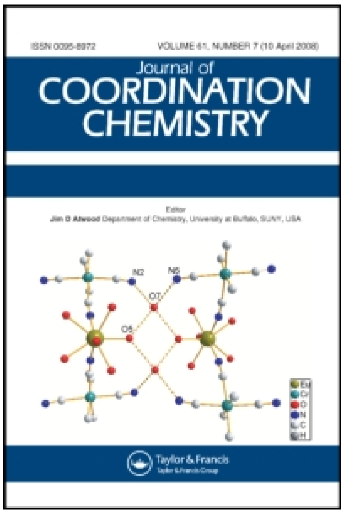

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Russell Knighton[a]; Xueqing Song[a]; Robert Pike[b]; Angel C. de Dios[c]; Leah Casabianca[c]; George Eng[a]
[a] Department of Chemistry and Physics, University of the District of Columbia, Washington, DC, 20008, USA [b] Department of Chemistry, College of William & Mary, Williamsburg, VA 23187, USA [c] Department of Chemistry, Georgetown University, Washington, DC, 20057, USA

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Synthesis and structural determination of two triphenyltin thiosalicylates

RUSSELL KNIGHTON†, XUEQING SONG†, ROBERT PIKE‡,
ANGEL C. DE DIOS§, LEAH CASABIANCA§ and GEORGE ENG*†

†Department of Chemistry and Physics, University of the District of Columbia,
Washington, DC, 20008, USA
‡Department of Chemistry, College of William & Mary, Williamsburg, VA 23187, USA
§Department of Chemistry, Georgetown University, Washington, DC, 20057, USA

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Two structurally different triphenyltin complexes of thiosalicylic acid were obtained depending on the amine used. Bis(triphenyltin) thiosalicylate was obtained when diethylamine was used while dicyclohexylammonium thiosalicylatotriphenylstannate resulted with dicyclohexylamine. Their structures have been characterized by IR and multi-nuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopies. In the solid state, both tins in the *bis*(triphenyltin) thiosalicylate complex are four-coordinate while the tin in dicyclohexylammonium thiosalicylatetriphenylstannate is five-coordinate. However, in solution, dissociation occurs in the dicyclohexylammonium thiosalicylatotriphenylstannate complex reducing the coordination of tin to four. The coordination of the tin atoms in the two triphenyltin complexes is confirmed by X-ray crystallographic studies.

Keywords: Crystal structure; IR; NMR; Thiosalicylic acid; Triphenyltin complexes

1. Introduction

The biocidal properties of triorganotins (R_3SnX) are well documented in the literature [1–4]. The toxicity of the compounds are generally species specific and have been shown to depend on the number and type of organic group attached to tin [1–4]. For example, triphenyltin complexes are commonly used as agricultural fungicides while trimethyltin complexes are active against insects [1–4]. The effect of the fourth group (X) attached to tin is not clear, as reports cite both the importance and insignificance of this group [2, 5–7]. It also has been reported that solubility plays a role in the efficacy of the compounds [8]. Increasing the aqueous solubility for a series of diphenyltin complexes increases their effectiveness. The *in vitro* anti-tumor activities (ID_{50}) of ionic diphenyltin complexes of thiosalicylate increases from 585 to 256 $\mathrm{ng\,cm^{-3}}$ against the MCF-7 cell lines and from 15,800 to 831 $\mathrm{ng\,cm^{-3}}$ against the *wiDr* cell lines when compared to the nonionic diphenyltin derivative [9]. In an attempt to synthesize a series of ionic triphenyltin complexes of thiosalicylic acid, an ionic and a nonionic triphenyltin

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*Corresponding author. Email: Geng@udc.edu

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complex were obtained based on the amine used in the synthesis. In this article, the structural characterizations as well as the comparison of the two complexes are reported.

2. Experimental

The IR spectra in the 400–4000 cm^{-1} region were recorded as KBr pellets on a Nicolet Magna-IR 760 spectrometer. All NMR measurements were made on a Varian Unity Inova 500 MHz spectrometer. Sample and instrument temperatures were at 298 K. Proton decoupled ^{13}C and ^{119}Sn spectra were acquired with a WALTZ decoupling sequence. ^{1}H and ^{13}C chemical shifts were referenced to internal TMS while ^{119}Sn chemical shifts were referenced to tetramethyltin, externally.

