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**STRUCTURE OF TRI-*n*-BUTYLTIN  
HYDROXYACETATE**

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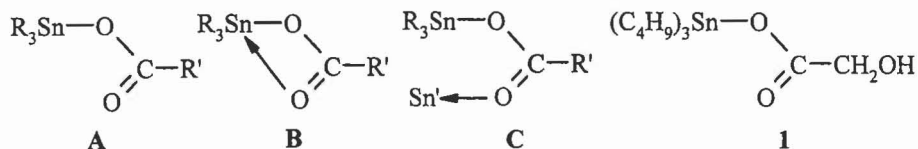
*The structure of tri-*n*-butyltin derivative of hydroxyacetic acid was prepared and structurally characterized by X-ray crystallographic techniques in the solid state. This compound reveals linear polymeric structural character with five-coordinated tin atoms. Coordination geometry of tin atoms is trigonal bipyramidal with all three carbon atoms in equatorial positions, monodentately bonded carboxylic oxygen and the hydroxo oxygen atom from the adjacent molecule in the axial positions forming thus the linear chain. Two independent molecules/chains are nearly perpendicularly oriented and interconnected by H-bonding by OH group from one chain to uncoordinated oxygen of carboxylic group of second chain in the crystal lattice.*

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## Introduction

The triorganotin(IV) esters of carboxylic acids have been known for a long time as catalysts and bio active compounds [1,2]. Organotin(IV) compounds have been studied and screened *in vitro* and *in vivo* for antitumor activity [3]. Another topic was to explore the biological activity of these compounds against potentially pathogenic fungi [4,5]. The structures of these compounds are well established and studied by X-ray [6], Mössbauer and CP MAS NMR techniques in the solid state, and mainly multinuclear NMR techniques in solution [1]. The tin atom in these compounds can be four-coordinated (Scheme 1, structure A) or five-coordinated with major occurrence in the solid state. In this case, the tin atom is surrounded by three carbon atoms originating from organo groups and two oxygen atoms from one asymmetrically bidentate carboxylate group (intramolecularly chelated; Scheme 1, structure B) or two different carboxylate groups (intermolecularly bridging; Scheme 1, structure C). The compounds with the intermolecularly bridging bond form infinite polymeric networks in the solid state [6], which can be often fragmented into oligomeric or monomeric particles in solution of various solvents [7]. Another structural motif in polymeric and/or chelate arrangement can be revealed when a further donor atom is implemented as a part of carboxylate ligand into the tin coordination sphere [6].



Scheme 1

In our previous work, we were interested in structure of organotin carboxylates containing mainly one organotin fragment in solution of different solvents [7]. Now we would like to pay much more attention to systems where two or more non-equivalent organotin groups exist (caused by chemical or geometrical (sterical) non-equivalency or dynamic exchange) and to study and compare such phenomena in both the solid state and solution.

In this concept, we reported [8] triorganotin derivatives of different bifunctional carboxylic acids previously. Some of the compounds can occur in two tautomeric forms, and there also is a theoretical possibility of increase in the tin coordination number *via* the coordination of intrinsic donor atoms. There are different possible coordination modes in such complexes: going from monomeric monodentate carboxylate, through bidentate ones (see Scheme 1) forming polymers, where the formation of small (five- to seven-), bigger ten-membered

chelate rings, or even bigger cycles throughout an intermolecular connection can be formed. Previously we observed such a variety of coordination modes in the case of diesters of ketopimelic acid [9].

For this paper we have selected the triorganotin esters of hydroxyacetic (glycolic) acid in order to observe two equivalent or non-equivalent tin fragments depending on sterical hindrance of organyl substituents and the possibility of formation of a supramolecular architecture. The preparation, basic spectral properties (IR,  $^1\text{H NMR}$ ) and thermal reactivity or decomposition of triorganotin (and also germanium and silicon analogues) and diorganotin derivatives of a bifunctionally bonded glycolic acid were studied in 1970's [10].

