Structural Characterization of 2,2-Di-*n*-butyl-4-methyl-1,3,2-dioxastannolane Isolated from Supercritical CO_2 Conditions

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The title compound has been isolated as single crystals from the synthesis of propylene carbonate from racemic 1,2-propanediol and carbon dioxide using *n*-Bu_2SnO as a catalyst precursor. The X-ray crystallographic structure analysis revealed the self-assembly of di-*n*-butyltin(IV) 1,2-propanediolate units, linked together through long-distance Sn–O interactions leading to a one-dimensional polymeric architecture organized in a syndiotactic arrangement. The coordination geometry around the tin atoms can be described as an unusual faced-capped trigonal bipyramidal environment.

Key words: Organotin(IV), 1,2-Propanediol, Dioxastannolane, Self-assembly, Crystal Structure

Introduction

Organotin(IV) compounds are known to be efficient catalysts for the transformation of carbon dioxide into useful chemicals such as linear dialkyl carbonates [1], cyclic carbonates [2], and oxazolidone [3]. In the past, *n*-Bu_2SnO was reported in particular as catalyst precursor for the formation of propylene carbonate from 1,2-propanediol and CO_2 under supercritical conditions [4]. The 2,2-di-*n*-butyl-4-methyl-1,3,2-dioxastannolane derivative (**1**) was then proposed by the authors as a possible key intermediate of the catalytic cycle. In our quest for a better understanding of the carbonation reaction mechanisms [5], and in revisiting the reaction, we successfully isolated **1** in the form of single crystals. Here, we report and discuss its unprecedented solid-state structure.

Results and Discussion

Reaction of racemic 1,2-propanediol with carbon dioxide under supercritical conditions (P = 180 bar, T = 413 K) for 20 h, in the presence of DMF and catalyzed by *n*-Bu_2SnO, leads to the formation of propylene carbonate. However, the IR fingerprint of the tin-based residue does not correspond to that of the starting tin compound. Indeed, new significant vibration bands are observed, in particular at 2829, 1051 and 612 cm^{-1}, which may correspond to the coordination of tin atoms by 1,2-propanediolate ligands. By slow evaporation of a saturated methanolic solution of **1**, we collected colorless crystals which were characterized as 2,2-di-*n*-butyl-4-methyl-1,3,2-dioxastannolane (**1**) by elemental analysis, IR and NMR spectroscopy, and single-crystal X-ray crystallography.

The X-ray structure analysis reveals a one-dimensional polymeric architecture built on the self-assembly of di-*n*-butyltin(IV) 1,2-propanediolate units. The tin atom of a monomer is bound to two *n*-butyl groups and is chelated by a bidentate 1,2-propanediolate ligand (L^{2-}), leading to a five-membered dioxastannolane ring. Both oxygen atoms of L^{2-} are also implicated in intermolecular interactions, with two different Sn–O distances, giving rise to the formation of planar Sn_2O_2 four-membered rings which leads to the propagation of the infinite 1D polymer. Interestingly, the L^{2-} fragments are positioned in a syndiotactic arrangement, and the chirality on the diolato fragment (C9) alternates along the Sn-based zigzag chain. An ORTEP view of the chain structure of **1**, together with selected bond lengths and angles, is given in Fig. 1.

The tin atoms are six-coordinated with a geometry which can be described as an unusual face-capped trigonal-bipyramidal environment (Fig. 2). The axial positions are occupied by the oxygen atoms O2 and $O2^i$ from two distinct L^{2-} ligands [O2–Sn–$O2^i$ = 151.75(7)°, Sn–O2 = 2.140(2) and Sn–$O2^i$ = 2.232(2) Å]. The equatorial plane contains the α-carbon atoms of the two *n*-butyl chains [C1–Sn–

