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Dicyclohexylammonium (dicarboxylato)triorganostannates. Crystal structure of bis(dicyclohexylammonium) tris(malonato)tetrakis(tributylstannate)

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Abstract

In the crystal structure of bis(dicyclohexylammonium) tris(malonato)tetrakis(tributylstannate) the asymmetric unit comprises a bis(tributyltin)malonate molecule $(C_4H_9)_3Sn^1O_2CCH_2CO_2Sn^3(C_4H_9)_3$ (Sn^1–O 2.218(6), Sn^3–O 2.185(6) Å) connected to two dicyclohexylammonium malonatotributylstannate $\{[(cyclo\text{-}C_6H_{11})_2N^1H_2]^+[(C_4H_9)_3Sn^2O_2CCH_2CO_2]^-$ (Sn^2–O 2.169(6) Å), $[(cyclo\text{-}C_6H_{11})_2N^2H_2]^+$ $[(C_4H_9)_3Sn^4O_2CCH_2CO_2]^-$ (Sn^4–O 2.151(7) Å)$\}$ ion pairs by covalent (Sn^1–O 2.304(6), Sn^3–O 2.321(6) Å) bonds. The tin atom in each ion pair is further coordinatively linked to the carbonyl oxygen atoms of adjacent bis(tributyltin) malonate molecules. In the ion pairs, the ammonium nitrogen is hydrogen bonded ($N^1 \cdots$ O 2.866(9), 3.030(9); $N^2 \cdots$ O 2.842(10), 3.057(10) Å) to the carbonyl oxygens to form a six-membered ring. All four tin atoms in the compound are five-coordinate in distorted *trans*-C_3SnO_2 trigonal bipyramidal environments.

Introduction

Triorganotin carboxylates often form one-dimensional chain structures [1,2]. In the case of bis(triorganotin) esters of dicarboxylic acids, the presence of an additional carboxyl group gives rise to three-dimensional networks [3,4]. The structures of three dicyclohexylammonium mono(triorganotin)dicarboxylates have recently been reported. In the 2,6-pyridinedicarboxylatotributylstannate the dicarboxylato group links the triorganotin groups into a linear infinite chain [5], as does the corresponding ligand in the succinatotriphenylstannate [6]. In tris(oxalato)te-

