probably explains the rapid transformation of the monohydrate to the anhydrous compound when exposed to air. Unlike the condensation of dibutyltin oxide with dicyclohexylammonium hydrogen 2,6-pyridinedicarboxylate that yielded this seven-coordinate ammonium stannate [1], that of dibutyltin oxide with diisopropylammonium hydrogen 2,6-pyridinedicarboxylate gave bis(diisopropylammonium) tris(2,6-pyridinedicarboxylato)bis(dibutylstannate) as an air-stable trihydrate, whose water molecules are involved in extensive hydrogen bonding interactions [2]. In continuation with the structural studies on the dibutylstannate derivatives of 2,6-pyridinedicarboxylic acid, dibutyltin oxide was treated with methylphenylammonium hydrogen 2,6-pyridinedicarboxylate to afford a yellow product that rapidly turned into an opaque powder when taken out of solution. The change implied the presence of lattice water. Several crystals used for room-temperature diffraction measurements decomposed in the X-ray beam, and low-temperature data were acquired in order to elucidate structure of the organotin compound.

Experimental

Dibutyltin oxide was reacted with two molar equivalents each of 2,6-pyridinedicarboxylic acid and *N*-methylaniline in hot ethanol; a mixture of colorless and yellow crystals separated from the solution. The 4038 reflections that were collected with a selected yellow crystal on a Siemens *P4* diffractometer (Mo-*K*α radiation, λ = 0.71073 Å) at -115°C (-20 < *h* < 0, 0 < *k* ≤ 13, -26 ≤ *l* ≤ 26) to 2θ = 50° [3] were corrected for absorption [4] and decay. The two Sn atoms were located [5] in the acentric *C*₂ space group; the origin was then shifted so that these were related by a center of inversion. Refinement on *F*² proceeded in the *C2/c* space group. One butyl chain is disordered, but the disorder could be modeled over only two sites. The C5-C6-C7-C8 and the C5'-C6'-C7'-C8' chains were assigned half site occupancies, with the C5 and C5' atoms restrained by *EXYZ* and *EADP* instructions in *SHELXL-93* [6]. The 1,2- and 1,3-related C-C distances in both the disordered and ordered chains with fixed at 1.54±0.01 and 2.52±0.02 Å. The temperature factors of the other primed C atoms were restrained to be the same as those of the unprimed atoms, and a *SIMU* instruction was also used on the disordered chain. The *N*-methylaniline molecule is disordered over the two-fold axis and the center of the phenyl ring lies on the 4*e* Wyckoff site; their atoms were assigned half site occupancies. Non-hydrogen atoms were refined anisotropically except for the atoms belonging to the *N*-methylaniline molecule, which were refined isotropically. H-atoms were generated and allowed to ride on their parent C-, N- or O-atoms with *U*(H) = 1.5*U*_{eq}(C,N,O). The refinement over all 3680 independent reflections converged with a shift-to-error ratio of 0.001 to *R* = 0.0650 for 3108 *I* > 2σ(*I*) reflections. Atomic coordinates and temperature factors are listed in Table 1. The structure is shown as a 50% probability *ORTEP* [7] plot in Fig. 1; the layer structure is illustrated as a *PLUTON* [8] plot in the Fig. 2.

Results and Discussion

Two crystalline products were obtained from the reaction between dibutyltin oxide and methylphenylammonium hydrogen 2,6-pyridinedicarboxylate in 1/2 molar stoichiometry.

