

C1a—Sn1a—C7a	115.2 (2)	C1b—Sn1b—C13b	120.4 (1)
C1a—Sn1a—C13a	132.3 (2)	C1b—Sn1b—C7b	117.1 (1)
C1a—Sn1a—O1a	94.6 (2)	C1b—Sn1b—O1b	101.2 (1)
C1a—Sn1a—O3a	84.8 (2)	C1b—Sn1b—O2a	81.7 (1)
C7a—Sn1a—C13a	111.7 (1)	C7b—Sn1b—C13b	119.8 (1)
C7a—Sn1a—O1a	89.3 (1)	C7b—Sn1b—O1b	88.4 (1)
C7a—Sn1a—O3a	89.9 (1)	C7b—Sn1b—O2a	87.6 (1)
C13a—Sn1a—O1a	93.9 (1)	C13b—Sn1b—O1b	96.5 (1)
C13a—Sn1a—O3a	87.4 (1)	C13b—Sn1b—O2a	84.5 (1)
O1a—Sn1a—O3a	178.7 (1)	O1b—Sn1b—O2a	175.8 (1)

The final difference map in (I) had a peak of about $1 \text{ e } \text{Å}^{-3}$ near the Sn atom. In (II), phenyl rings were refined as rigid hexagons. The dimethyl sulfoxide coordinated to the Sn2a atom is disordered with respect to the ethanol, and each molecule was refined with 0.5 occupancy. The C—C distance in the ethanol molecule was fixed at $1.54 \pm 0.01 \text{ Å}$. The final difference map also had peaks of about $1 \text{ e } \text{Å}^{-3}$ near the Sn atoms. In (III), the three dimethylamino groups are disordered over two positions and were refined with restraints (P—N = 1.65 ± 0.01 , N—C = 1.45 ± 0.01 and C··C = 2.37 Å); *EADP* (*SHELXL93*; Sheldrick, 1993) restraints were imposed on these atoms. All phenyl rings were refined as rigid hexagons. One of the phenyl rings bonded to the Sn1a atom is also disordered over two positions; an *EADP* restraint was also applied to that ring having 0.333 occupancy. In (II) and (III), disorder affected the refinement of the phenyl rings, some of which had C—C distances that were either too long or too short when the phenyl rings were not restrained as planar hexagons.

For all compounds, data collection: *CAD-4 VAX/PC* (Enraf–Nonius, 1988); cell refinement: *CAD-4 VAX/PC*; data reduction: *Xtal3.0* (Hall & Stewart, 1990); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1059). Services for accessing these data are described at the back of the journal.

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2[(C₆H₁₁)₂NH₂]⁺·[Sn(O₂CCH₂CH₂CO₂)⁻(C₄H₉)₃]⁻·1/2(O₂CCH₂CH₂CO₂)²⁻·H₂O, an Organostannate Consisting of Linear Polyanionic Tributyl(succinato)stannate Chains Hydrogen Bonded into Layers by a [Tetrakis(dicyclohexylammonium) Succinate Dihydrate] Dicationic Network

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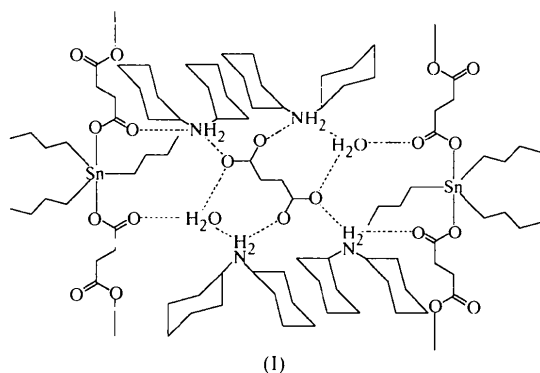
(Received 4 July 1997; accepted 8 December 1997)

Abstract

In bis(dicyclohexylammonium) *catena*-poly[tributylstannate- μ -succinato] hemi(succinate) monohydrate, (C₁₂H₂₄N)₂[Sn(C₄H₄O₄)(C₄H₉)₃](C₄H₄O₄)_{1/2}·H₂O, the polyanionic tributyl(succinato)stannate chains are hydrogen bonded into layers by a [tetrakis(dicyclohexylammonium) succinate dihydrate] dicationic network. The linear polyanionic chain consists of planar tributyltin groups that are axially linked by the succinato groups.