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Table 1

Non-hydrogen positional and isotropic displacement parameters

Atom	x	y	z	U_{eq} (Å^2)
Sn(1)	0.80115(2)	0.08654(2)	0.24142(3)	0.0833(3)
Sn(2)	0.68131(2)	0.42258(2)	0.23423(4)	0.0932(3)
Sn(3)	0.60116(3)	0.17159(2)	0.22416(3)	0.0858(3)
Sn(4)	0.84410(2)	0.13759(3)	−0.05899(3)	0.0831(3)
C(1)	0.6624(3)	0.0503(3)	0.3140(4)	0.076(4)
C(11)	0.6455(3)	0.0998(3)	0.3015(4)	0.082(4)
O(111)	0.6275(2)	0.1037(2)	0.2517(3)	0.101(3)
O(112)	0.6487(2)	0.1303(2)	0.3375(3)	0.092(3)
C(12)	0.7092(3)	0.0399(3)	0.2897(4)	0.078(4)
O(121)	0.7344(2)	0.0748(2)	0.2841(3)	0.094(3)
O(122)	0.7202(2)	−0.0012(2)	0.2774(3)	0.101(3)
C(2)	0.5932(3)	0.2990(3)	0.2561(4)	0.090(4)
C(21)	0.6111(3)	0.3470(3)	0.2464(4)	0.091(4)
O(211)	0.5840(2)	0.3793(2)	0.2414(3)	0.119(3)
O(212)	0.6534(2)	0.3531(2)	0.2469(3)	0.105(3)
C(22)	0.5614(3)	0.2805(3)	0.2101(4)	0.079(4)
O(221)	0.5683(2)	0.2403(2)	0.1909(3)	0.091(3)
O(222)	0.5305(2)	0.3063(2)	0.1944(3)	0.099(3)
C(3)	0.8524(3)	0.1588(3)	0.1276(4)	0.085(4)
C(31)	0.8868(3)	0.1328(3)	0.1653(4)	0.081(4)
O(311)	0.8707(2)	0.1050(2)	0.2012(3)	0.095(3)
O(312)	0.9271(2)	0.1408(2)	0.1593(3)	0.103(3)
C(32)	0.8647(3)	0.1595(3)	0.0654(4)	0.076(4)
O(321)	0.8354(2)	0.1413(2)	0.0321(3)	0.093(3)
O(322)	0.9006(2)	0.1776(2)	0.0478(3)	0.100(3)
C(11A)	0.7831(6)	0.0523(7)	0.1610(8)	0.30(1)
C(11B)	0.7459(7)	0.0709(7)	0.1443(7)	0.29(1)
C(11C)	0.721(1)	0.0421(9)	0.0895(9)	0.46(2)
C(11D)	0.749(1)	0.013(1)	0.055(1)	0.49(2)
C(12A)	0.7913(5)	0.1586(4)	0.2646(5)	0.150(7)
C(12B)	0.8173(6)	0.1863(6)	0.293(1)	0.30(1)
C(12C)	0.8029(7)	0.2333(5)	0.3104(9)	0.32(1)
C(12D)	0.819(1)	0.2488(8)	0.354(2)	0.65(4)
C(13A)	0.8389(4)	0.0432(6)	0.2946(8)	0.26(1)
C(13B)	0.8329(6)	0.0203(7)	0.327(1)	0.32(1)
C(13C)	0.8686(8)	−0.0238(8)	0.3534(8)	0.36(2)
C(13D)	0.863(1)	−0.0131(9)	0.3999(9)	0.44(2)
C(21A)	0.6633(4)	0.4258(4)	0.1456(5)	0.138(6)
C(21B)	0.7061(7)	0.4231(7)	0.1006(9)	0.34(2)
C(21C)	0.708(1)	0.3911(8)	0.083(1)	0.65(3)
C(21D)	0.747(1)	0.394(1)	0.039(1)	0.55(3)
C(22A)	0.7465(4)	0.3959(4)	0.2489(6)	0.173(7)
C(22B)	0.7664(5)	0.4000(6)	0.2998(8)	0.26(1)
C(22C)	0.8214(6)	0.3895(8)	0.304(1)	0.39(2)
C(22D)	0.8331(9)	0.394(1)	0.361(1)	0.61(3)
C(23A)	0.6443(4)	0.4572(4)	0.2986(5)	0.121(6)
C(23B)	0.6410(5)	0.4327(4)	0.3554(6)	0.163(7)
C(23C)	0.6163(5)	0.4575(6)	0.4011(6)	0.21(1)
C(23D)	0.6108(8)	0.4319(9)	0.4528(7)	0.35(2)
C(31A)	0.6667(4)	0.2002(3)	0.2154(5)	0.129(6)
C(31B)	0.6773(5)	0.2236(5)	0.1590(7)	0.23(1)
C(31C)	0.7164(7)	0.2339(8)	0.1435(8)	0.32(1)
C(31D)	0.7284(7)	0.2525(7)	0.0914(9)	0.32(1)