2.1. *Synthesis of bis(triphenyltin) thiosalicylate (complex 1)*

Thiosalicylic acid (2 mmol) in 15 mL of acetone was mixed with an equal molar amount of diethyl amine in 15 mL of acetone at room temperature to yield the ammonium salt of thiosalicylic acid. Two millimole of triphenyltin hydroxide was dissolved in 20 mL of hot acetone and any undissolved material was filtered off. The two solutions were then mixed and refluxed for 1.5 h, filtered and allowed to cool to room temperature. The solvent was then removed by a rotary evaporator to yield a solid product. The product was dissolved in dilute ethanol and colorless crystals, suitable for X-ray crystal diffraction analysis, were obtained upon slow evaporation. Yield 64%, m.p. 138.0–139.5°C. Analysis calculated for $C_{43}H_{34}O_2SSn_2$(%): C, 59.47; H, 6.72; Sn, 20.49. Found(%): C, 59.40; H, 6.76; Sn, 20.59.

2.2. *Synthesis of dicyclohexylammonium thiosalicylatotriphenylstannate (complex 2)*

Equal molar ratios of thiosalicylic acid (2 mmol) and dicyclohexylamine (2 mmol) were mixed in 15 mL ethanol and the resultant solution was added to 2 mmol of triphenyltin hydroxide in 15 mL of ethanol. After refluxing for 30 min, a white precipitate was collected upon cooling. Fine crystals suitable for X-ray study were obtained by slow evaporation of the dilute ethanol solution. Yield 72%, m.p. 152.0–153.0°C. Analysis calculated for $C_{37}H_{43}NO_2SSn$(%): C, 64.92; H, 6.33; Sn, 17.34%. Found(%): C, 65.22; H, 6.18; Sn, 17.08.

2.3. *X-ray crystallography*

Crystal structure data were collected using a Bruker SMART Apex II X-ray diffractometer with an Oxford Cryosystream low temperature device using graphite-monochromated Cu-Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct method (SHELXS97) [10] and refined by full-matrix least-squares on all F^2 data (SHELXL97) [10]. Nonhydrogen atoms were refined with an anisotropic thermal parameter and the hydrogens included

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**.

Complex	**1**	**2**
Chemical formula	$C_{43}H_{34}O_2SSn_2$	$C_{25}H_{19}O_2SSn \cdot C_{12}H_{24}N$
Formula weight	$M_r = 852.14$	$M_r = 684.47$
Crystal system, space group	Monoclinic, $P2(1)/c$	Monoclinic, $P2(1)/n$
Unit cell dimensions (Å, °)		
a	14.1451(2)	11.13870(10)
b	17.2144(3)	17.6465(2)
c	15.4565(3)	17.0629(2)
β	107.1030(10)	105.2994(4)
Volume (Å^3), Z	3597.21(11), 4	3235.01(6), 4
F_{000}	1696	1416
Calculated density (mg m^{-3})	1.573	1.405
Absorption coefficient (mm^{-1})	11.86	7.14
Max. and min. transmission	0.206, 0.145	0.424, 0.294
θ range for data collection (°)	3.3–67.0	3.7–67.0
Reflection collected	6195	5716
Independent reflection	5772 [$R_{(int)} = 0.037$]	5552 [$R_{(int)} = 0.037$]

from the geometry of the molecules were refined isotropically. The crystallographic data for the two complexes are shown in table 1.

3. Results and discussion

3.1. *Spectral studies*

The infrared spectrum of thiosalicylic acid showed a strong broad band between 3200 and 2800 cm^{-1} assignable to the carboxyl group (–COOH) and a medium band at 2564 cm^{-1} assigned to the thio group (–SH). Both bands were absent in spectra of the two complexes indicative of deprotonation of both the –SH and –COOH groups. Sharp bands were observed in both complexes at 560 cm^{-1} indicating formation of the Sn–O bond.

The mode of coordination of the carboxylate to metals including tin, has been deduced using the differences between the asymmetric and symmetric stretching vibrations of the OCO group [11]. The observed differences for **1** and **2** are 288 and 171 cm^{-1}, respectively. In **1**, the difference of 288 cm^{-1} is indicative of a monodentate ligand giving rise to a tetrahedral complex. The observed difference of 171 cm^{-1} for **2** indicates the carboxylate is a bridged ligand within the complex. It is suggested that the carboxylate oxygen is bonded to tin while the carbonyl oxygen is bonded to the ammonium ion through H-bonding. Based on these observations, it can be concluded that the thiosalicylato group is coordinated to tin via its sulfur atom and the carboxylate oxygen atom, giving a five-coordinate complex with H-bonding.

The ^{1}H and ^{13}C NMR spectra show the presence of two $SnPh_3$ and one $SnPh_3$ moieties for **1** and **2**, respectively. The observation of two tin resonances in **1** indicates that two different phenyl groups are present, supporting a *bis*-triphenyltin complex. Additional support for the proposed structure is the absence of the diethylammonium cation. ^{1}H NMR spectra of **2** shows the presence of dicyclohexylammonium supporting an ionic structure.

