

Synthesis and Crystal Structure of One Trinuclear di-*n*-butyltin(IV) Complex with Salicylaldoxime

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Abstract One trinuclear di-*n*-butyltin(IV) complex with salicylaldoxime (*o*-HON=CHC₆H₄OH=HONZO), (Bu₂Sn)(Bu₂SnO)(Bu₂SnOH)(ONZO)(ONZO), has been synthesized and characterized by elemental analyses, IR spectrum, and single crystal X-ray diffraction. This complex is a small cluster displaying two unequivalent salicylaldoximate with one seven-coordinate pentagonal-bipyramidal tin atom linked two five-coordinate trigonal-bipyramidal tin atoms via a network of oxygen atoms by Sn–O–Sn bridges. The hydrogen bonds (*o*-HON=CHC₆H₄–O...H–O) are observed in the complex. These hydrogen bonds include intramolecular hydrogen bonds and intermolecular hydrogen bonds. (Bu₂Sn)(Bu₂SnO)(Bu₂SnOH)(ONZO)(ONZO) belongs to monoclinic: space group *P*2₁/*n*, with *a* = 12.2307(15) Å, *b* = 17.361(2) Å, *c* = 20.976(3) Å, β = 94.424(2)°, *V* = 4440.5(10) Å³, *Z* = 4, *D*_c = 1.500 g/cm³, μ(MoKα) = 1.715 mm⁻¹, *F*(000) = 2024, and final *R*₁ = 0.0426, *wR*₂ = 0.1064 for observed reflections 7779 (*I* > 2σ(*I*)).

Keywords Diorganotin(IV) · Synthesis · Crystal structure

Introduction

Organotin complexes of oximido compound are a kind of interesting organotin oxo clusters and have attracted considerable attention during the last decades, In view of their unique multinuclear structural features as well as their

applications as biocides and in homogenous catalysis [1–5]. Great efforts have been devote to study multinuclear organotin complexes [6–9]. However, the establishment of a clear relationship between coordination structure of multinuclear tin cluster and different ligands has been very difficult owing to absolute lack of available crystal structure data.

Tin oxo compounds have been of the variety of geometries [10–14]. In the present work, we synthesized one new trinuclear di-*n*-butyltin(IV) complex with salicylaldoxime, (Bu₂Sn)(Bu₂SnO)(Bu₂SnOH)(ONZO)(ONZO). They were characterized by elemental analyses, IR spectrum, and single crystal X-ray diffraction.

Experimental

Materials

Di-*n*-butyltin oxide and salicylaldoxime were analytical grade and used without further purification. Ethanol and benzene were chemical reagent, and redistilling before using.

Physical Measurements

Elemental analyses for C, H, and N were determined on a Perkin-Elmer 2400 II analyzer. IR spectrum was obtained for KBr pellets on a Nicolet 460 spectrophotometer in the 4,000–400 cm⁻¹.

Preparation of the Complex



Bu₂SnO (0.3734 g, 1.5 mmol) was dissolved in 15 ml benzene and HONZO (0.1371 g, 1.0 mmol) was dissolved in

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Table 1 Crystal data and structure refinement parameters of the complex

Complex	(Bu ₂ Sn)(Bu ₂ SnO)(Bu ₂ SnOH)(ONZOH)(ONZO)	
CCDC	CCDC-274465	
Color	Colorless	
Chemical formula	C ₃₈ H ₆₆ N ₂ O ₆ Sn ₃	
Formula weight	1003.00	
Temperature, K	298(2)	
Wavelength, Å	0.71073	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Volume, Å ³	4440.5(10)	
Unit cell dimensions	$a = 12.2307(15) \text{ \AA}$	$\beta = 94.924(2)^\circ$
	$b = 17.361(2) \text{ \AA}$	
	$c = 20.976(3) \text{ \AA}$	
Z	4	
Density(calculated), Mg/m ³	1.500	
Absorption coefficient, mm ⁻¹	1.715	
Diffractometer, scan	Siemens SMART/CCD area, detector/ ω -scans	
$F(000)$	2024	
θ range for data collection	2.00–25.03°	
Reflections collection	22671	
Independent	7779($R_{\text{int}} = 0.0400$)	
Max. and min. transmission	0.6545 and 0.5543	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	7779/48/442	
Goodness of fit on F^2	1.005	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0426$, $wR_2 = 0.1064$	
R indices (all data)	$R_1 = 0.0767$, $wR_2 = 0.1397$	
Largest diff. peak and hole, e/Å ³	0.941 and -0.601	

10 ml ethanol, mixed two solution and then the mixture stirred for 4 h. The resulting clear solution was rotary evaporated under vacuum to a small volume and was held at 6 °C for 5 days. Then the colorless crystal suitable for single crystal X-ray diffraction was obtained. IR $\nu(4,000\text{--}400 \text{ cm}^{-1})$: 3455–3395 (NO–H), 2955 (CH₂), 686 (Sn₃O), 632 (Sn–O–Sn), 586 (Sn–C), 440 (Sn–N). Anal. Calcd for C₃₈H₆₆N₂O₆Sn₃ (%): C 45.50, H 6.63, N 2.79; Found: C 45.38, H 6.55, N 2.84.