Table 1 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(32A)	0.5570(4)	0.1778(4)	0.2941(5)	0.130(6)
C(32B)	0.5101(5)	0.1780(6)	0.2875(7)	0.23(1)
C(32C)	0.4811(5)	0.1813(6)	0.3415(7)	0.23(1)
C(32D)	0.4369(7)	0.1838(8)	0.3276(9)	0.34(2)
C(33A)	0.5779(6)	0.1434(4)	0.1492(6)	0.209(9)
C(33B)	0.5611(6)	0.1053(6)	0.1437(6)	0.24(1)
C(33C)	0.5458(6)	0.0858(5)	0.0836(8)	0.25(1)
C(33D)	0.5151(7)	0.0522(6)	0.0858(8)	0.28(1)
C(41A)	0.9033(4)	0.0973(4)	−0.0579(5)	0.130(6)
C(41B)	0.9153(5)	0.0655(5)	−0.0096(7)	0.207(9)
C(41C)	0.8830(5)	0.0283(5)	−0.0051(7)	0.206(9)
C(41D)	0.898(1)	−0.0060(7)	0.040(1)	0.41(2)
C(42A)	0.8525(7)	0.2131(4)	−0.0852(7)	0.27(1)
C(42B)	0.8297(9)	0.2359(9)	−0.0529(8)	0.41(2)
C(42C)	0.828(1)	0.2824(9)	−0.097(1)	0.49(3)
C(42D)	0.807(1)	0.3074(6)	−0.071(1)	0.42(2)
C(43A)	0.7765(3)	0.1098(4)	−0.0669(4)	0.114(5)
C(43B)	0.7400(4)	0.1398(6)	−0.0333(5)	0.185(8)
C(43C)	0.6920(5)	0.1209(7)	−0.0403(7)	0.25(1)
C(43D)	0.6568(6)	0.151(1)	−0.0101(9)	0.43(2)
N(1)	0.4872(2)	0.3948(2)	0.2404(3)	0.083(3)
C(111)	0.4669(3)	0.3860(4)	0.2996(4)	0.100(5)
C(112)	0.4997(4)	0.4019(4)	0.3436(5)	0.141(6)
C(113)	0.4810(5)	0.3886(5)	0.4039(5)	0.182(8)
C(114)	0.4705(5)	0.3390(5)	0.4087(6)	0.179(8)
C(115)	0.4387(4)	0.3244(4)	0.3635(5)	0.152(7)
C(116)	0.4583(4)	0.3350(4)	0.3038(5)	0.120(6)
C(121)	0.5013(3)	0.4450(3)	0.2261(4)	0.099(5)
C(122)	0.4633(4)	0.4782(4)	0.2337(6)	0.139(6)
C(123)	0.4787(5)	0.5279(4)	0.2170(7)	0.178(8)
C(124)	0.4959(5)	0.5292(4)	0.1562(7)	0.184(8)
C(125)	0.5331(4)	0.4947(4)	0.1471(7)	0.174(8)
C(126)	0.5163(4)	0.4463(4)	0.1646(5)	0.125(6)
N(2)	0.9804(2)	0.2174(2)	0.0971(3)	0.092(4)
C(211)	1.0087(4)	0.2044(4)	0.0465(5)	0.112(5)
C(212)	1.0516(4)	0.2341(4)	0.0465(5)	0.148(7)
C(213)	1.0791(5)	0.2214(7)	0.0002(6)	0.23(1)
C(214)	1.0939(5)	0.1705(6)	0.0035(6)	0.214(9)
C(215)	1.0505(5)	0.1379(5)	0.0079(6)	0.200(9)
C(216)	1.0206(4)	0.1544(4)	0.0550(5)	0.131(6)
C(221)	0.9672(4)	0.2680(3)	0.1029(5)	0.124(6)
C(222)	0.9419(5)	0.2826(4)	0.0482(6)	0.182(8)
C(223)	0.9220(7)	0.3344(5)	0.0600(9)	0.34(1)
C(224)	0.8881(7)	0.3304(6)	0.100(1)	0.37(2)
C(225)	0.9149(5)	0.3194(5)	0.1586(8)	0.24(1)
C(226)	0.9357(4)	0.2702(4)	0.1517(6)	0.154(7)

trakis(tributylstannate), two oxalatotributylstannate anions flank a neutral bis(tributyltin) oxalate molecule to form a short tetranuclear chain [7]. The structure of the tris(malonato)tetrakis(tributylstannate) has now been determined as an extension of the study of the oxalatostannate.