Comment

The dicyclohexylammonium hydrogen carboxylates, [(C₆H₁₁)₂NH₂]⁺·[HO₂C(CH₂)_nCO₂]⁻, when condensed with half a molar equivalent of bis(tributyltin) oxide in ethanol, yield bis(dicyclohexylammonium) tris(oxalato)tetrakis(tributylstannate)·2ethanol for the $n = 0$ (oxalato) homolog (Ng *et al.*, 1990) and bis(dicyclohexylammonium) tris(malonato)tetrakis(tributylstannate) for the $n = 1$ (malonato) derivative (Ng *et al.*, 1992). The condensation of dicyclohexylammonium hydrogen succinate ($n = 2$) with bis(tributyltin) does not afford the simple ammonium stannate, but instead gives [(C₆H₁₁)₂NH₂]⁺·[Sn(C₄H₉)₃(O₂CCH₂CH₂CO₂)⁻] as a 2:1 complex with 2[(C₆H₁₁)₂NH₂]⁺·[O₂CCH₂CH₂CO₂]²⁻·2H₂O, (I).



The tributyl(succinato)stannate anion exists as a linear *catena*-poly[tributylstannate- μ -succinato] polyanion and its Sn atom shows *trans*-C₃SnO₂ trigonal bipyramidal coordination [Σ_{C-Sn-C} 359.9 (9) and O—Sn—O 174.5 (2)°]. One of the C—Sn—C angles [134.4 (3)°] has been opened up in order to accommodate the two double-bonded carbonyl O atoms. The Sn—O bond distances [2.279 (5) and 2.230 (5) Å] are longer than that [2.214 (2) Å] found in the analogous aromatic triphenyl(succinato)stannate chain (Ng *et al.*, 1991); its Sn atom lies on a crystallographic twofold axis, so that the C₃Sn girdle is perfectly flat.

The negative charge of the tributyl(succinato)stannate anion is balanced by the positive charge of half the [tetrakis(dicyclohexylammonium) succinate dihydrate]

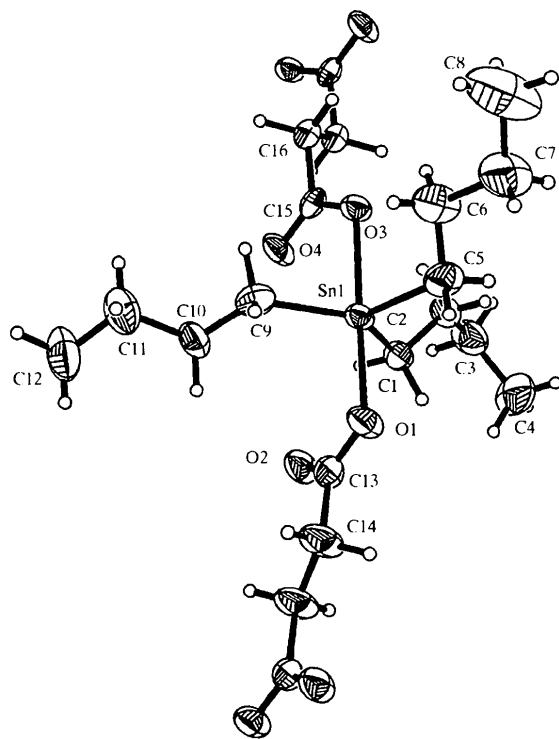


Fig. 1. ORTEP (Johnson, 1976) plot of the polyanionic tributyl(succinato)stannate chain of (I) at the 75% probability level. H atoms are drawn as spheres of arbitrary radii.

dicationic network. This dicationic entity comprises a centrosymmetric succinato dianion that uses its four carboxyl O-atom ends to interact with four dicyclohexylammonium groups [N···O 2.709 (7), 2.743 (7), 2.749 (7) and 2.771 (9) Å] and two water molecules [O···O 2.733 (8) and 2.775 (8) Å]. The dicationic entities are hydrogen bonded to the polyanionic chains [O2···O7 2.733 (8) and O4···N1 2.743 (7) Å] to give a sheet structure.

