Synthesis of a cyclic dinuclear organotin carboxylate via simultaneous debenzylation and decarbonylation reactions: X-ray crystal structure of \[\{(\text{PhCH}_2)_2\text{O}_2\text{C}_6\text{H}_4\{\text{N(H)}\text{N}=(\text{C}_6\text{H}_3-4(=\text{O})-5-\text{O})\}-\text{o}\}\text{Sn}]_2\]

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Abstract

The complex, \[\{(\text{PhCH}_2)_2\text{O}_2\text{C}_6\text{H}_4\{\text{N(H)}\text{N}=(\text{C}_6\text{H}_3-4(=\text{O})-5-\text{O})\}-\text{o}\}\text{Sn}]_2\] (I), is obtained as the exclusive reaction product from the reaction of sodium 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate and (PhCH2)3SnCl. The reaction possibly proceeds via Dakin type rearrangements where arylazosalicylaldehyde is oxidized to arylazocatechol, followed by facile Sn–C bond cleavage. Complete assignments were achieved by \(^1\text{H}, \ ^{13}\text{C}, \ ^{2}\text{D} \ ^{1}\text{H}–^{119}\text{Sn} \text{HMQC (}^{119}\text{Sn chemical shift), \ ^{1}\text{D} \ ^{1}\text{H}–^{15}\text{N} \text{HMQC (}^{15}\text{N}, \ ^{1}\text{H} \text{coupling constant) NMR and ESI-MS. The crystal structure of compound I as determined by X-ray diffraction analyses shows a cyclic centrosymmetric dinuclear moiety linked into extended chains by pairs of long Sn–O contacts of approximately 3.2 Å. Two polymorphs were identified and their structures differ primarily in the packing arrangement afforded by the benzyl groups. In one polymorph, when viewed along the Sn–Sn vector, the benzyl groups at each Sn-atom are oriented to form an S-shape, while they form a U-shape in the second polymorph. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Investigation of the organotin compounds \(\text{R}_n\text{SnX}_4(n=1–4)\) (\(n=1–4\)) is of interest because of their biological activity, reactivity, and industrial applications [1–4]. Several organostannoxanes have been shown to be extremely versatile catalysts for polyurethane, RTV silicone polymerisation and for trans esterification reactions [5–9]. Some dibenzyltin dicarboxylates have also been used as catalysts for the synthesis of urethanes [10]. Owing to these applications, the structure and mechanisms of action of these organotin compounds remain a matter of great interest [6,11–17]. In view of this, in recent years there have been constant efforts to develop new synthetic strategies and consequently dearylation and dealkylation [18–24] reactions proved to be useful for synthesizing new organotin clusters. The reaction of (PhCH2)3SnCl with sulfuric acid leads to a mixture of ditin and diorganotin derivatives.
2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate proceeded effectively via debenzylation and subsequent oxidative decarbonylation reactions, and affords the cyclic dinuclear dibenzyltin complex I, in contrast to the carboxylate-bridged polymeric structures obtained for the Me$_2$Sn (2) [25] and Bu$_3$Sn (3) [26] analogues and the monomeric complex with the Ph$_3$Sn (4) [27] analogue. In this communication, the synthesis, characterization, and the tin coordination of the novel cyclic and pseudo-polymeric moiety that crystallized as the two polymorphs 1a and 1b are reported.

2. Experimental

2.1. Materials

The solvents used in the reactions were of AR grade and dried using standard procedures. (PhCH$_2$)$_3$SnCl [28] and LHNa [25] were prepared by following the reported methods.

2.2. Physical measurements

Elemental analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm$^{-1}$ were obtained on a BOMEM DA-8 FT-IR spectrophotometer with samples investigated as KBr discs. The $^1$H-, $^{13}$C NMR and $^{119}$Sn chemical shifts were referenced to Me$_4$Si set at 0.00 ppm, CDCl$_3$ set at 77.0 ppm and tetramethyltin set at 0.00 ppm, respectively. 2D gs (gradient selected)-H,H-COSY, gs 1H–13C HMBC (optimized for 3J(C,H) = 100 Hz) and gs 1H–15N HMBC (optimized for 3J(N,H) = 100 Hz) were used for the measurement of the $^{119}$Sn chemical shift and 1J($^{119}$Sn,$^1$H) coupling constants, respectively. Positive- and negative-ion electrospray ionization mass spectra (ESI-MS) were measured on an Esquire 3000 (Bruker Daltonics) in the range m/z 50–1500. Compound 1 was dissolved in acetonitrile and analysed by direct infusion at a flow rate of 1 µl/min. The selected precursor ions were further analysed by MS/MS analyses (isolation width m/z = 8 for ions containing one tin atom and m/z = 12 for ions containing more tin atoms, collision amplitude: 0.8–1.0 V, ion source temperature: 300 °C, tuning parameter compound stability 20%, flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively).

