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Linear chains in polymeric dicyclohexylammonium tributyl(4-oxo-4*H*-pyran-2,6-dicarboxylato)stannate and methylphenylammonium tributyl(pyridine-2,6-dicarboxylato)stannate containing trigonal bipyramidal tin

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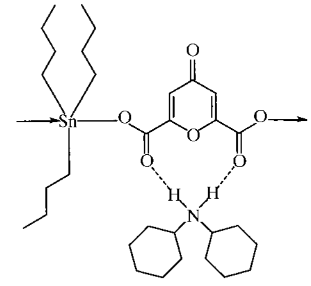
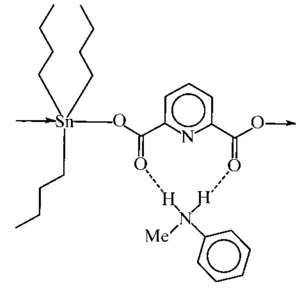
catena-Poly[dicyclohexylammonium [tributyltin-μ-(4-oxo-4*H*-pyran-2,6-dicarboxylato-O^2:O^6)]], $(C_{12}H_{24}N)[Sn(C_7H_2O_6)(C_4H_9)_3]$, consists of 4-oxo-4*H*-pyran-2,6-dicarboxylato groups that axially link adjacent tributyltin units into a linear polyanionic chain. The ammonium counter-ions surround the chain, and each cation forms a pair of hydrogen bonds to the double-bond carbonyl O atoms of the same dianionic group. The chain propagates in a zigzag manner along the *c* axis of the monoclinic cell. In *catena*-poly[methyl(phenyl)ammonium [tributyltin-μ-(pyridine-2,6-dicarboxylato-O^2:O^6)]], $(C_7H_{10}N)[Sn(C_7H_3NO_4)(C_4H_9)_3]$, the pyridine-2,6-dicarboxylato groups also link the tributyltin groups into a chain, but the hydrogen-bonded chain propagates linearly on the *ac* face of the monoclinic cell.

Comment

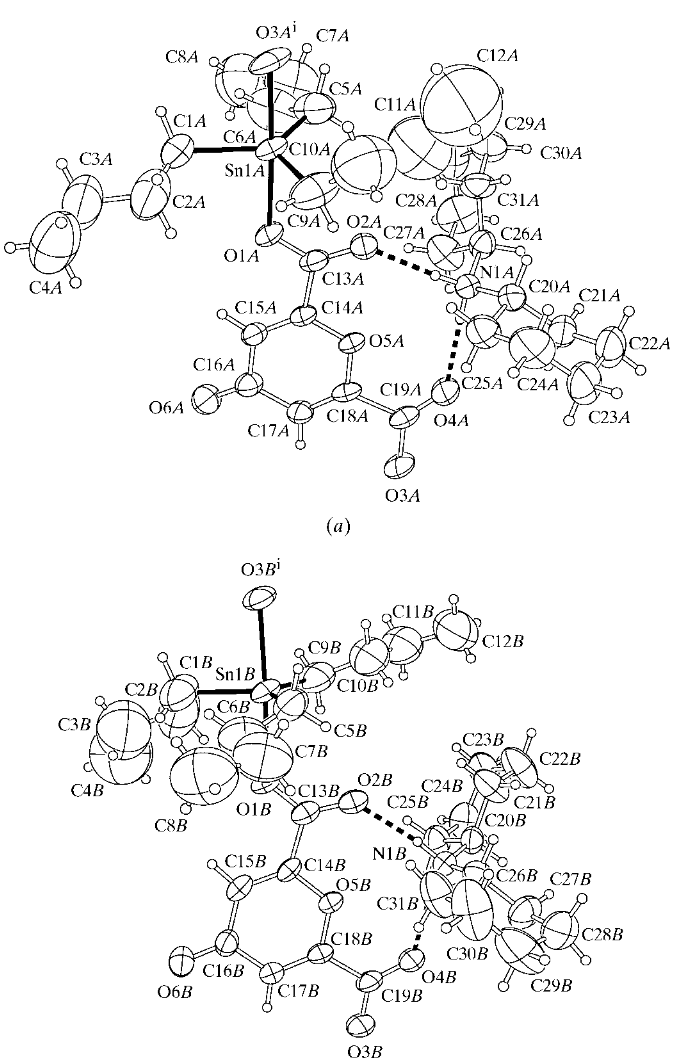
Among the triorganotin derivatives of polycarboxylic acids, the ammonium triorganotin dicarboxylates represent a class of stannates whose biological properties are expected to be improved compared with those of neutral triorganotin monocarboxylates or bis(triorganotin) dicarboxylates because of the potentially greater degree of aqueous solubility. Dicyclohexylammonium tributyltin pyridine-2,6-dicarboxylate exists as a linear hydrogen-bonded polyanionic chain motif; the ammonium counter-ions surround the chain and they interact with the double-bond carbonyl O atoms through hydrogen bonds [N···O = 2.75 and 2.79 Å; Ng, Kumar Das & Tiekink, 1991]. Replacement of the pyridyl unit by the 4-oxo-4*H*-pyranyl entity results in the formation of a similar hydrogen-bonded architecture for dicyclohexylammonium tributyl(4-oxo-4*H*-pyran-2,6-dicarboxylato)stannate, (I), which crystallizes as two symmetry-independent hydrogen-bonded chains. These are approximately related by (0.5 + *x*, *y*, 0.45 − *z*), such a relationship suggesting the possibility of a stacking fault. The Sn atoms show *trans*-C_3SnO_2 trigonal bipyramidal coordination [chain *A*: Sn—O = 2.285 (4) and 2.292 (4) Å, and O—Sn—O = 174.3 (2)°; chain *B*: Sn—O = 2.286 (5) and 2.292 (5) Å, and O—Sn—O = 176.0 (2)°]; the