The solid-state ¹¹⁹Sn NMR chemical shift of -42.3 p.p.m. is similar to those found for five-coordinate tributyltin systems (Nadvornik *et al.*, 1984). In solution, the chemical shift of 103.1 p.p.m. indicates tetrahedral coordination; this geometry is also supported by the magnitude of the one-bond ¹¹⁹Sn-¹³C coupling constant of 367.7 Hz. The value is similar to that (365.8 Hz) measured for bis(tributyltin) oxide in chloroform (Nadvornik *et al.*, 1984).

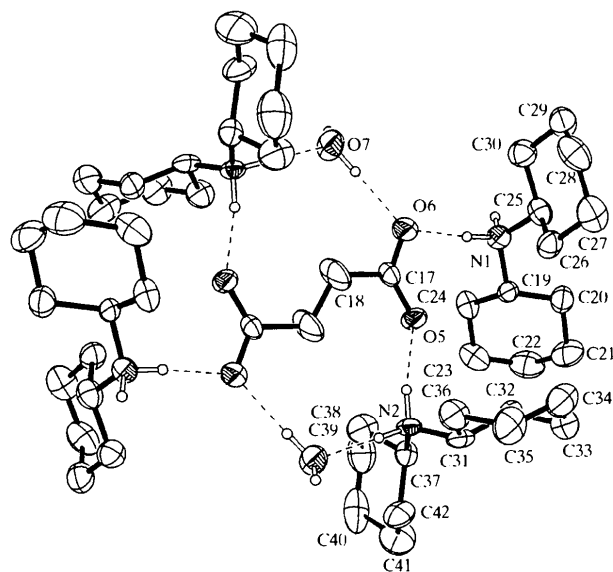


Fig. 2. ORTEP (Johnson, 1976) plot of the [tetrakis(dicyclohexylammonium) succinate dihydrate] dicationic network at the 75% probability level. H atoms are drawn as spheres of arbitrary radii.

Experimental

Dicyclohexylamine and succinic acid (1:1 molar ratio) were dissolved in a small volume of ethanol, and to the solution was added a 0.5 molar equivalent of bis(tributyltin) oxide. The mixture was heated briefly and slow cooling of the filtered solution yielded the ammonium stannate, which was recrystallized from ethanol. Analysis found C 59.70, H 10.00, N 3.26%; C₄₂H₈₃N₂O₇Sn requires C 59.57, H 9.88, N 3.31%. ¹¹⁹Sn Mössbauer (77 K): isomer shift 1.34, quadrupole splitting 3.26, τ_1 0.86, τ_2 0.86 mm s⁻¹. IR (Nujol): 3300 (water), 1661, 1552 cm⁻¹ (carboxyl). ¹³C NMR in CDCl₃ [chemical shift in p.p.m., ⁿJ(¹¹⁹Sn-¹³C) coupling constant in Hz]: C₁ = 16.18 (367.7), C₂ = 27.58 (19.9), C₃ = 26.79 (65.9), C₄ = 13.41 (-); -CO₂ = 178.36. -CH₂ (succinate) = 33.20; cyclohexyl C₁ = 52.43, C₂ = 29.61, C₃ = 24.66, C₄ =

