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Crystal Structure of Di-*iso*-butylammonium Thiolactatotriphenylstannate

Olaniran ATCHADE,* Xueqing SONG,* Robert PIKE,** and George ENG*†

*Department of Chemistry and Physics, University of District of Columbia, Washington, DC 20008, USA

**Department of Chemistry, College of William & Mary, Williamsburg, VA 23187, USA

The title compounds, $[(\textit{iso}\text{-C}_4\text{H}_9)_2\text{NH}_2][\text{SnPh}_3(\text{O}_2\text{CCH}(\text{CH}_3)\text{S})]$, crystallized in a monoclinic space group $P2_1/n$ with the following cell parameters: $a = 9.8537(2)\text{\AA}$, $b = 16.7775(3)\text{\AA}$, $c = 17.5845(3)\text{\AA}$, $\beta = 103.7740(10)^\circ$, $V = 2823.48(9)\text{\AA}^3$, $Z = 4$ and $D_x = 1.375\text{ Mg m}^{-3}$. The structure was refined to a final R value of 0.0222 for 5042 reflections [$I > 2\sigma(I)$]. The structure of the complex is ionic consisting of an anionic triphenyltin moiety and a cationic di-*iso*-butylammonium portion. In addition, a hydrogen bonding network between the cations and anions was observed.

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Triorganotin compounds are toxic to various organisms and their biocidal properties are well-documented in the literature.¹⁻⁴ The biological activity of a compound can be affected by its solubility. A large number of pharmaceutical compounds, including organotin, are sparingly soluble in water. Increasing the solubility of a compound may increase its biological activity. Thus, ionic complexes with partial ionic characteristics may lessen the solubility problem. Thus, we report the crystal structure of a dimeric ionic triorganotin complex, di-*iso*-butylammonium thiolactatotriphenylstannate (Fig. 1).

The title complex was prepared by the addition, with stirring, of 2 mmol of thiolactic acid to 30 mL of acetone containing 2 mmol of triphenyltin hydroxide. To this solution was added, dropwise, 2 mmol of di-*iso*-butylamine in 20 mL acetone. A cloudy solution formed immediately and after refluxing for 2 h, the solution became clear. The crude product was obtained as a solid by removing the solvent on a rotary evaporator. It was then recrystallized from 95% ethanol, and upon slow evaporation, crystals were obtained suitable for X-ray diffraction analyses, yield 71%, mp 108 - 109°C. Analysis Calculated for $\text{C}_{29}\text{H}_{39}\text{NO}_2\text{SSn}$: C, 59.40; H, 6.76; Sn, 20.59%. Found: C, 59.47; H, 6.72; Sn, 20.49%.

The structure was solved by direct methods and refined by a full-matrix least squares technique anisotropically. Details of the refinement parameters are listed in Table 1. The positions of

the hydrogen atoms were placed at geometrically idealized positions and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The final positions of all the non-hydrogen atoms are given in Table 2. An ORTEP plot of the molecular structure with the atomic numbering scheme is depicted in Fig. 2. Selected bond lengths and bond angles are summarized in Table 3.

Shown in Fig. 2 is the formula unit which consists of a di-*iso*-butylammonium cation and a thiolactatotriphenylstannate anion. The tin atom in the anion has essentially a *cis*-TBP geometry with O(1) and C(4) in the axial positions with C(10), C(16), and S(1) forming the equatorial plane. The Sn-C bond lengths for the two equatorial phenyl groups (2.144(2)Å and 2.152(2)Å) are slightly shorter than for the axial phenyl group (2.189(2)Å). The axial skeleton is slightly bent with a C4-Sn1-O1 angle of 171.20(6)°. The S1-Sn1-O1 angle was significantly reduced (76.79(3)°) due to steric effects in the thiolactatotriphenylstannate