## Materials and Methods

*General remarks:* All syntheses were made in the air. Hydroxyacetic acid, hexane and *n*-hexabutyl distannoxane were obtained from commercial sources (Sigma-Aldrich) and used without further purification. The tri-*n*-butyltin derivative of hydroxyacetic acid (*I*) was prepared as published elsewhere [10] from hydroxyacetic acid and hexa-*n*-butyldistannoxane in toluene using Dean–Stark apparatus.

*X-Ray crystallography:* The single crystals of *I* were grown from saturated hexane solution by a slow evaporation in the air at room temperature.

The X-Ray data were collected on a Nonius Kappa CCD diffractometer fitted with  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150(1) K. The absorption correction was performed using a Gaussian procedure [11], the structure was solved by direct methods (SIR92[12]) and full-matrix least-squares refinements on  $F^2$  were carried out using the program SHELXL97[13]. There is a dynamic disorder of the last two butyl carbon atoms in *I* caused by the thermal motion even at 150 K, these atoms were split into two positions with highest electron density statistically.

Crystallographic data for *I*;  $\text{C}_{14}\text{H}_{30}\text{O}_3\text{Sn}$ ,  $M = 365.08$ , trigonal,  $P 3_1 2_1$ ,  $a = 14.9250(2)$ ,  $b = 14.9250(2)$ ,  $c = 27.6090(3)$ ,  $Z = 12$ ,  $V = 5326.11(12) \text{ \AA}^3$ ,  $D_c = 1.313 \text{ g.cm}^{-3}$ ,  $\mu = 1.433 \text{ mm}^{-1}$ , 16269 reflections measured ( $q_{\text{max}} = 27.5^\circ$ ), 8136 independent ( $R_{\text{int}} = 0.0155$ ), 7756 with  $I > 2\sigma(I)$ , 235 parameters,  $S = 1.219$ ,  $R_1(\text{obs. data}) = 0.0392$ ,  $wR_2(\text{all data}) = 0.1312$ ; max, min residual electron density = 0.995,  $-0.756 \text{ e\AA}^{-3}$ . CCDC Deposition number: 702605.

## Results and Discussion

A set of triorganotin(IV) derivatives of hydroxyacetic acid was prepared according to the previously published results [10] in order to investigate and compare struc-