(I)



(II)



(*a*)

(*b*)

Figure 1
*ORTEP*II (Johnson, 1976) plot of molecules *A* and *B* of (I) at the 30% probability level. H atoms are shown as spheres of arbitrary radii (symmetry codes are as in Table 1).

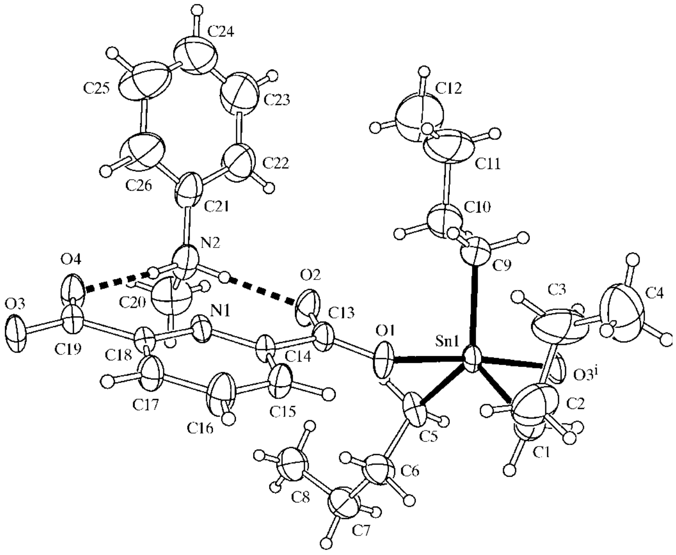


Figure 2
*ORTEP*II (Johnson, 1976) plot of (II) at the 30% probability level. H atoms are shown as spheres of arbitrary radii [symmetry code: (i) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$].

negatively charged carboxyl O atoms of the dicarboxylato dianion bind to two adjacent tributyltin cations. The Sn—O bond distances are longer than covalent Sn—O bonds, but shorter than dative Sn—O bonds found in most triorganotin carboxylates (Tiekink, 1991, 1994). The bond distances are somewhat longer than those [Sn—O = 2.26 (1) and 2.31 (1) Å] found in poly(dicyclohexylammonium 2,6-pyridinedicarboxylatotributylstannate) (Ng, Kumar Das & Tiekink, 1991) and that [Sn—O = 2.214 (2) Å] found in poly(dicyclohexylammonium succinatotriphenylstannate) (Ng, Kumar Das, Xiao *et al.*, 1991); in (I), the Sn atom lies on a special position so that the two Sn—O bonds are equivalent.

