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Crystal Structure of Dicyclohexylammonium Succinatotriphenylstannate at 138 K

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ABSTRACT

Dicyclohexylammonium succinatotriphenylstannate, synthesized by condensing $[(c\text{-}C_6H_{11})_2NH_2][HO_2C(CH_2)_2CO_2]$ *with* $(C_6H_5)_3SnOH$*, has a zig-zag structure consisting of polymeric chains in which planar triphenyltin cations* (Σ *C–Sn–C* = *360.0(2)°*) *are axially linked by succinato dianions (Sn–O = 2.214(2) Å; O–Sn–O = 172.52(6)°); the dicyclohexylammonium cations surround the chain and are hydrogen-bonded to the acyl oxygens of the ligand (N···O = 2.829(3) Å). The stannate is four-coordinate in* $CDCl_3$ *solution.*

INTRODUCTION

Dicyclohexylammonium hydrogen oxalate when treated with bis(tributyltin) oxide (TBTO) in ethanol affords $[(c\text{-}C_6H_{11})_2NH_2]$ $[(C_4H_9)_3SnO_2CCO_2]\cdot C_2H_5OH$, which co-crystallizes in a 2:1 ratio with bis(tributyltin) oxalate as a tetranuclear stannate whose tin atoms adopt essentially *trans*-C_3SnO_2 trigonal bipyramidal geometries [1]. Dicyclohexylammonium hydrogen 2,6-pyridinedicarboxylate, on the other hand, condenses with TBTO to give the ammonium stannate, $[(c\text{-}C_6H_{11})_2NH_2]$ $[(C_4H_9)_3SnO_2CC_5H_3NCO_2]$, whose crystal structure reveals an anionic chain comprising near-planar $(C_4H_9)_3Sn$ cations axially linked by $C_5H_3N(CO_2)_2$ dianions with similar tin–oxygen bond lengths (2.26(1), 2.31(1) Å) [2]. Reacting the mono-$[(c\text{-}C_6H_{11})_2NH_2]^+$ salt of succinic acid with $(C_6H_5)_3SnOH$ also yields a simple ammonium stannate, $[(c\text{-}C_6H_{11})_2NH_2]$ $[(C_6H_5)_3SnO_2C(CH_2)_2CO_2]$. Its crystal structure was determined in order to ascertain the preferred mode of coordination of this dicarboxylato ligand.

EXPERIMENTAL

Synthesis

Triphenyltin hydroxide was added to an ethanol solution containing equimolar amounts of dicyclohexylamine and succinic acid, and the solution was heated on a hot water bath to remove the ethanol. The product was collected, washed with ether, and recrystallized from ethanol. Anal. Calcd. for $C_{34}H_{43}NO_4Sn$: C, 62.98; H, 6.68; N, 2.16%. Found: C, 63.00; H, 6.77; N, 2.19. Infrared (Nujol mull) data: CO_2 (asymmetric) 1650, 1592, 1562; CO_2 (asym-

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metric) 1247; Sn–O 449 cm^{-1}. ^{13}C NMR in $CDCl_3$ at 300 K (chemical shift δ (coupling constant J_{Sn-C} in Hz)): phenyl C_{ipso} = 138.3 (647.9), C_{ortho} = 136.8 (48.0), C_{meta} = 128.8 (63.2), C_{para} = 130.0 (13.7); cyclohexyl C_1 = 53.1, C_2 = 31.4, C_3 = 25.0, C_4 = 25.5; methylene C = 31.6; carboxyl C = 178.5. The compound shows a ^{119}Sn NMR chemical shift δ = −110.9 relative to $(CH_3)_4Sn$.

X-ray Crystallography

A crystal of $[(c\text{-}C_6H_{11})_2NH_2]$ $[(C_6H_5)_3SnO_2C(CH_2)_2CO_2]$, 0.23 × 0.35 × 0.47 mm, was used for diffraction analysis. Intensity data were collected at 138 K on a CAD4 diffractometer by using the ω-scan mode up to $2\theta_{max}$ = 53° (graphite-filtered Mo-Kα radiation, λ 0.71069 Å). Of the 3558 unique reflections, the 2664 reflections obeying $F_0 > 2\sigma(F_0)$ were used in the full-matrix least-squares refinement after correction for Lorentz and polarization factors and for absorption effects (μ_{Mo} = 7.8 cm^{-1}, max/min transmission = 0.8387, 0.7571). As the heavy atom lies on the two-fold axis in the *Pnaa* space group, all the h = odd reflections were of zero intensity when the model was phased with Sn only. This was resolved without ambiguities or disorder to give a low R index of 0.0261 (R_w = 0.0377; $w = [\sigma^2(F_0) + 0.04(F_0)^2]^{-1}$; S = 1.57), although two residual e-density peaks (0.92 and 0.94 eÅ^{-3}) were found near the Sn atom. The H-atoms were all located. Atomic coordinates and bond dimensions are listed in Tables 1 and 2, respectively; the structure is depicted in Figure 1.