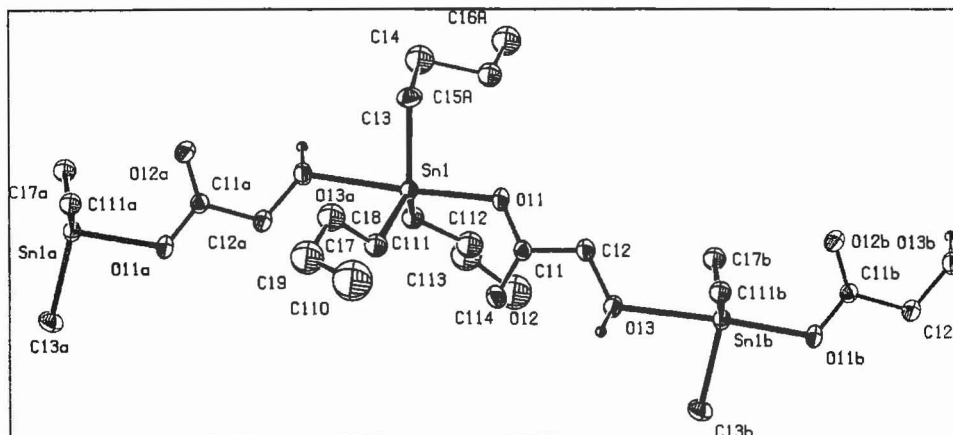


Fig. 1 Molecular structure of compound *1* with atom numbering scheme: (ORTEP 40% probability level), hydrogen atoms (except of the hydroxo ones) and symmetry related C2-C4 atoms of butyl groups are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1 C13 2.139(5), Sn1 C111 2.143(5), Sn1 C17 2.149(5), Sn1 O11 2.155(3), Sn1 O13a 2.495(3), C11 O12 1.233(5), C11 O11 1.268(5), C12 O13 1.424(6), O13 H13 0.9443; for the second chain: Sn2 C27 2.146(7), Sn2 O21 2.151(3), Sn2 C211 2.150(5), Sn2 C23 2.169(7), C21 O22 1.219(5), C21 O21 1.294(5), C22 O23 1.400(6), O23 Sn2 2.534(3), O23 H23 0.9770. C13 Sn1 C111 116.2(2), C13 Sn1 C17 117.4(2), C111 Sn1 C17 123.00(19), C13 Sn1 O11 92.47(19), C111 Sn1 O11 99.59(17), C17 Sn1 O11 96.03(16), C13 Sn1 O13 84.21(18), C111 Sn1 O13 81.95(16), C17 Sn1 O13 85.52(16), O11 Sn1 O13 176.68(12), O12 C11 O11 124.6(4); for the second chain: C27 Sn2 O21 91.6(2), C27 Sn2 C211 118.2(2), O21 Sn2 C211 98.46(17), C27 Sn2 C23 118.5(3), O21 Sn2 C23 96.42(18), C211 Sn2 C23 120.5(3), C27 Sn2 O23 83.4(2), O21 Sn2 O23 175.04(11), C211 Sn2 O23 84.01(17), C23 Sn2 O23 85.95(17)

ture in the solid state and in solution. Unfortunately, single crystals of sufficient quality were obtained for the triorgatin(IV) derivative (*1*) only.

Compound *1* crystallizes in highly symmetrical system (trigonal), where two geometrically independent molecules are present in the crystal unit cell. The difference between these two fragments is negligible from the point of view of mutual comparison of interatomic distances and angles, but the orientation of both moieties forming with further contacts infinite nearly linear chains (Figs 1 and 2) is perpendicular-like (89.2°). The coordination geometry of both tin atoms is trigonal bipyramidal ( $\tau$  [14] values for Sn1 and Sn2 are 0.89 and 0.91, respectively) with three carbon atoms in ideally equatorial positions (the sum of equatorial angles is 356.6 and 357.2°), monodentate bonded carboxylic oxygen and the coordinated hydroxo oxygen atom (Sn1 O13a 2.495(3) and O23 Sn2 2.534(3) Å) from the adjacent molecule in the axial positions forming thus the mentioned linear chain (axial O-Sn-O angles: 176.68(12) and 175.04(11)°). The remaining uncoordinated carboxylic oxygen atoms are out of the primary coordination spheres of tin atoms (Sn-O > 3.1 Å). On the other hand, they are in-

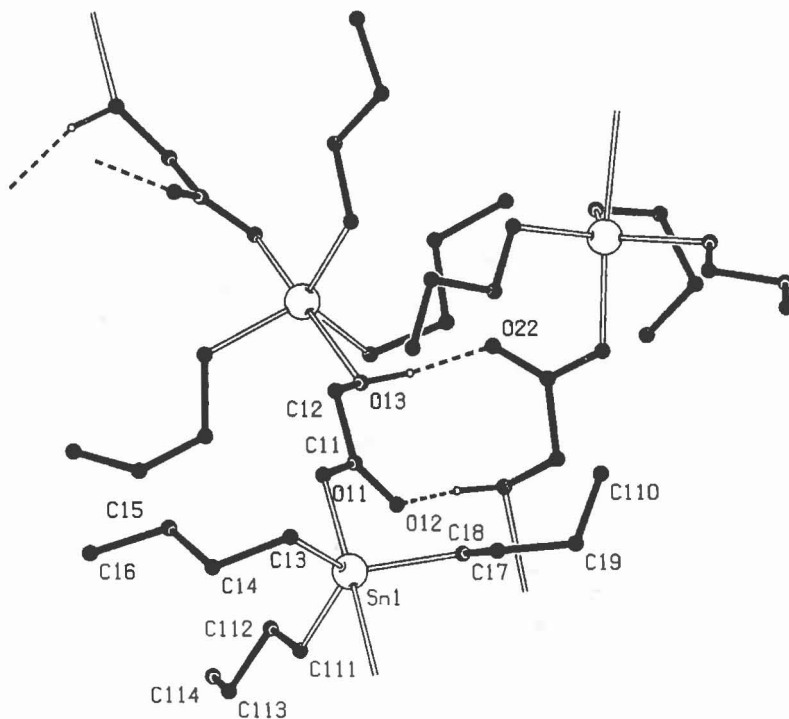


Fig. 2 Molecular structure of compound *1*, view of H-bonding. Hydrogen atoms (except of the hydroxo ones) are omitted for clarity. H-bonds: O13-H13...O22 2.635(1) Å, 158°; O23-H23...O12 2.638(2) Å, 156°

terconnected with OH groups from adjacent chain to form ten-membered rings *via* H-bridges (Fig. 2).