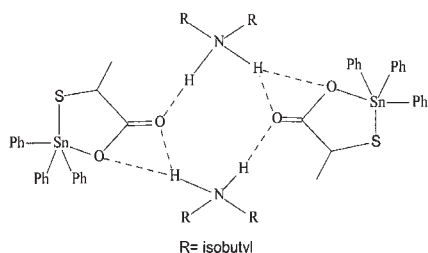


Fig. 1 Dimeric structure of the title complex

† To whom correspondence should be addressed.
 E-mail: geng@udc.edu

Table 1 Crystal and experimental data

Formula:	$\text{C}_{29}\text{H}_{39}\text{NO}_2\text{SSn}$
Formula weight:	584.36
Crystal system:	monoclinic
Space group	$P2_1/c$, $Z=4$
$a = 9.8537(2)\text{\AA}$	
$b = 16.7775(3)\text{\AA}$	$\beta = 103.7740(10)^\circ$
$c = 17.5845(3)\text{\AA}$	
$V = 2823.48(9)\text{\AA}^3$	$D_x = 1.375\text{ Mg/m}^{-3}$
Temperature	100 K
θ range for data collection	3.7 to 69.1°
Reflections collected/unique	31580/5042 [$R(\text{int}) = 0.029$]
Data/restraints/parameters	5042/3/312
Goodness-of fit on F^2	1.02
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0222$, $wR2 = 0.0215$
R indices (all data)	$R1 = 0.0575$, $wR2 = 0.0569$
$(\Delta/\sigma)_{\text{max}}$	0.003
$(\Delta\rho)_{\text{max}}$	$0.38\text{ e}\text{\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$	$-0.63\text{ e}\text{\AA}^{-3}$
Measurement:	Bruker-AXS SMART Apex II CCD
Program system	Bruker-AXS SMART, SHELXL-97
Refinement method	full-matrix least-squares on F^2

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (\AA^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Sn1	0.385471 (13)	0.665001 (7)	0.059245 (7)	0.01572 (6)
S1	0.30658 (5)	0.74117 (3)	0.15862 (3)	0.02087 (11)
O1	0.38729 (15)	0.80200 (8)	0.01339 (8)	0.0196 (3)
O2	0.40808 (16)	0.92788 (9)	0.05162 (8)	0.0245 (3)
C1	0.3666 (2)	0.85761 (13)	0.05724 (11)	0.0185 (4)
C2	0.2801 (2)	0.84135 (12)	0.11684 (13)	0.0225 (5)
C3	0.1278 (2)	0.85668 (14)	0.07655 (15)	0.0321 (5)
C4	0.3858 (2)	0.55003 (11)	0.11815 (11)	0.0175 (4)
C5	0.2650 (2)	0.51152 (12)	0.12770 (12)	0.0207 (4)
C6	0.2714 (2)	0.43747 (13)	0.16433 (13)	0.0251 (5)
C7	0.3997 (2)	0.40012 (12)	0.19191 (13)	0.0257 (5)
C8	0.5203 (2)	0.43652 (13)	0.18206 (13)	0.0246 (4)
C9	0.5130 (2)	0.51066 (12)	0.14562 (12)	0.0222 (4)
C10	0.2495 (2)	0.64122 (12)	-0.05381 (12)	0.0174 (4)
C11	0.2053 (2)	0.56268 (12)	-0.07044 (12)	0.0212 (4)
C12	0.1251 (2)	0.54114 (13)	-0.14363 (13)	0.0241 (4)
C13	0.0882 (2)	0.59798 (13)	-0.20218 (13)	0.0247 (4)
C14	0.1306 (2)	0.67628 (13)	-0.18657 (14)	0.0261 (5)
C15	0.2105 (2)	0.69797 (12)	-0.11324 (13)	0.0225 (4)
C16	0.6050 (2)	0.68092 (12)	0.06953 (12)	0.0185 (4)
C17	0.6763 (2)	0.64133 (12)	0.02129 (13)	0.0217 (4)
C18	0.8209 (2)	0.64840 (13)	0.03350 (14)	0.0262 (5)
C19	0.8962 (2)	0.69504 (14)	0.09395 (15)	0.0296 (5)
C20	0.8255 (3)	0.73590 (16)	0.14132 (15)	0.0357 (6)
C21	0.6815 (2)	0.72924 (14)	0.12916 (14)	0.0292 (5)
N1	0.49623 (17)	0.08331 (10)	0.08864 (10)	0.0184 (3)
C22	0.3794 (2)	0.14223 (12)	0.08125 (13)	0.0215 (4)
C23	0.3148 (2)	0.14518 (13)	0.15153 (13)	0.0223 (4)
C24	0.1973 (2)	0.20722 (13)	0.13545 (15)	0.0299 (5)
C25	0.2590 (3)	0.06423 (14)	0.16870 (15)	0.0315 (5)
C26	0.6182 (2)	0.09655 (12)	0.15706 (12)	0.0202 (4)
C27	0.7544 (2)	0.06628 (12)	0.14057 (12)	0.0214 (4)
C28	0.8758 (2)	0.08935 (14)	0.20878 (13)	0.0266 (5)
C29	0.7532 (2)	-0.02317 (13)	0.12537 (14)	0.0283 (5)