2.3. Synthesis of [(PhCH$_2$)$_2$O$_2$CC$_6$H$_4$ $\{N(\text{H})-N\rightarrow\text{C}_6H_3(\equiv\text{O})-\equiv\text{O}\} \cdot ^1\text{Sn}$_2$] (I)

A warm solution of (PhCH$_2$)$_3$SnCl (0.71 g, 1.66 mmol) in anhydrous methanol (ca. 30 ml) was added slowly to a solution of LHNa (0.50 g, 1.67 mmol) in hot anhydrous methanol (ca. 70 ml) under stirring conditions. The dark red solution was refluxed for 8 h. It was then evaporated to dryness and the residue was dried in vacuo. The dried mass was washed with hot petroleum ether (60–80 °C, 4 x 5 ml), dried in vacuo, extracted by boiling in anhydrous benzene (ca. 60 ml) and filtered while hot. The filtrate was then concentrated to one-sixth of its volume, precipitated with hot petroleum ether (60–80 °C), filtered and the crude product was dried in vacuo. The dark red solid was dissolved by boiling in benzene, filtered to remove any undissolved particles and the filtrate was left to evaporate slowly at room temperature for 3 days to afford dark red crystals (prism and needle types) of the title compound I, 0.53 g yield (43%); m.p.: 205–208 °C. Anal. Found: C, 58.25; H, 4.01; N, 5.00. Calc. for C$_5$H$_4$NaO$_2$Sn$_2$: C, 58.21; H, 3.90; N, 5.02. IR (KBr, cm$^{-1}$): 1589 ν(OCO)$_{ asym}$. $^1$H NMR (CDCl$_3$/125.76 MHz) $^1$H: 12.26 [brs, 1H, (NH)]. 8.01 [m, 1H, (A) H3]. 7.85 [m, 1H, (A) H6]. 7.55 [m, 1H, (A) H5]. 7.36 [dd, $\Delta$(H,H) = 9.0 Hz and 2.4 Hz, 1H, (B) H6]. 7.19 [m, 1H, (A) H4]. 7.02 [m, 1H, (C) H2]. 6.91 [m, 1H, (C) H3]. 6.80 [tt, 1H, (C) H4]. 6.59 [d, $\Delta$(H,H) = 2.4 Hz, 1H, (B) H2]. 6.51 [d, $\Delta$(H,H) = 9.0 Hz, 1H, (B) H5]. 3.09 and 3.06 [AB system (H,H) = 9.0 Hz, $\Delta$(H,H) = 2.4 Hz, 2H, (B) H2]. Suggested interpretation of observed ions: a: 1589; 1379 (42%); 1155 (100%); 955 (97%); 775; 671; 597 (54%); b: 1589; 1379 (100%); 955 (97%); 775; 671; 597; 531 (48%). MS/MS of 1139: m/z 973; 937; 415. MS/MS of 1139: m/z 1047; 955; 775; 671; 597; 489; 399. MS/MS of 973: m/z 597 (100%); 531; 415. Suggested interpretation of observed ions: a: 1155 [M + K]$^+$. 1139 [M + Na]$^+$. 1047 [M + Na – CH$_3$C$_6$H$_3$]$^+$. 973 [M + K-2*CH$_3$C$_6$H$_3$]$^+$. 955 [M + Na – 2*CH$_3$C$_6$H$_3$]$^+$. 937 [M + Na – 2*CH$_3$C$_6$H$_3$]$^+$. 1 Refer to the following figure for the numbering scheme for $^1$H and $^{13}$C NMR.


