Journal of Organometallic Chemistry, 371 (1989) C1–C3
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20010PC

Preliminary communication

Structural chemistry of organotin carboxylates

I. The crystal structure of di-n-butylbis(thiophenoxyacetato)-tin(IV): $^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_2\mathrm{SC}_6\mathrm{H}_5)_2$

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(Received January 3rd, 1989)

Abstract

A crystal structure study of $^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_2\mathrm{SC}_6\mathrm{H}_5)_2$ reveals the compound to be monomeric with the tin atom situated on a crystallographic 2-fold axis in a skew-trapezoidal bipyramidal geometry. The basal plane is defined by two asymmetrically chelating carboxylate groups; Sn–O 2.134(4) and 2.559(5) Å and the ^{n}Bu–Sn–^{n}Bu angle is 140.7(2)°. The sulphur atoms do not participate in any significant interactions to the tin atom. Crystals are monoclinic with space group $C2$ and unit cell dimensions a 18.668(6), b 15.761(6), c 5.106(5) Å, β 117.55(5)°; $Z = 2$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.034$ and $R_w = 0.033$ for 1294 reflections with $I \geq 2.5\sigma(I)$.

The industrial importance of organotin compounds is well documented but questions of their mode of action still remain [1,2]. Relevant to this paper are diorganotin dicarboxylates for which the first crystal structure was reported recently i.e. $\mathrm{Me}_2\mathrm{Sn}(\mathrm{OAc})_2$ [3]. The incorporation of sulphur into the R group of carboxylic acids generates a series of compounds with useful properties such as thermal stabilization of PVC [2,4]. The results of a crystal structure determination of dibutyltin 3-thiopropinate were reported by Lockhart [4] which showed it to form cyclic hexamers in the solid state via bridging carboxylate groups and coordinating S atoms. We report here the preparation and characterization by X-ray diffraction techniques of the dibutyltin dithiocarboxylate $^n\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_2\mathrm{SC}_6\mathrm{H}_5)_2$, which was studied in order to reveal the influence of the presence of the sulphur atom.

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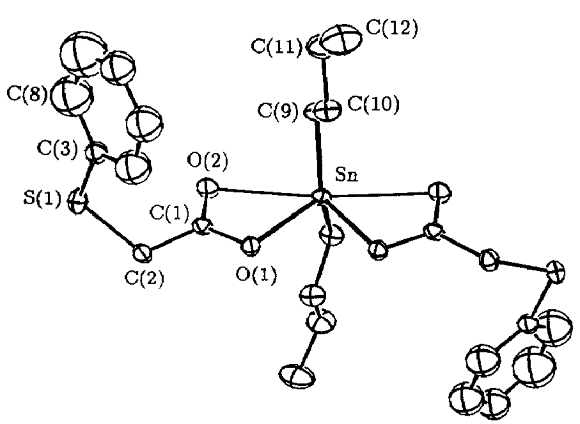

Fig. 1. Molecular structure and crystallographic numbering scheme for $^{n}Bu_2Sn(O_2CCH_2SC_6H_5)_2$. Selected interatomic parameters: Sn–O(1) 2.134(4), Sn–O(2) 2.559(5), Sn–C(9) 2.099(6) Å; O(1)–Sn–O(2) 55.0(2), O(1)–Sn–O(1)′ 79.5(2), O(2)–Sn–O(2)′ 170.5(2), C(9)–Sn–C(9)′ 140.7(1)°. (Primed atoms related by crystallographic 2-fold axis).

The compound $^{n}Bu_2Sn(O_2CCH_2SC_6H_5)_2$ was prepared by reaction of dibutyltin oxide with thiophenoxyacetic acid (1/2) in a mixture of anhydrous alcohol and benzene [5*]. Crystals for an X-ray structure determination were grown by slow evaporation of a petroleum ether (60–80 °C) solution of the compound. Intensity data were measured on an Enraf–Nonius CAD4 diffractometer fitted with graphite monochromatized Mo-K_α radiation. A total of 2355 reflections were measured (θ_{max} 25°) of which 1294 absorption corrected data [6] were unique and satisfied the $I \geq 2.5\sigma(I)$ criterion. The unit cell contains two unique molecules of the $^{n}Bu_2Sn(O_2CCH_2SC_6H_5)_2$, each located about a crystallographic 2-fold axis of symmetry. Full-matrix least-squares refinement based of F [6] converged to final $R = 0.034$ and $R_w = 0.033$ with anisotropic thermal parameters for non-phenyl (phenyl rings as hexagonal rigid groups) and non-hydrogen atoms (hydrogen atoms in calculated positions), and a weighting scheme of the form $w = [\sigma^2 F + 0.0019F^2]^{-1}$. The absolute configuration of the structure was not determined unambiguously as there was no significant difference between the refinements of the two isomers; the configuration yielding the lowest residual is presented here. The numbering scheme employed is shown in Fig. 1 with selected interatomic parameters given in the figure caption. Other details are available from the authors (E.R.T.T.).

The crystal structure (Fig. 1) is seen to be comprised of discrete molecules of $^{n}Bu_2Sn(O_2CCH_2SC_6H_5)_2$ with the tin atom hexa-coordinated. The ^{n}Bu–Sn–^{n}Bu angle of 140.7(2)° 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 [7]. The carboxylate groups coordinate in an asymmetric mode forming both short Sn–O bonds (2 × 2.134(4) Å) and long Sn–O bonds (2 × 2.559(5) Å). The anisobidentate mode of coordination of the two carboxylate structures is reflected in the disparity of the associated C–O bonds; the C–O bond distances for the weakly coordinating oxygen atoms of 1.24(1) Å is

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* Reference number with asterisk indicates a note in the list of references.

shorter than the C–O bond distances associated with the strongly bound oxygen atoms of 1.298(7) Å. Nevertheless, the longer Sn–O bond distances are significantly below the sum of the Van der Waals radii for these atoms (3.70 Å [8]), and therefore these oxygen atoms must be considered as bonding. The geometry found about the tin atom in $^{n}Bu_2Sn(O_2CCH_2SC_6H_5)_2$ is best described as a skew-trapezoidal bipyramid geometry [7] and closely resembles that found for the $Me_2Sn(OAc)_2$ structure [3].

The most interesting aspect of the structure concerns the non-coordination of the sulphur atom to tin. As can be seen from Fig. 1 the sulphur atom is directed away from the tin atom. Furthermore, the sulphur atoms do not make close intermolecular contacts to tin in the crystal lattice. Coordination numbers greater than six are known for diorganotin species [e.g. 4,9,10], and it would seem that the presence of the bulky phenyl group bound to the sulphur atom precludes close contacts with neighbouring tin centres.

The structure determination reported here, and that of $Me_2Sn(OAc)_2$ [3], combined with NMR evidence [3], suggests that the $R_2Sn(O_2CR')$ compounds adopt monomeric structures rather than polymeric structures arising from bridging carboxylate groups.

Acknowledgements. The Australian Research Grants Scheme is thanked for support. A referee is thanked for helpful comments concerning the crystallography.

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