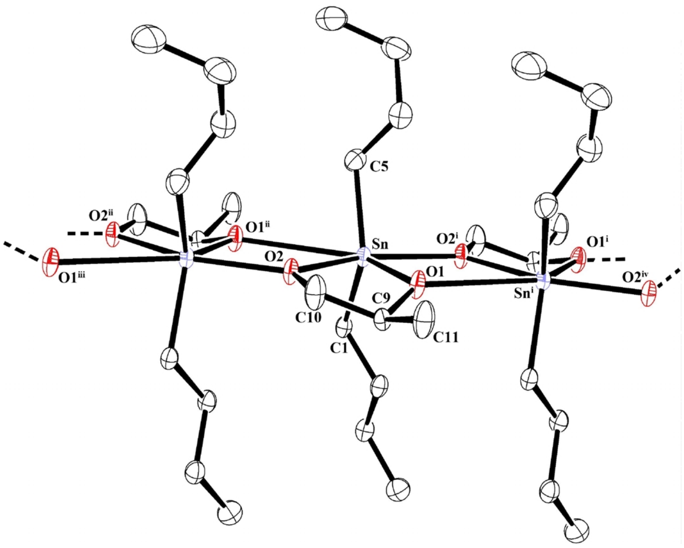

Fig. 1. Chain structure of **1** (ORTEP; color online). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn–O1 2.030(2), Sn–O2 2.140(2), Sn–O2^{i} 2.232(2), Sn–O1^{ii} 2.873(2), Sn–C1 2.134(3), Sn–C5 2.128(3); O1–Sn–O2 78.31(7), O1–Sn–O1^{ii} 137.40(6), O1–Sn–O2^{i} 73.44(7), O1–Sn–C1 115.28(10), O1–Sn–C5 117.74(12), O2–Sn–O1^{ii} 59.09(7), O2–Sn–O2^{i} 151.75(7), O2–Sn–C1 102.54(10), O2–Sn–C5 102.13(11), O1^{ii}–Sn–O2^{i} 149.16(6), O1^{ii}–Sn–C1 76.44(9), O1^{ii}–Sn–C5 75.39(9), O2^{i}–Sn–C1 89.93(10), O2^{i}–Sn–C5 90.83(10), C1–Sn–C5 124.75(13). Symmetry transformations used to generate equivalent atoms: ^{i} $-x+1/2$, $y+1/2$, z; ^{ii} $-x+1/2$, $y-1/2$, z; ^{iii} x, $1-y$, z; ^{iv} x, $1+y$, z.

C5 = 124.75(13)°, Sn–C1 = 2.134(3) and Sn–C5 = 2.128(3) Å] and the second oxygen atom (O1) of one of the two L^{2-} ligands, which is chelating the tin atom [O1–Sn–C1 = 115.28(10)°, O1–Sn–C5 = 117.74(12)°, and Sn–O1 = 2.030(2) Å]. In addition, one face of the trigonal bipyramid is capped by a supplementary oxygen atom of a neighboring unit (O1^{ii}) at a long Sn–O distance [Sn–O1^{ii} = 2.873(2) Å] (Fig. 2). The bending of the O2–Sn–O2^{i} axis can be explained by the close location of the capping oxygen atom O1^{ii} [O1^{ii}–Sn–O2 = 59.09(7)°, O1^{ii}–Sn–C1 = 76.44(9)°, O1^{ii}–Sn–C5 = 75.39(9)°]. In a recent study, we observed a comparable environment around tin atoms of a 2D organostannoxane network [6], but nevertheless such a coordination geometry remains a rare case in the literature.