25.06. ¹¹⁹Sn NMR in CDCl₃ = 103.1 p.p.m. (relative to tetramethyltin). The solid-state ¹¹⁹Sn NMR spectrum was recorded on a Bruker MSL 200 spectrometer equipped with a double-bearing CP/MAS probe: ¹¹⁹Sn NMR = -42.3 p.p.m. (relative to tetracyclohexyltin, δ = 176.0 p.p.m.). The solid-state ¹³C NMR spectrum was also recorded, but some of the butyl and cyclohexyl signals could not be assigned because of extensive overlap. The spectrum showed three carbonyl (177.11, 177.49 and 179.28 p.p.m.) and three methylene (37.11, 35.32 and 33.58 p.p.m.) signals. The carbon signals were referenced to the carbonyl C atom of glycine (δ = 176.0 p.p.m.). Positive chemical shifts denote downfield shifts with respect to the standard.

Crystal data

(C₁₂H₂₄N)₂[Sn(C₄H₄O₄)-
(C₄H₉)₃](C₄H₄O₄)_{1/2}·H₂O

M_r = 846.79

Triclinic

P $\bar{1}$

a = 13.068 (3) Å

b = 13.715 (3) Å

c = 14.312 (3) Å

α = 84.48 (2)°

β = 65.25 (2)°

γ = 86.76 (2)°

V = 2318.4 (9) Å³

Z = 2

D_x = 1.213 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 32 reflections

θ = 2.24–12.46°

μ = 0.596 mm⁻¹

T = 158 (2) K

Rhombohedral block

0.50 × 0.30 × 0.20 mm

Colorless

Data collection

Siemens P4 diffractometer

ω scan

Absorption correction:

ψ scan (North *et al.*, 1968)

T_{min} = 0.843, *T_{max}* = 0.888

8129 measured reflections

8081 independent reflections

5229 reflections with

I > 2σ(*I*)

R_{int} = 0.055

θ_{max} = 24.99°

h = -15 → 15

k = -16 → 16

l = 0 → 15

3 standard reflections

every 97 reflections

intensity decay: 6.84%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.069

wR(*F*²) = 0.160

S = 1.032

8080 reflections

477 parameters

H atoms riding, *U*(H) =

1.5*U*_{eq}(C,N); water H

atoms located and refined

w = 1/[σ²(*F_o*²) + (0.0506*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.665 e Å⁻³

Δρ_{min} = -0.555 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Sn1—C1	2.123 (7)	N1···O6	2.749 (7)
Sn1—C5	2.156 (7)	N2···O5	2.709 (7)
Sn1—C9	2.132 (7)	N2···O7'	2.771 (9)
Sn1—O1	2.230 (5)	O2···O7	2.733 (8)
Sn1—O3	2.279 (5)	O6···O7	2.775 (8)
N1···O4	2.743 (7)		
C1—Sn1—C5	112.4 (3)	C5—Sn1—O1	88.0 (2)
C1—Sn1—C9	134.4 (3)	C5—Sn1—O3	87.6 (2)

C1—Sn1—O1	93.3 (2)	C9—Sn1—O1	90.2 (2)
C1—Sn1—O3	91.4 (2)	C9—Sn1—O3	88.6 (2)
C5—Sn1—C9	113.1 (3)	O1—Sn1—O3	174.5 (2)

Symmetry code: (i) -1 - *x*, 1 - *y*, 1 - *z*.

Data collection: XSCANS (Siemens, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

We thank Professor Ward T. Robinson of the University of Canterbury for the diffraction measurements, and the National Science Council for R&D (IRPA 09-02-03-0371) for supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1058). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 752–755

Octabutyl-1κ²C,2κ²C,3κ²C,4κ²C-bis-μ₃-oxo-1:2:3κ³O;1:3:4κ³O-tetrakis-[μ-(2-pyridinecarboxylato *N*-oxide)]-1κ²O,O':2κO;2κO:3κ²O,O';3κ²O,O':4κO;-1κ²O,O':4κO-tetratin Hydrate

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Abstract

The unit cell of the title compound, bis[1,1,3,3-tetrabutyl-1,3-bis(picolinato *N*-oxide)distannoxane] hy-