Table 2

Bond distances (Å) and angles (°) [a]

Sn(1)–O(121)	2.218(6)	C(12A)–C(12B)	1.29(2)	C(121)–C(126)	1.50(2)
Sn(1)–O(311)	2.304(6)	C(12B)–C(12C)	1.46(2)	C(122)–C(123)	1.54(2)
Sn(1)–C(11A)	2.19(2)	C(12C)–C(12D)	1.21(4)	C(123)–C(124)	1.51(2)
Sn(1)–C(12A)	2.15(1)	C(13A)–C(13B)	1.02(3)	C(124)–C(125)	1.48(2)
Sn(1)–C(13A)	2.08(2)	C(13B)–C(13C)	1.75(3)	C(125)–C(126)	1.52(2)
Sn(2)–O(212)	2.169(6)	C(13C)–C(13D)	1.14(3)	N(2)–C(211)	1.49(1)
Sn(2)–O(122′)	2.473(6)	C(21A)–C(21B)	1.64(2)	N(2)–C(221)	1.50(1)
Sn(2)–C(21A)	2.14(1)	C(21B)–C(21C)	1.00(3)	C(211)–C(212)	1.52(2)
Sn(2)–C(22A)	2.08(1)	C(21C)–C(21D)	1.54(4)	C(211)–C(216)	1.49(2)
Sn(2)–O(23A)	2.10(1)	C(22A)–C(22B)	1.33(2)	C(212)–C(213)	1.40(2)
Sn(3)–O(111)	2.185(6)	C(22B)–C(22C)	1.64(2)	C(213)–C(214)	1.52(3)
Sn(3)–O(221)	2.321(6)	C(22C)–C(22D)	1.39(4)	C(214)–C(215)	1.58(2)
Sn(3)–C(31A)	2.10(1)	C(23A)–C(23B)	1.51(2)	C(215)–C(216)	1.48(2)
Sn(3)–C(32A)	2.09(1)	C(23B)–C(23C)	1.47(2)	C(221)–C(222)	1.54(2)
Sn(3)–C(33A)	2.05(1)	C(23C)–C(23D)	1.42(2)	C(221)–C(226)	1.47(2)
Sn(4)–O(321)	2.151(7)	C(31A)–C(31B)	1.51(2)	C(222)–C(223)	1.62(2)
Sn(4)–O(112″)	2.443(7)	C(31B)–C(31C)	1.23(2)	C(223)–C(224)	1.37(3)
Sn(4)–C(41A)	2.08(1)	C(31C)–C(31D)	1.38(3)	C(224)–C(225)	1.61(3)
Sn(4)–C(42A)	2.26(1)	C(32A)–C(32B)	1.38(2)	C(225)–C(226)	1.54(2)
Sn(4)–C(43A)	2.14(1)	C(32B)–C(32C)	1.53(2)		
C(1)–C(11)	1.53(1)	C(32C)–C(32D)	1.33(3)		
C(1)–C(12)	1.51(1)	C(33A)–C(33B)	1.20(2)		
C(11)–O(111)	1.29(1)	C(33B)–C(33C)	1.58(2)		
C(11)–O(112)	1.22(1)	C(41A)–C(41B)	1.49(2)		
C(12)–O(121)	1.25(1)	C(41B)–C(41C)	1.43(2)		
C(12)–O(122)	1.25(1)	C(41C)–C(41D)	1.50(3)		
C(2)–C(21)	1.49(1)	C(42A)–C(42B)	1.20(3)		
C(2)–C(22)	1.52(1)	C(42B)–C(42C)	1.69(3)		
C(21)–O(211)	1.22(1)	C(42C)–C(42D)	1.13(4)		
C(21)–O(212)	1.25(1)	C(43A)–C(43B)	1.58(2)		
C(22)–O(221)	1.25(1)	C(43B)–C(43C)	1.51(2)		
C(22)–O(222)	1.22(1)	C(43C)–C(43D)	1.52(3)		
C(3)–C(31)	1.53(1)	N(1)–C(111)	1.53(1)		
C(3)–C(32)	1.50(1)	N(1)–C(121)	1.53(1)		
C(31)–O(311)	1.25(1)	C(111)–C(112)	1.48(2)		
C(31)–O(312)	1.21(1)	C(111)–C(116)	1.49(1)		
C(32)–O(321)	1.27(1)	C(112)–C(113)	1.56(2)		
C(32)–O(322)	1.24(1)	C(113)–C(114)	1.46(2)		
C(11A)–C(11B)	1.27(3)	C(114)–C(115)	1.47(2)		
C(11B)–C(11C)	1.69(3)	C(115)–C(116)	1.54(2)		
C(11C)–C(11D)	1.41(4)	C(121)–C(122)	1.47(1)		