The ^{119}Sn{^{1}H} spectrum of **1** in $CDCl_3$ at 273 K displays a major broad resonance centered at $\delta = -122$ ppm. According to the literature, this chemical shift indicates that penta-coordination of the tin centers is favored in solution, and that compound **1** is present mainly as a dimer [7]. Indeed, three additional low-intensity signals at $\delta = -139$, -148 and -270 ppm are also observed and can be assigned to higher oligomers (tri-, tetra- and pentamers) with penta- and hexa-coordination modes. In the ^{13}C{^{1}H} NMR spectrum, in addition of the characteristic resonances of the 1,2-propanediolato ligand, two sets of signals are observed for the diastereotopic *n*-butyl groups. MALDI-TOF and ES mass spectrometry analyses of **1** have corroborated the observations made by ^{119}Sn{^{1}H} NMR spectroscopy, showing effectively in the range of 300 – 2000 Da the presence of several intense mass clusters, which can be assigned to related oligomers of **1**. Finally, the IR spectrum of crystals of **1** is strictly identical to that measured of the tin-based residue resulting from the supercritical CO_2 conditions, which confirms that **1** is the major tin-containing product of the reaction.

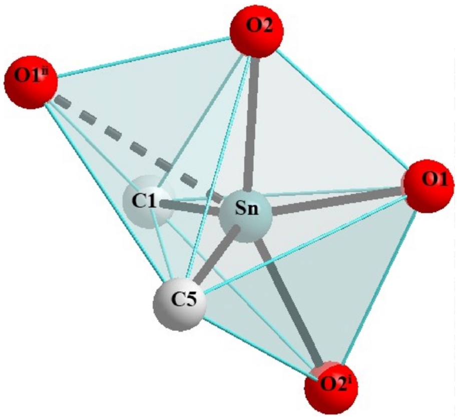

Fig. 2. The coordination environment around the tin centers of **1** displaying an unusual distorted face-capped trigonal-bipyramidal geometry (DIAMOND presentation; color online).

1,3,2-Dioxastannolanes have been known for a long time, but in the past the elucidation of their structure has been the subject of several conflicting reports [8]. To this date, six crystallographic reports of five-membered 1,3,2-dioxastannolanes rings have been registered in the Cambridge Structural Database [9].

The isolation of crystalline 2,2-di-*n*-butyl-4-methyl-1,3,2-dioxastannolane (**1**) has added a new example of this class of compounds and moreover has given a relevant clue to the key intermediate in the mechanism of propylene carbonate formation from 1,2-propanediol and CO_2 promoted by organotin(IV) species. Further work is in progress to study the reactivity of **1** toward carbon dioxide and to clarify its catalytic role.

Experimental Section

The organic solvents were refluxed over appropriate desiccants, distilled, and saturated with argon prior to use. Chemicals were purchased from Aldrich and Acros Organics. Di-*n*-butyltin oxide was used without further purification. High-pressure reactions were conducted in a 120 mL stainless-steel batch reactor. The ^{1}H, ^{119}Sn{^{1}H}, and ^{13}C{^{1}H} NMR experiments were run on Bruker Avance 300 and II 600 spectrometers, and calibrated with Me_4Si or Me_4Sn as internal standard. Chemical shift δ values are given in ppm. IR spectra were recorded on a Bruker Vector 22 equipped with a Specac Golden Gate^{TM} ATR device. The MALDI-TOF mass spectrum was obtained with a Bruker Daltonics Ultraflex II spectrometer in the reflectron positive mode by using dithranol as a matrix. The ES mass spectrum was collected on a Bruker microOTOF-Q instrument using a methanol mobile phase. Elemental analyses (C, H) were performed at the Institut de Chimie Moléculaire de l'Université de Bourgogne, Dijon.

2,2-Di-n-butyl-4-methyl-1,3,2-dioxastannolane

Caution: Since high pressures are involved, appropriate safety precautions must be taken.