Table 1. Atomic coordinates and equivalent temperature factors ($\text{\AA}^2$)

Atom	x	y	z	U_{eq}
Sn1	0.23836(4)	0.26409(6)	-0.09701(3)	0.0258(3)
O1	0.2595(4)	0.3742(6)	-0.0019(3)	0.027(2)
O2	0.2563(5)	0.5598(7)	0.0393(3)	0.035(2)
O3	0.2285(5)	0.2987(6)	-0.1959(3)	0.031(2)
O4	0.2334(5)	0.4323(7)	-0.2707(3)	0.043(2)
O5	0.2162(5)	0.0722(7)	-0.1387(3)	0.037(2)
N1	0.2522(6)	0.4667(7)	-0.1119(4)	0.030(2)
C1	0.3561(6)	0.2234(9)	-0.0936(5)	0.032(2)
C2	0.4152(6)	0.328(1)	-0.0854(5)	0.041(3)
C3	0.4996(7)	0.285(1)	-0.0848(8)	0.071(4)
C4	0.559(1)	0.390(2)	-0.075(1)	0.114(8)
C5	0.1191(7)	0.265(1)	-0.0853(5)	0.042(3)
C6	0.069(1)	0.318(3)	-0.140(1)	0.076(7)
C7	-0.017(1)	0.315(4)	-0.129(1)	0.094(9)
C8	-0.034(3)	0.402(6)	-0.077(3)	0.17(3)
C6' (50%)	0.067(1)	0.375(2)	-0.101(2)	0.076(7)
C7' (50%)	-0.018(1)	0.337(3)	-0.098(2)	0.094(9)
C8' (50%)	-0.073(2)	0.447(4)	-0.107(3)	0.17(3)
C9	0.2608(6)	0.488(1)	-0.0032(4)	0.027(2)
C10	0.2621(7)	0.5445(9)	-0.0670(4)	0.030(2)
C11	0.2770(7)	0.664(1)	-0.0755(5)	0.037(3)
C12	0.2778(7)	0.707(1)	-0.1355(5)	0.037(3)
C13	0.2669(7)	0.6239(9)	-0.1827(5)	0.032(2)
C14	0.2515(7)	0.5030(9)	-0.1703(5)	0.031(2)
C15	0.2365(6)	0.4064(9)	-0.2160(4)	0.029(2)
N2 (50%)	0.063(3)	-0.029(4)	-0.243(2)	0.13(2)
C16 (50%)	0.019(4)	0.091(4)	-0.248(4)	0.14(2)
C17 (50%)	0.030(1)	-0.134(1)	-0.245(2)	0.060(8)
C18 (50%)	-0.050(1)	-0.156(2)	-0.252(2)	0.10(2)
C19 (50%)	-0.078(1)	-0.274(2)	-0.253(1)	0.065(9)
C20 (50%)	-0.026(1)	-0.370(1)	-0.248(2)	0.10(2)
C21 (50%)	0.054(1)	-0.349(2)	-0.242(2)	0.060(8)
C22 (50%)	0.082(1)	-0.231(2)	-0.241(1)	0.055(7)

U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

Crystal data: $C_{37}H_{55}N_3O_{10}Sn_2$, $FW = 939.22$, monoclinic, $C2/c$, $a = 17.22(1)$, $b = 11.052(4)$, $c = 22.110(8)$ Å, $\beta = 94.74(3)^\circ$, $V = 4194(3)$ Å³, $Z = 4$, $D_{x-ray} = 1.488$ g cm⁻³, $F(000) = 1912$, $\mu = 1.246$ mm⁻¹.

As only one equivalent of methylphenylammonium hydrogen 2,6-pyridinedicarboxylate has been consumed to yield bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] N-methylaniline solvate (Fig. 1), the condensation reaction liberates N-methylaniline, which is probably not sufficiently basic to deprotonate the excess methylphenylammonium hydrogen 2,6-pyridinedicarboxylate. The methylphenylammonium hydrogen pyridinedicarboxylate, which separates as the colorless crystals, has also been structurally identified [9].