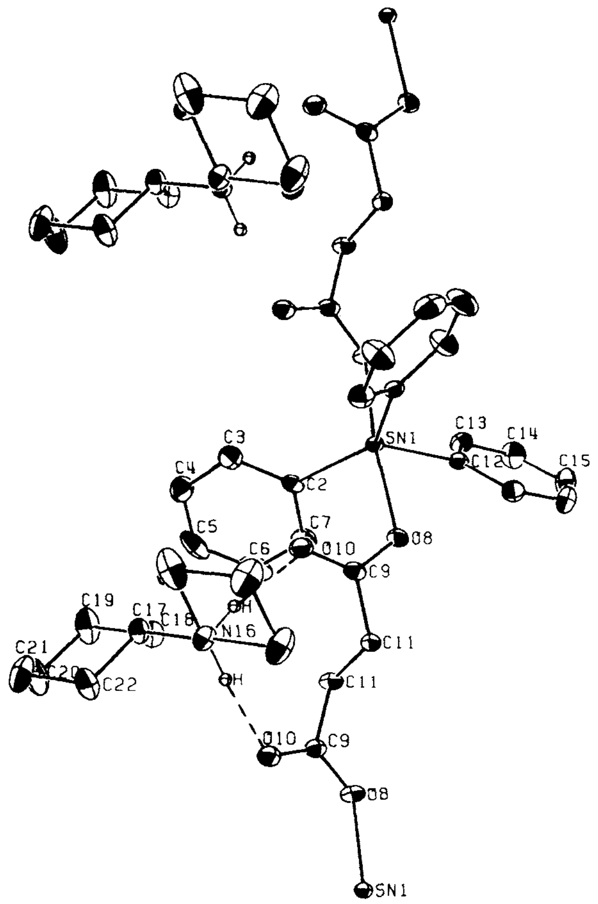

FIGURE 1 View of $[(c\text{-}C_6H_{11})_2NH_2]$ $[(C_6H_5)_3SnO_2C(CH_2)_2CO_2]$

TABLE 1 Positional Parameters

Atom	*x*	*y*	*z*
Sn(1)	0.18649(1)	0.25000	0.75000
C(2)	0.2291(1)	0.1425(1)	0.6800(2)
C(3)	0.2904(4)	0.1082(1)	0.7302(3)
C(4)	0.3135(1)	0.0380(2)	0.6744(4)
C(5)	0.2742(2)	0.0007(1)	0.5702(3)
C(6)	0.2129(2)	0.0333(2)	0.5225(4)
C(7)	0.1905(1)	0.1040(2)	0.5750(3)
O(8)	0.1789(1)	0.2091(1)	0.9731(2)
C(9)	0.2304(1)	0.2132(1)	1.0613(2)
O(10)	0.2935(1)	0.2225(1)	1.0272(2)
C(11)	0.2104(1)	0.2087(1)	1.2174(2)
C(12)	0.0743(2)	0.2500	0.7500
C(13)	0.0357(1)	0.1940(1)	0.8246(3)
C(14)	−0.0377(1)	0.1934(1)	0.8224(3)
C(15)	−0.0746(2)	0.2500	0.7500
N(16)	0.3911(1)	0.2500	1.2500
C(17)	0.4331(1)	0.1774(2)	1.2766(3)
C(18)	0.3821(1)	0.1104(1)	1.3025(3)
C(19)	0.4226(2)	0.0354(2)	1.3293(4)
C(20)	0.4735(2)	0.0178(2)	1.2084(4)
C(21)	0.5232(2)	0.0849(2)	1.1836(4)
C(22)	0.4829(1)	0.1602(2)	1.1527(3)

Crystal Data. $C_{34}H_{43}NO_4Sn$, *MW* = 648.40, *F*(000) = 1344, orthorhombic space group *Pnaa* (nonstandard setting for *Pccn*, No. 56); a = 18.931(4), b = 17.280(6), c = 9.379(2), V = 3068(2) Å^3, $D_{X\text{-ray}}$ = 1.403 g cm^{-3} for Z = 4.

RESULTS AND DISCUSSION

Five-coordinate triorganotin compounds invariably adopt the *trans*-trigonal bipyramidal (tbp) geometry in which the donor atoms of the electronegative ligands occupy the apical positions. Among triphenyltin compounds, the *cis*-tbp geometry is found only in the chelated complexes in which the chelating group spans the axial–equatorial positions of the tbp [3]. The succinato ligand in the present study was selected in the hope that it would chelate efficiently to yield a strain-free, seven-membered ring, but the results of the crystal structure analysis on the succinatotriphenyltin complex once again demonstrate the preference for the trans- over the cis- geometry.