A 120 mL stainless-steel batch reactor was charged with 1.24 g of di-*n*-butyltin oxide (5 mmol), 7.3 mL of 1,2-propanediol (100 mmol), 2.0 mL of DMF and 38.5 g of CO_2 (875 mmol). The reaction was carried out for 20 h at 413 K. At the end of the reaction, the reactor was cooled down to 273 K, and then depressurized. Finally, the content was extracted with 30 mL of methanol, and after decantation the organic phase was separated by filtration from the remaining insoluble tin-containing residue. Several weeks later, suitable single crystals grew from the filtrate at r. t. and were characterized as **1**. – $C_{11}H_{24}O_2Sn$ (306.99): calcd. C 43.03, H 7.88; found C 42.86, H 7.77. – IR: ν = 2957s, 2919s, 2871m, 2855m, 2829m (OC-H), 1459m, 1364m, 1340m, 1141s, 1051vs (SnO-C), 935s, 859s, 770w, 680m, 612vs (Sn-OC), 574s cm^{-1}. – ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K): δ = 0.88 (m, 6H, *n*-butyl CH_3), 1.08 (d, 3H, J = 5.8 Hz, CH*Me*), 1.20 – 1.70 (m, 12H, *n*-butyl, CH_2), 2.97 (m, 1H, C*H*Me), 3.68 (m, 2H, CH_2CHMe). – ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 298 K): δ = 13.62 (*n*-butyl, CH_3), 13.65 (*n*-butyl, CH_3), 20.85 (CH*Me*), 22.69 (br, *n*-butyl, CH_2), 26.95 (*n*-butyl, CH_2), 27.04 (*n*-butyl, CH_2), 27.44 (*n*-butyl, CH_2), 27.55 (*n*-butyl, CH_2), 68.39 (*C*HMe), 69.31(*C*H_2CHMe). – ^{119}Sn{^{1}H} NMR (223.79 MHz, $CDCl_3$, 273 K): δ = −122 (br, major), −139 (minor), −148 (minor), and −270 (br, minor). – MS (MALDI-TOF): *m*/*z* = 306.722 (calcd. 307.020 for $C_{11}H_{24}O_2Sn$, $[M]^+$), 344.600 (calcd. 344.506 for $C_3H_7O_4Sn_2$), 361.347 (calcd. 360.505 for $C_3H_7O_5Sn_2$), 458.784 (calcd. 458.784 for $C_{11}H_{25}O_4Sn_2$), 514.904 (calcd. 514.844 for $C_{15}H_{33}O_4Sn_2$), 801.017 (calcd. 801.227 for $C_{14}H_{30}O_8Sn_4$), 915.138 (calcd. 915.458 for $C_{22}H_{48}O_8Sn_4$). – MS (ES, positive mode): *m*/*z* = 305.05465 (calcd. 305.00118 for $C_{11}H_{22}O_2Sn$).

X-Ray structure determination

$C_{11}H_{24}O_2Sn$, M = 306.99, colorless crystal: $0.37 \times 0.10 \times 0.05$ mm^3, a = 14.198(5), b = 7.527(5), c = 25.235(5) Å, V = 2697(2) Å^3, D_{calcd} = 1.512 g cm^{-3}, μ = 1.874 mm^{-1}, experimental absorption correction (T_{min} = 0.651, T_{max}= 0.871), Z = 8, orthorhombic, space group *Pbca* (no. 61), λ = 0.71073 Å, T = 115 K, mixture of ϕ rotations and φ scans, 14063 reflections collected on a Nonius Kappa CCD diffractometer (index ranges: h = −12/+18; k = ±9; l = ±32), $((\sin\theta)/\lambda)_{max}$ = 0.65 Å^{-1}, 3083 independent (R_{int} = 0.0575) and 2350 observed reflections [$I \geq 2\sigma(I)$], 137 refined parameters, R indices for observed reflections: R_1 = 0.0314, wR_2 = 0.0655, R indices for all data: R_1 = 0.0486, wR_2 = 0.0709, goodness-of-fit = 1.027, $\Delta\rho_{fin}$ (max/min): 0.70/−0.85 e Å^{-3}. Comments: The structure was solved using Direct Methods (SIR 92) [10] and refined with full-matrix least-squares methods based on F^2 (SHELXL-97) [11] with the aid of the WINGX program suite [12]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined as riding atoms. The carbon atoms C9, C10 and C11 were found disordered over two positions with occupation factors converging to 0.43 : 0.57.

CCDC 727018 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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