The connectivity between the dianionic and cationic groups leads to the formation of a polyanionic zigzag chain structure. The *sec*-ammonium cations surround the chain, and each cation forms a pair of hydrogen bonds [chain *A*: N···O = 2.785 (7) and 2.788 (7) Å; chain *B*: N···O = 2.765 (7) and 2.786 (8) Å]. The ketonic O atom of the 4-oxo-4*H*-pyran moiety is not involved in hydrogen bonding.

Whereas poly(2,6-pyridinedicarboxylatotributylstannate) adopts a zigzag chain motif in the dicyclohexylammonium derivative (Ng, Kumar Das & Tiekink, 1991), the polyanion in methylphenylammonium tributyl(pyridine-2,6-dicarboxylato)stannate, (II), adopts a linear arrangement that is neither zigzag nor helical as the chain propagates on the *ac* face of the monoclinic cell. The repeat distance of (II) is half the *ac* diagonal (*a*/*c* = 11.10 Å); this distance is nearly identical to that (*c*/2 = 11.06 Å) of the dicyclohexylammonium derivative. The similarity of the two repeat distances suggests that the nature of the ammonium counter-ion governs packing. However, the packing of both compounds appears to be inefficient, as noted from the accessible voids. In (II), there are two such voids of 37.6 Å^3 in the unit cell. The hydrogen bonds in (II) [N···O = 2.732 (5) and 2.763 (4) Å] are much shorter than that [N···O = 2.904 (3) Å] found in the methylphenylammonium hydrogen 2,6-pyridinedicarboxylate (Ng & Turnbull, 1998) reactant.

Experimental

Dicyclohexylamine (1.81 g, 10 mmol) and 4-oxo-4*H*-pyran-2,6-dicarboxylic (chelidonic) acid (1.84 g, 10 mmol) were heated in a small volume of ethanol until the acid dissolved completely. The addition of bis(tributyltin) oxide (2.98 g, 5 mmol) gave an immediate precipitate. More ethanol was added to dissolve the solid, and slow evaporation of the filtered solution led to yellow blocks of (I). The solid-state ^{119}Sn NMR spectrum consists of three signals (4:3:1 intensity ratio) at −55, −60 and −64 p.p.m. relative to tetramethyltin. A similar reaction with *N*-methylaniline, 2,6-pyridinedicarboxylic acid and bis(tributyltin) oxide gave (II) as long plates.

Compound (I)

Crystal data

$(C_{12}H_{24}N)[Sn(C_7H_2O_6)(C_4H_9)_3]$
$M_r = 654.43$
Monoclinic, $P2_1/c$
$a = 18.1212$ (3) Å
$b = 18.0363$ (2) Å
$c = 21.8937$ (1) Å
$\beta = 98.454$ (1)°
$V = 7078.0$ (1) Å^3
$Z = 8$

$D_x = 1.228$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7059 reflections
$\theta = 1.14$–28.31°
$\mu = 0.759$ mm^{-1}
$T = 298$ (2) K
Parallelepiped, colorless
0.38 × 0.24 × 0.20 mm

Data collection

Siemens CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.761$, $T_{max} = 0.863$
36 773 measured reflections