The crystal structure of title complex consists

TABLE 2 Bond Distances (Å) and Angles (°)

Sn(1)–C(2)	2.129(2)	C(11)–C(11)'	1.553(3)
Sn(1)–C(12)	2.123(3)	C(12)–C(13)	1.400(3)
Sn(1)–O(8)	2.214(2)	C(13)–C(14)	1.389(4)
C(2)–C(3)	1.386(4)	C(14)–C(15)	1.380(3)
C(2)–C(7)	1.395(4)	N(16)–C(17)	1.506(3)
C(3)–C(4)	1.391(4)	C(17)–C(18)	1.527(4)
C(4)–C(5)	1.387(4)	C(17)–C(22)	1.526(4)
C(5)–C(6)	1.365(4)	C(18)–C(19)	1.527(4)
C(6)–C(7)	1.384(4)	C(19)–C(20)	1.518(5)
O(8)–C(9)	1.281(3)	C(20)–C(21)	1.512(4)
C(9)–O(10)	1.247(3)	C(21)–C(22)	1.534(4)
C(9)–C(11)	1.515(3)	O(10)–H(33)	1.92(3)
N(16)–H(33)	0.91(3)		
C(2)–Sn(1)–C(2)"	135.41(9)	O(8)–C(9)–C(11)	115.5(2)
C(2)–Sn(1)–C(12)	112.29(6)	C(9)–C(11)–C(11)'	109.5(2)
C(2)–Sn(1)–O(8)	92.17(7)	O(10)–C(9)–C(11)	119.6(2)
O(8)–Sn(1)–C(12)	86.26(4)	C(12)–C(13)–C(14)	121.4(2)
O(8)–Sn(1)–O(8)"	172.52(6)	C(13)–C(12)–C(13)"	117.0(3)
Sn(1)–C(2)–C(3)	125.9(2)	C(13)–C(14)–C(15)	120.5(3)
Sn(1)–C(2)–C(7)	115.8(2)	C(14)–C(15)–C(14)"	119.2(3)
Sn(1)–O(8)–C(9)	122.9(1)	N(16)–C(17)–C(18)	109.0(2)
Sn(1)–C(12)–C(13)	121.5(2)	N(16)–C(17)–C(22)	111.3(2)
C(2)–C(3)–C(4)	120.5(2)	C(17)–N(16)–C(17)'	116.2(2)
C(2)–C(7)–C(6)	120.8(3)	C(17)–C(18)–C(19)	110.7(2)
C(3)–C(2)–C(7)	118.4(2)	C(17)–C(22)–C(21)	109.2(3)
C(3)–C(4)–C(5)	120.2(3)	C(18)–C(17)–C(22)	111.3(2)
C(4)–C(5)–C(6)	119.6(3)	C(18)–C(19)–C(20)	111.4(3)
C(5)–C(6)–C(7)	120.5(3)	C(19)–C(20)–C(21)	110.9(3)
O(8)–C(9)–O(10)	124.8(2)	C(20)–C(21)–C(22)	111.7(2)
O(10)–H(33)–N(16)	172(3)		

Symmetry transformations: (') *x*, 0.5 − *y*, 2.5 − *z*; (") *x*, 0.5 − *y*, 1.5 − *z*.

of polymeric chains in which planar triphenyltin cations (Σ C–Sn–C = 360.0(2)°) are axially linked by succinato dianions; the dicyclohexylammonium cations surround the chain and are hydrogen-bonded to the acyl oxygens of the ligand. The chain runs parallel to the *c*-axis of the unit cell. A somewhat distorted *trans*-C_3SnO_2 trigonal bipyramidal geometry at tin is evident from the oxygen–tin–oxygen angle.

The Sn(1) atom lies on the crystallographic two-fold axis, which passes through the center of the bond joining the methylene carbons of the succinato group. This two-fold axis relates two phenyl rings to each other and also one half of the third phenyl ring to its other half (symmetry transformation: *x*, 0.5 − *y*, 1.5 − *z*). The two cyclohexyl rings are symmetry-related by another two-fold axis, which passes through the N(14) atom. One interesting outcome of the crystallographic symmetry of the structure is the isotropic bridging nature of the ligand: there is neither a short nor a long tin–oxygen bond. The tin–oxygen bond length is intermediate between the covalent and dative tin–oxygen bonds found in neutral carboxylate-bridged triorganotin esters [4].

In $CDCl_3$ solution the stannate dissociates into a four-coordinate species, as shown by the values for its ^{119}Sn NMR chemical shift (δ = −110.9) and one-bond coupling constant ($^1J_{Sn-C}$ = 647.9 Hz), which lie in the range typical of four-coordinate triphenyltin compounds [5].

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SUPPLEMENTARY MATERIAL AVAILABLE

Anisotropic thermal displacement factors, F_{obs} and F_{calc} tables, have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England, and are available on request.

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