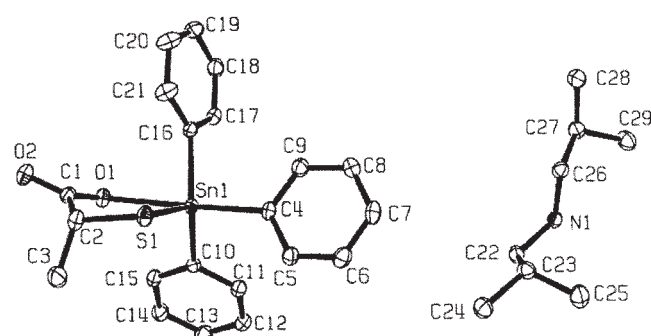


Fig. 2 ORTEP drawings of the title complex with the atom labels. Displacement ellipsoids are shown at 50% level (H atoms are excluded for clarity).

anion. There are two significant interactions between the cation and the anion moieties through hydrogen bonding. Each of the

Table 3 Selected bond lengths (\AA) and angles ($^\circ$).

Sn1—C16	2.144 (2)	S1—C2	1.828 (2)
Sn1—C10	2.154 (2)	O1—C1	1.258 (3)
Sn1—C4	2.1890 (19)	O2—C1	1.259 (3)
Sn1—S1	2.4368 (5)	N1—C22	1.500 (3)
Sn1—O1	2.4373 (13)	N1—C26	1.501 (3)
C16—Sn1—C10	119.62 (8)	S1—Sn1—O1	76.79 (3)
C16—Sn1—C4	100.49 (7)	C2—S1—Sn1	103.49 (7)
C10—Sn1—C4	101.78 (7)	C1—O1—Sn1	118.80 (13)
C16—Sn1—S1	111.21 (6)	O2—C1—O1	122.92 (18)
C10—Sn1—S1	121.65 (5)	O2—C1—C2	117.81 (18)
C4—Sn1—S1	95.02 (5)	O1—C1—C2	119.17 (18)
C16—Sn1—O1	79.84 (6)	C3—C2—S1	111.91 (15)
C10—Sn1—O1	85.48 (6)	C1—C2—S1	113.04 (15)
C4—Sn1—O1	171.20 (6)	C22—N1—C26	115.06 (16)

di-*iso*-butylammonium cation has significant hydrogen bonding with the carbonyl oxygen atoms, N1-H1A—O2ⁱ and N1-H1B—O2ⁱⁱ. Slightly weaker hydrogen bonding is observed with the N1-H1A—O1ⁱ atoms [symmetry codes: (i) 1-*x*, 1-*y*, -*z*; (ii) *x*, *y*-1, *z*]. Hydrogen bonding substantially affects the distribution of the electrons on the carbonyl groups, as can be seen by the observation of two identical C—O bond distances, 1.258(3) \AA for the C(1)—O(1) bond and 1.259(3) \AA for the C(1)—O(2) bond. These results would indicate that the complex is a loosely associated dimer bridged by two di-*iso*-butylammonium cations in the lattice as shown in Fig. 1.

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