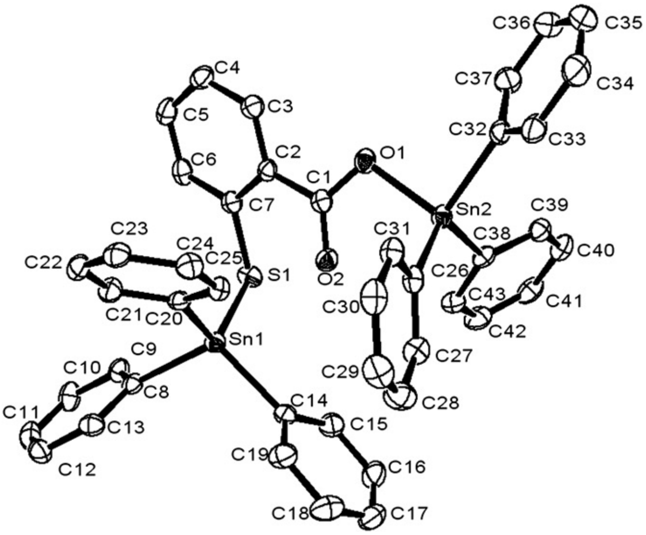

Figure 1. Crystal structure of **1**.

The ^{119}Sn chemical shifts of **1** in $CDCl_3$ showed two signals at −68.8 and −109.0 ppm, further supporting the existence of two four-coordinate tins in solution. Complex **2** exhibited only a single sharp resonance at −106.9 ppm, similar to values reported for other four-coordinate triphenyltin carboxylates [12], supporting a four-coordinate complex in solution.

Based on the spectral studies it can be concluded that tins in **1** are four-coordinate in the solid state as well as solution, while the tin in **2** is five-coordinate in the solid state and four-coordinate in solution.

3.3. *Crystal structures of complexes 1 and 2*

The crystal structure of **1** (figure 1) shows that the complex is monomeric and neutral, and that the two tins are four coordinate. The Sn–O1 bond length is 2.0721(15) Å. The carbonyl of the ligand coordinates very weakly to Sn with a long Sn–O2 bond of 2.7453(15) Å. This interaction causes distortion of the tetrahedral geometry. Thus, the best geometry to describe the carboxylatotin in the complex is a distorted tetrahedron. Similar structures have been reported in the literature for tin complexes [13], which have a short Sn–O bond length [2.04–2.12 Å] and a longer one in the range of 2.56–3.07Å. The Sn–S bond lengths of 2.4372(4) agrees with the Sn–S bond length for other organotin thiolates reported in the literature [14]. Selected bond lengths and angles of **1** are presented in table 2.

Based on the crystallographic data, **2** consists of an anionic moiety, thiosalicylatotriphenylstannate, and a dicyclohexylammonium cation (figure 2). This structure is similar to dicyclohexylammonium thiolactatotriphenylstannate reported earlier [15]. The anionic tin complex has a distorted *cis*-trigonal bipyramid (TBP) geometry with two carbons and one sulfur occupying the equatorial positions and an oxygen and phenyl occupying axial positions. The Sn–C bond lengths for the two equatorial

Table 2. Selected bond lengths and angles (Å, °) for **1**.

Sn1–C14	2.131(2)	C14–Sn1–C20	111.84(9)
Sn1–C20	2.134(2)	C14–Sn1–C8	109.75(8)
Sn1–C8	2.158(2)	C20–Sn1–C8	103.62(8)
Sn1–S1	2.4173(6)	C14–Sn1–S1	108.99(6)
Sn2–O1	2.0721(15)	C20–Sn1–S1	120.12(6)
Sn2–C26	2.116(2)	C8–Sn1–S1	101.53(6)
Sn2–C38	2.125(2)	O1–Sn2–C26	113.25(8)
Sn2–C32	2.134(2)	O1–Sn2–C38	104.23(7)
Sn2–O2	2.7453(15)	C26–Sn2–C38	120.75(9)
S1–C7	1.789(2)	O1–Sn2–C32	94.82(8)
O1–C1	1.318(3)	C26–Sn2–C32	110.81(9)
O2–C1	1.230(3)	C38–Sn2–C32	109.76(9)