X-ray Crystallography

Single crystal of suitable size of the complex was mounted on Bruker Smart-1000 CCD diffractometer. Intensity data were collected with a graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. The structure was solved by directed method and the positions of the rest non-hydrogen atoms were determined from successive Fourier syntheses. The hydrogen atoms were placed in the geometrically calculated positions and allowed to ride on their respective parent atoms. The position and anisotropic

parameters of all non-hydrogen atoms were refined on F^2 by full-matrix least-squares method using the SHELXL-97 program package. Crystal data and structure refinement parameters of the complex are summarized in Table 1. Selected bond lengths and angles are presented in Table 2.

Result and Discussion

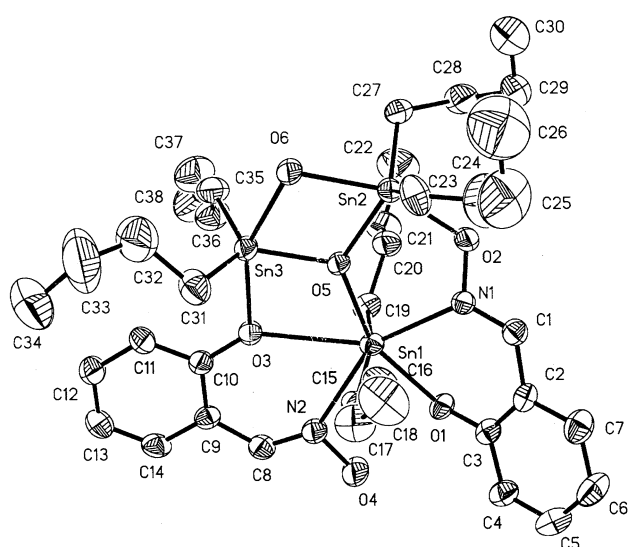
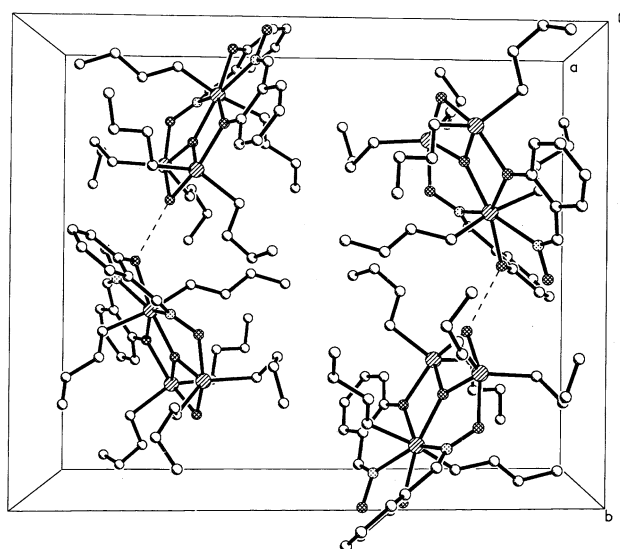
The molecular structure and the packing diagram of the complex are depicted in Figs. 1, 2.

The Sn(1) is seven-coordinate in pentagonal bipyramidal geometry containing two nonequivalent salicylaldoximate, one oxygen atom and two *n*-butyl groups. Here, two salicylaldoxime are bidentate ligands coordinating to tin atom Sn(1) via the phenoxide oxygen atoms and the oxime nitrogen atoms respectively. The O(5), N(1), N(2), O(1), O(3) take up the equatorial position, while C(19) and C(15) take up the axial sites. The mean deviation of five-coordinated atoms in the equatorial plane is 0.0394 Å, and the distance of Sn(1) from the plane is 0.0125 Å.