The water-coordinated tin atom [Sn-O_{water} = 2.331(7) Å] of the centrosymmetric dinuclear bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] moiety is seven-coordinate in a *trans*-C₂SnNO₄ pentagonal bipyramidal geometry [C-Sn-C = 164.7(4)°]. It is *O,N,O*-chelated by the 2,6-pyridinedicarboxylate anion; both carboxyl groups are unidentate, but one of the esteryl oxygen atoms of the monomeric unit [Sn-O = 2.431(7) Å] forms an intradimer bond with the tin atom of the other monomeric unit. This intradimer bond distance [Sn-O = 2.667(7) Å] is significantly shorter than that [2.783(4) Å] found in bis[aquadibutyl(2,6-pyridinedicarboxylato)tin], which adopts a linear chain structure arising from intermolecular hydrogen bonding [2.707(7) Å] [10]. However, the differences in the tin-oxygen bond distances between the solvated and unsolvated complexes do not manifest in an similarly large difference in the carbon-tin-skeletal angle [C-Sn-C = 164.7(4)° in the solvated complex; C-Sn-C = 166.2(2)° in the unsolvated complex]. The intradimer bond distance is also shorter than that [2.805(3) Å] found in the 1/1 complex of bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] di-2-pyridylamine. In the crystal structure, the di-2-pyridylamine molecules occupy the space between hydrogen-bonded layers of the dimer; the hydrogen bonds [2.653(5), 2.764(5) Å] involve the coordinated water molecule and adjacent carbonyl oxygen atoms. The layers, which are crystallographically imposed to be flat, are separated by a distance of 5.57 Å [11].

Fig. 1. Geometry of the tin atom in bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] *N*-methylaniline. Selected bond distances and angles: Sn1-C1 = 2.07(1), Sn1-C5 = 2.09(1), Sn1-N1 = 2.278(8), Sn1-O1 = 2.431(7), Sn1-O1a = 2.666(7), Sn1-O3 = 2.213(7), Sn1-O5 = 2.331(7) Å; C1-Sn1-C5 = 164.7(4), C1-Sn1-N1 = 96.0(4), C1-Sn1-O1 = 90.1(3), C1-Sn1-O1a = 84.2(3), C1-Sn1-O3 = 93.9(4), C1-Sn1-O5 = 86.8(3), C5-Sn1-N1 = 97.5(4), C5-Sn1-O1 = 88.3(4), C5-Sn1-O1a = 81.2(3), C5-Sn1-O3 = 97.2(4), C5-Sn1-O5 = 85.5(4), N1-Sn1-O1 = 67.8(3), N1-Sn1-O1a = 133.4(3), N1-Sn1-O3 = 71.8(3), N1-Sn1-O5 = 148.5(3), O1-Sn1-O1a = 65.6(3), O1-Sn1-O3 = 139.7(2), O1-Sn1-O5 = 143.6(2), O1a-Sn1-O3 = 154.8(2), O1a-Sn1-O5 = 78.1(2), O3-Sn1-O5 = 76.7(3)°. Symmetry transformation: $a = \frac{1}{2} - x, \frac{1}{2} - y, -z$.

Fig. 2. Hydrogen bonds linking the bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] molecules [$O5 \cdots O2' = 2.646(9)$, $O5 \cdots O4'' = 2.729(9)$ Å] viewed along the *a*-axis. Symmetry transformation: $' = \frac{1}{2} - x, \frac{1}{2} - y, -z$; $'' = \frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$.

In the *N*-methylaniline solvate, the coordinated water of the dinuclear molecule forms hydrogen bonds with adjacent molecules [$O \cdots O = 2.729(9)$ Å]. The hydrogen bonding interactions furnish a layer structure (Fig. 2). The layers are separated by a distance equal to half the *a*-axis (i.e., 8.61 Å), and the

disordered N-methylaniline molecules occupy the space between them. The molecules are not linked by hydrogen bonds to the dimer, which may explain the air-sensitive nature of the compound. The manner the solvent is packed between the layers is reminiscent of the packing found in bis[aquaethylphenyl(2,6-pyridinedicarboxylato)tin] di-chloroform solvate [12]. For this compound, the larger phenyl and the smaller ethyl substituents on tin have relatively minor effect on the hydrogen-bonded layer structure; the chloroform molecules occupy the space between the layers.

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