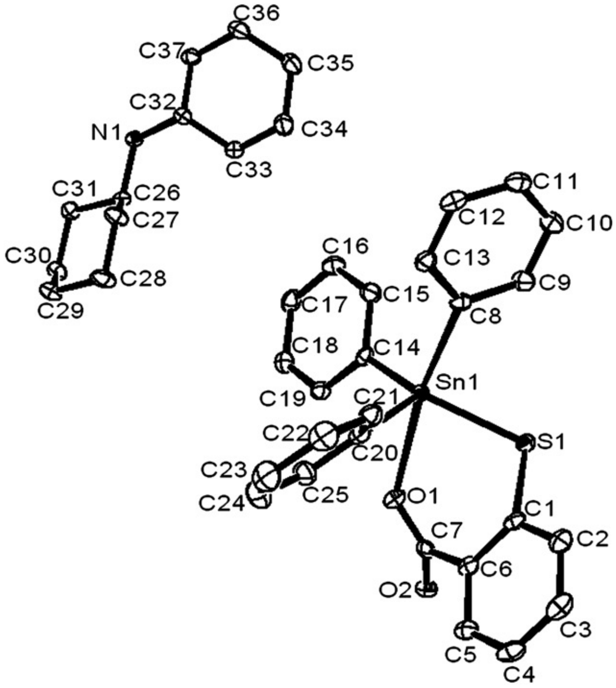

Figure 2. Crystal structure of **2**.

phenyls (2.1436(18) Å and 2.1515(17) Å) are slightly shorter than that for the axial phenyl (2.1872(18) Å. The S1–Sn1–O1 angle is significantly reduced (75.98(3)°) due to the steric effects in the thiosalicylatotriphenylstannate anion. Selected bond lengths and angles for **2** are listed in table 3.

The compound is essentially a dimer formed via an extensive hydrogen-bonding network between the carbonyl groups (C=O) from the thiosalicylatotriphenylstannate and nitrogen from the dicyclohexylammonium. The hydrogen bond distances and angles are listed in table 4. There are two significant interactions between the cation and the anion moieties through hydrogen bonding. The distances for N1–H1B–O2^{i} (2.868(2) Å) and N1–O1 (2.946(4) Å) bonds are much shorter than the sum of the van der Waals radii for the N and O (3.2 Å). Hydrogen bonding between N1–H1A–O2^{ii}

Table 3. Selected bond lengths and angles (Å, °) for **2**.

Sn1–C20	2.1436(18)	C20–Sn1–C14	113.16(7)
Sn1–C14	2.1515(17)	C20–Sn1–C8	104.66(7)
Sn1–C8	2.1872(18)	C14–Sn1–C8	101.05(7)
Sn1–S1	2.4372(4)	C20–Sn1–S1	115.64(5)
Sn1–O1	2.6034(13)	C14–Sn1–S1	122.66(5)
S1–C1	1.7795(18)	C8–Sn1–S1	94.08(5)
O1–C7	1.249(2)	C20–Sn1–O1	84.71(6)
O2–C7	1.270(2)	C14–Sn1–O1	80.45(6)
		C8–Sn1–O1	168.73(6)
		S1–Sn1–O1	75.98(3)

Table 4. Hydrogen-bond parameters (Å, °) for **2**.

D–H···A	D–H	H···A	D···A	D–H···A
N1–H1B···O2^{i}	0.92	1.98	2.868(2)	161
N1–H1A···O2^{ii}	0.92	1.89	2.7896(19)	165

Symmetry codes: (i) x, y, $z+1$; (ii) $-x+2$, $-y$, $-z+1$.

[symmetry code: (ii) $2-x$, $-y$, $1-z$] was also observed. O2 is also linked to an adjacent dicyclohexylammonium cation by a slightly weaker hydrogen bonding N1–H1B–O2^{i} [symmetry code: (i) x, y, $z+1$]. Hydrogen bonding substantially affects the distribution of electrons on the carbonyl group, which can be seen by observation of two nearly identical C–O bond distances, 1.235(5) Å for the C19–O2 bond and 1.259(4) Å for the C19–O1 bond. Additional evidence for weak hydrogen bonding between atoms N1–H1A–O1 can be observed by a significantly longer Sn–O distance (2.6034(13) Å) in dicyclohexylammonium thiosalicylatotriphenylstannate as compared to other similar complexes such as dicyclohexylammonium thiolactatotriphenylstannate [15] (2.498(2) Å), trimethylammonium chlorodiphenylmercaptoacetato stannnate [16] (2.228(4) Å), and 2-methylpyrimidium chlorodiphenylmercaptostannate [17] (2.214(9) Å).

Supplementary material

CCDC-704322 and CCDC-704321 contains crystallographic data for complexes **1** and **2**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic data center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk).

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