Globally, there are cavities (Fig. 3) present in the crystal lattice of *1* (70.4 Å<sup>3</sup> per unit cell) caused by macrocyclic 36-membered rings (Fig. 4) of rhomboidal shape (14.322 × 8.944 Å; Fig. 4) formed by eight organotin fragments and four H-bridges.

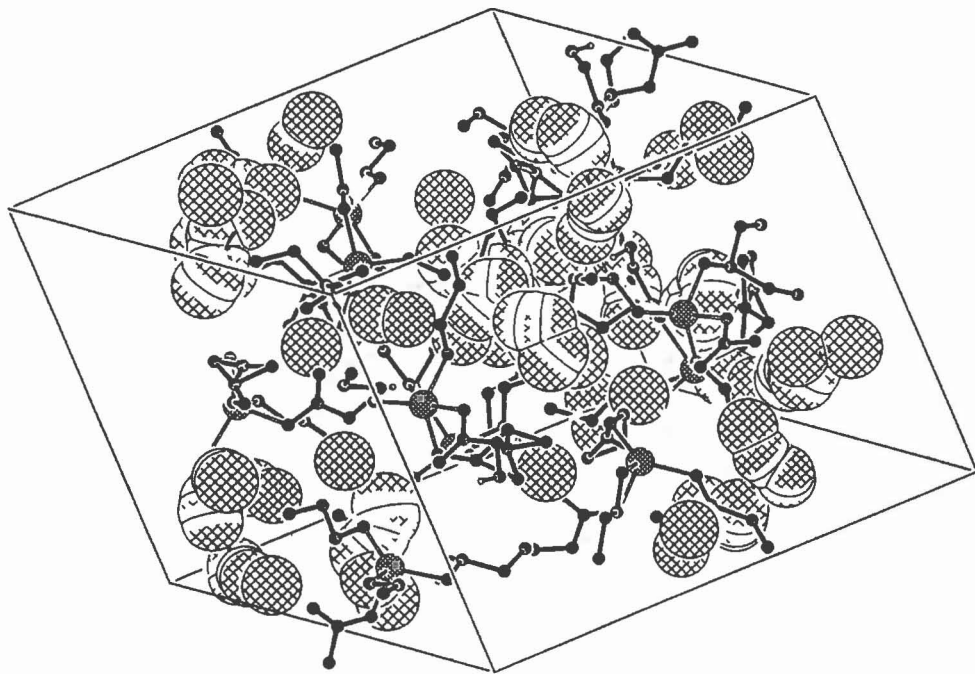


Fig. 3 Plot of cavities present within crystal lattice of *1*

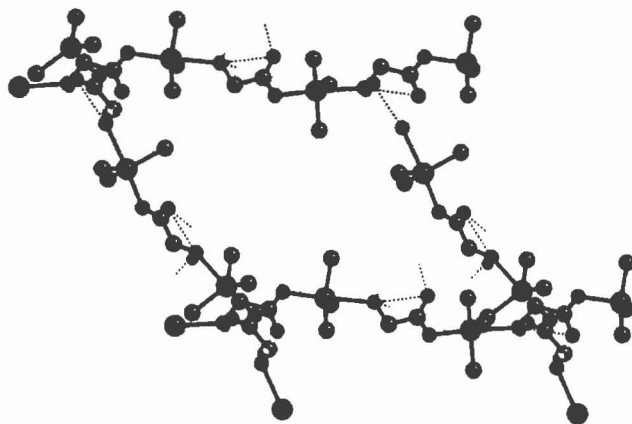


Fig. 4 Presentation of 36-membered ring in *1*

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