12 367 independent reflections
6929 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 25.00°$
$h = -21 \rightarrow 15$
$k = -19 \rightarrow 21$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.189$
$S = 1.072$
12 367 reflections
703 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 9.8444P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Sn1*A*—C1*A*	2.127 (9)	Sn1*B*—C1*B*	2.20 (1)
Sn1*A*—C5*A*	2.13 (1)	Sn1*B*—C5*B*	2.15 (1)
Sn1*A*—C9*A*	2.08 (1)	Sn1*B*—C9*B*	2.14 (1)
Sn1*A*—O1*A*	2.285 (4)	Sn1*B*—O1*B*	2.286 (5)
Sn1*A*—O3*A*^{i}	2.292 (4)	Sn1*B*—O3*B*^{ii}	2.292 (5)
C1*A*—Sn1*A*—C5*A*	118.2 (4)	C1*B*—Sn1*B*—C5*B*	115.6 (5)
C1*A*—Sn1*A*—C9*A*	117.0 (5)	C1*B*—Sn1*B*—C9*B*	119.1 (5)
C1*A*—Sn1*A*—O1*A*	86.5 (3)	C1*B*—Sn1*B*—O1*B*	87.8 (4)
C1*A*—Sn1*A*—O3*A*^{i}	91.4 (3)	C1*B*—Sn1*B*—O3*B*^{ii}	88.6 (4)
C5*A*—Sn1*A*—C9*A*	124.8 (5)	C5*B*—Sn1*B*—C9*B*	125.3 (4)
C5*A*—Sn1*A*—O1*A*	91.6 (3)	C5*B*—Sn1*B*—O1*B*	88.3 (3)
C5*A*—Sn1*A*—O3*A*^{i}	94.0 (3)	C5*B*—Sn1*B*—O3*B*^{ii}	94.9 (3)
C9*A*—Sn1*A*—O1*A*	89.8 (3)	C9*B*—Sn1*B*—O1*B*	93.8 (3)
C9*A*—Sn1*A*—O3*A*^{i}	86.5 (3)	C9*B*—Sn1*B*—O3*B*^{ii}	86.2 (3)
O1*A*—Sn1*A*—O3*A*^{i}	174.3 (2)	O1*B*—Sn1*B*—O3*B*^{ii}	176.0 (2)

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

Compound (II)

Crystal data

$(C_7H_{10}N)[Sn(C_7H_3NO_4)(C_4H_9)_3]$
$M_r = 563.29$
Monoclinic, $P2_1/n$
$a = 17.7536$ (3) Å
$b = 9.3746$ (1) Å
$c = 17.8985$ (2) Å
$\beta = 102.981$ (1)°
$V = 2902.77$ (7) Å^3
$Z = 4$
$D_x = 1.289$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5832 reflections
$\theta = 2.82$–$28.27°$
$\mu = 0.910$ mm^{-1}
$T = 298$ (2) K
Block, colorless
0.44 × 0.22 × 0.18 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.690$, $T_{max} = 0.853$
19786 measured reflections
7133 independent reflections
4770 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 28.27°$
$h = -23 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.155$
$S = 1.060$
7133 reflections
307 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 0.3874P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -1.08$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Sn1—C1	2.146 (5)	Sn1—O1	2.275 (2)
Sn1—C5	2.152 (4)	Sn1—O3^i	2.279 (2)
Sn1—C9	2.113 (5)		
C1—Sn1—C5	115.3 (2)	C5—Sn1—O1	91.9 (1)
C1—Sn1—C9	124.2 (2)	C5—Sn1—O3^i	85.3 (1)
C1—Sn1—O1	87.0 (1)	C9—Sn1—O1	92.3 (2)
C1—Sn1—O3^i	90.2 (2)	C9—Sn1—O3^i	93.0 (2)
C5—Sn1—C9	120.5 (2)	O1—Sn1—O3^i	174.7 (1)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

For (I), the 1,2- and 1,3-related carbon–carbon distances in the butyl chains and cyclohexyl rings were restrained by DFIX 1.54±0.01 and DFIX 2.52±0.02 Å; displacement parameter restraints (SIMU 0.02) were imposed on the six butyl groups. Additionally, the displacement parameters were restrained so that the ellipsoids would not be too elongated by an ISOR 0.02 command in *SHELXL*97 (Sheldrick, 1997). The crystal was measured to $2\theta = 56.5°$; however, as the refinement converged to $R >> 7\%$, an OMIT −3 50 instruction was used to eliminate the high angle reflections. For (II), one of the butyl chains is disordered over two positions, and this was refined as two half-site occupancy chains sharing a common C_α atom; the distances were similarly DFIXed.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1382). Services for accessing these data are described at the back of the journal.

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