2.4. X-ray crystallography

Crystals of polymorphs 1a and 1b suitable for an X-ray crystal structure determination were initially obtained from the same benzene solution, although the reported data for 1a are for a crystal obtained from chloroform. All measurements were made at low temperature on a Nonius KappaCCD diffractometer [29] with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [30]. The intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections based on the multi-scan method [31] were applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1. Each structure was solved by employing heavy-atom Patterson methods [32] followed by the Fourier expansion routine of DIRDIF94 [33]. The non-hydrogen atoms were refined anisotropically. The protonated amine H atom in each structure was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameters. All remaining H atoms were placed in geometrically calculated positions and refined using a riding model where each H atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2Ueq of its parent atom. The refinement of each structure was carried out on F² using full-matrix least-squares procedures, which minimized the function Σw(Fo – Fc)². A correction for secondary extinction was applied only for 1a. Neutral-atom scattering factors for non-hydrogen atoms were taken from Maslen et al. [34] and the scattering factors for H-atoms were taken from Stewart et al. [35]. The values of the mass attenuation coefficients are those of Creagh and Hubbel [36]. All calculations were performed using the SHELX97 [37] program.

3. Results and discussion

3.1. Synthesis

Triorganotin(IV) carboxylates are normally prepared by simple metathesis reactions, and in a similar way, the complexes R₃Sn[O₂CC₆H₄][N=N(C₆H₃-4-OH-5-CHO)]-o were obtained in one step reactions between (i) sodium 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate (LHNₐ) and R₃SnCl in methanol (R = Me (2)) [25], (ii) 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid [27] (LHH’, where H and H’ refer to phenolic and carboxylic protons, respectively) and (R₂Sn)₂O (R = ³Bu (3)) [26] and R₃SnOH in toluene (R = Ph (4·OH₃)) [27] under different experimental conditions.
conditions (Scheme 1). However, when the reaction was performed using LHNa and \((\text{PhCH}_2)_3\text{SnCl}\) in methanol under reflux conditions, a noteworthy change in the composition of the product to \(\text{[(PhCH}_2)_2\{O_2\text{-CC}_6\text{H}_4\{N(H)\text{-N=}(C_6\text{H}_5-4(=O)-5-O)\text{-O})\text{-Sn}\]_2}\) (1) is observed. In this reaction, a remarkably facile debenzylation occurs, which is presumably mediated by adventitious moisture present in the solvent, which, in turn, interacts further with the ligand used or vice versa. The same product was obtained after several attempts under strictly controlled conditions. Such dearylations have previously been reported [38] but have not been found to play a role in the interconversion of tin carboxylate complexes. The oxidative decarbonylation reaction of the ligand probably proceeds via Dakin type rearrangements where arylazosalicylaldehyde is oxidized to arylazocatechol [39] followed by facile Sn–C bond cleavage. In this reaction, one of the benzyl groups on the tin atom is eliminated as toluene (1, Scheme 1). Further, it should be noted here that dihydric phenol, such as catechol \([1,2-\text{C}_6\text{H}_4(\text{OH})_2]\), is preferentially oxidized by diazonium ions and can be substituted only under narrowly defined conditions [40]. Consequently, there are no reports available on arylazocatechol systems. The formation of 1 in the present investigation furnishes the first example of a metal complex containing arylazocatechol, which has been achieved by simple simultaneous debenzylation and decarbonylation reactions.

3.2. Spectroscopy

The presence of the dinuclear Sn molecule 1 is confirmed by complementary data obtained in positive- and negative-ion ESI-MS. The molecular adducts with sodium or potassium ions are the base peaks or abundant ions in the positive-ion mode (100% and 42%, respectively), while the deprotonated molecule \([\text{M} - \text{H}]^-\) and the adduct ion \([\text{M} - 2\text{H} + \text{Na}]^-\) are observed in the negative-ion mode, which enables an unambiguous molecular weight determination (MW = 1116 for the monoisotopic mass). Tandem mass spectra (MS/MS) of ions observed in the first-order ESI
mass spectra provide other abundant fragment ions. The suggested fragment ions are in a good correlation with the cyclic moiety elucidated from the X-ray crystal structure data (vide infra). The typical neutral losses are the subsequent losses of benzyl or toluene. Another important neutral loss is CO$_2$ as a typical fragmentation path in the negative-ion ESI mass spectra of carboxylic acids.