Table 2 Selected bond lengths (Å) and angles (°) of the complex

Sn(1)–O(5)	2.139(4)	Sn(1)–O(1)	2.254(5)
Sn(1)–N(1)	2.284(6)	Sn(1)–N(2)	2.623(6)
Sn(1)–O(3)	2.674(5)	Sn(2)–O(5)	2.037(4)
Sn(2)–C(23)	2.112(8)	Sn(2)–C(27)	2.125(8)
Sn(2)–O(2)	2.128(5)	Sn(2)–O(6)	2.163(5)
Sn(3)–O(5)	2.008(4)	Sn(3)–O(6)	2.142(5)
Sn(3)–O(3)	2.185(4)	N(2)–Sn(1)–O(3)	65.48(16)
O(5)–Sn(1)–O(3)	65.91(15)	O(1)–Sn(1)–N(1)	76.34(19)
O(1)–Sn(1)–N(2)	73.27(18)	C(19)–Sn(1)–C(15)	162.4(3)
O(5)–Sn(1)–N(1)	79.14(18)	O(5)–Sn(2)–C(27)	117.0(3)
O(5)–Sn(2)–C(23)	115.9(3)	O(2)–Sn(2)–O(6)	156.74(18)
C(23)–Sn(2)–C(27)	126.2(4)	C(23)–Sn(2)–C(27)	126.2(4)
O(5)–Sn(3)–C(31)	116.8(3)	O(5)–Sn(3)–C(35)	114.3(3)
C(31)–Sn(3)–C(35)	128.5(4)	O(3)–Sn(3)–O(6)	152.50(18)
Sn(3)–O(3)–Sn(1)	95.05(16)	Sn(3)–O(6)–Sn(2)	101.5(2)
Sn(3)–O(5)–Sn(1)	120.4(2)	Sn(3)–O(5)–Sn(2)	110.9(4)
Sn(1)–O(5)–Sn(2)	128.7(2)		

The Sn(2) is five-coordinated in trigonal-bipyramidal geometry. The three atoms [O(5), C(23), C(27)] in the equatorial plane and the distance of Sn(2) from the plane is 0.1172 Å, while the two oxygen atoms [O(2), O(6)] occupy the axial position. The sum of the angles of O(5)–Sn(2)–C(23), O(5)–Sn(2)–C(27), and C(23)–Sn(2)–C(27) is 359.1° which deviates from 360° only 0.9°. The angle of O(2)–Sn(2)–O(6) is 156.74(18)°, which deviate from 180°. The Sn(3) atom is similar to the Sn(2) atom, existing in a five-coordinated environment. The three atoms [O(5), C(31), C(35)] in the equatorial plane and the distance of

**Fig. 1** The molecular structure of the complex showing 30% probability displacement ellipsoids**Fig. 2** Packing diagram of the complex showing the hydrogen-bonded interactions as dashed line

Sn(3) from the plane is 0.0685 Å, while the two oxygen atoms [O(3), O(6)] occupy the axial position. The O(3) coordinating to Sn(3) in axial situation is a μ_2 -phenolate oxygen atom, while O(2) coordinating to Sn(2) in axial situation is an oxime oxygen atom.

In the complex, three tin atoms are linked via a network of oxygen atoms by Sn–O–Sn bridges. Sn(1)–O(3) bond length is longer than Sn(3)–O(3) bond length. Sn(3)–O(6) bond length is closed to Sn(2)–O(6) bond length. The oxygen atom O(5) bond with all three tin atoms, The four atoms define one plane and the mean deviation of four atoms is 0.001 Å. The bond lengths of Sn(2)–O(5) and Sn(3)–O(5) are closed to each other but longer than Sn(1)–O(5).

When the crystal structure was solved, the C atoms of each butyl chain in the unit are rotationally disordered over two positions. The stacking geometry (Fig. 2) is such that the hydrogen-bonded linkage of adjacent units forming infinite chain. The *n*-butyl chains are loosely packed by van der Waals interactions, as reflected by the Ueq values of the C atoms, which increase on approaching the methyl termini.

Hydrogen bonds lie in the complex. These hydrogen bonds include intramolecular hydrogen bonds and intermolecular hydrogen bonds. The oxime oxygen atoms form intramolecular hydrogen bonds (NO–H...O) with the phenoxide oxygens atom O(1) which coordinated only to Sn(1), the hydroxy oxygen atom [O(6)] form intermolecular hydrogen bonds (O–H...O) with the phenoxide oxygens atom O(1) which coordinated only to Sn(1). Detailed hydrogen bonds of the complex are listed in Table 3.

Table 3 Hydrogen Bond Interaction (Å, °) of the complex

D–H...A	d(D...H)	d(H...A)	d(D...A)	<(DHA)
O(4)–H(4)...O(1)	0.820	1.859	2.601	149.96
O(6)–H(4)...O(1) [#]	0.930	1.927	2.823	161.30

Note: Symmetry transformations used to generate equivalent atoms

[#] $-x + 1/2, y - 1/2, -z = 1/2$

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