The $^1$H-, $^{13}$C- and $^{119}$Sn chemical shifts for 1 are given in Section 2. The proton–proton connectivity was determined from a correlated spectroscopy (H,H-COSY) experiment. The $^{13}$C chemical shift assignments were straightforward and have been achieved from heteronuclear single quantum correlation (HSQC) and heteronuclear multiple-bond connectivity (HMBC) spectra. The solubility of compound 1 in deuterochloroform was very low and, thus, 2D $^1$H-$^{119}$Sn heteronuclear multiple quantum correlation (HMQC) had to be used for the measurement of the $^{119}$Sn chemical shift. The $^{119}$Sn resonance was found at $-256.1$ ppm, which corresponds to the value found for dibenzyltin(IV) dibenzoate ($-252.5$ ppm) [41] in deuterochloroform. In dibenzyltin(IV) dibenzoate, two benzyl groups and all four oxygen atoms (bidenate carboxylates) are bound to the tin atom analogously to the situation in compound 1.

The 1D $^1$H-$^{15}$N HMQC (optimized for $^{1}J(^{15}$N,$^1$H) = 100 Hz) technique was used to determine the $^{1}J(^{15}$N,$^1$H) coupling constant, which is $96.0$ Hz. Such a value is typical of a hydrazone form (keto-) [42,43] in deuterochloroform. This indicates that complex 1 retains its dinuclear cyclic solid-state structure in solution, although there may be a breakdown of the polymeric linkages (see Section 3.3). Further, the existence of the keto-form of the compound 1 is also reflected clearly in the $^{13}$C chemical shift of C4 (182.5 ppm) of the ring B [42,43].

### 3.3. X-ray crystallography

Compound 1 crystallizes as two polymorphs, 1a and 1b. The structure of the principal centrosymmetric cyclic dinuclear moiety in each polymorph is depicted in Figs. 1 and 2, respectively, while selected geometric parameters are given in Table 2. Each Sn-atom is coordinated by two benzyl groups and the opposite ends of two azo ligands. Each azo ligand coordinates to two Sn-atoms via bidentate coordination of the carboxylate group to one Sn-atom and bidentate coordination of the adjacent O-atoms of the o-substituted ring to the other Sn-atom. One of the azo N-atoms is protonated to compensate for the deprotonation of the original hydroxy group in the ligand and the bond lengths within the o-substituted ring show a quinoline pattern (see Scheme 1). The coordination of the Sn-atom leaves one face of the coordination sphere quite open. This space is filled by a long Sn···O(1)$^1$ contact of 3.248(2) Å in 1a and 3.199(2) Å in 1b from an adjacent cyclic moiety to give a distorted pentagonal bipyramidal coordination geometry about the Sn-atom. These Sn···O(1)$^1$ distances are well inside the sum of the van der Waals radii of these atoms, so represent significant secondary interactions. The long Sn···O contacts link dinuclear moieties across a centre of inversion to form...
a cooperative four-membered Sn–O⋯Sn–O loop. As the same pair of interactions occurs at each end of the dinuclear moiety, these moieties are linked into extended chains which run along the [101] (in 1a) and [100] (in 1b) directions (Figs. 3 and 4). The protonated amine group forms an intramolecular hydrogen bond with the adjacent carboxylate O-atom in the same ligand.

The two polymorphs of 1 were found in the same batch of crystals, so had apparently crystallized simulta-

Fig. 3. The molecular packing of 1a showing the links between the cyclic dinuclear moieties to form a polymeric chain.
neously. The structures of the polymorphs differ primarily in the arrangement of the benzyl groups, which apparently allows different, but energetically similar, packing motifs to be adopted. In 1a, when viewed along the Sn–Sn vector, the benzyl groups at each Sn-atom are oriented such that they appear to form an S-shape through the Sn-atom and those from the front Sn-atom directly eclipse those from the rear Sn-atom. In 1b, the benzyl groups at each Sn-atom are oriented such that they appear to form a U-shape through the Sn-atom and those from the front Sn-atom point in the opposite direction to those from the rear Sn-atom in an up–down relationship.

4. Supplementary material

CCDC-253636 (1a) and CCDC-253637 (1b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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