O(121)–Sn(1)–O(311)	175.0(2)	C(21A)–Sn(2)–O(122′)	88.2(3)
O(121)–Sn(1)–C(11A)	96.1(5)	C(22A)–Sn(2)–C(23A)	121.7(5)
O(121)–Sn(1)–C(12A)	85.1(4)	C(22A)–Sn(2)–O(122′)	85.5(4)
O(121)–Sn(1)–C(13A)	96.1(4)	C(23A)–Sn(2)–O(122′)	84.3(3)
O(311)–Sn(1)–C(11A)	87.9(5)	O(111)–Sn(3)–O(221)	175.1(2)
O(311)–Sn(1)–C(12A)	90.1(4)	O(111)–Sn(3)–C(31A)	93.1(3)
O(311)–Sn(1)–C(13A)	85.0(4)	O(111)–Sn(3)–C(32A)	93.6(4)
C(11A)–Sn(1)–C(12A)	127.9(6)	O(111)–Sn(3)–C(33A)	91.2(4)
C(11A)–Sn(1)–C(13A)	112.2(7)	O(221)–Sn(3)–C(31A)	90.9(3)
C(12A)–Sn(1)–C(13A)	119.4(6)	O(221)–Sn(3)–C(32A)	86.2(3)
O(212)–Sn(2)–C(21A)	94.5(4)	O(221)–Sn(3)–C(33A)	84.7(4)
O(212)–Sn(2)–C(22A)	89.2(4)	C(31A)–Sn(3)–C(32A)	127.5(4)
O(212)–Sn(2)–C(23A)	98.0(3)	C(31A)–Sn(3)–C(33A)	111.9(6)
O(212)–Sn(2)–O(122′)	174.6(2)	C(32A)–Sn(3)–C(33A)	119.9(6)
C(21A)–Sn(2)–C(22A)	113.6(5)	O(321)–Sn(4)–C(41A)	96.6(4)
C(21A)–Sn(2)–C(23A)	123.2(4)	O(321)–Sn(4)–C(42A)	103.5(4)

Table 2 (continued)

O(321)–Sn(4)–C(43A)	89.7(3)	C(23B)–C(23C)–C(23D)	115(2)
O(321)–Sn(4)–O(112″)	177.3(2)	Sn(3)–C(31A)–C(31B)	116.5(9)
C(41A)–Sn(4)–C(42A)	116.3(6)	C(31A)–C(31B)–C(31C)	123(2)
C(41A)–Sn(4)–C(43A)	124.4(4)	C(31B)–C(31C)–C(31D)	126(2)
C(41A)–Sn(4)–O(112″)	83.8(4)	Sn(3)–C(32A)–C(32B)	122(1)
C(42A)–Sn(4)–C(43A)	115.6(6)	C(32A)–C(32B)–C(32C)	117(1)
C(42A)–Sn(4)–O(112″)	78.6(4)	C(32B)–C(32C)–C(32D)	110(2)
C(43A)–Sn(4)–O(112″)	87.9(3)	Sn(3)–C(33A)–C(33B)	126(1)
C(11)–C(1)–C(12)	113.8(7)	C(33A)–C(33B)–C(33C)	122(1)
C(1)–C(11)–O(11)	112.8(8)	C(33B)–C(33C)–C(33D)	115(2)
C(1)–C(11)–O(112)	120.5(8)	Sn(4)–C(41A)–C(41B)	122.8(9)
O(111)–C(11)–O(112)	126.6(8)	C(41A)–C(41B)–C(41C)	111(1)
Sn(3)–O(111)–C(11)	119.3(5)	C(41B)–C(41C)–C(41D)	110(2)
C(11′)–O(112′)–Sn(4)	139.0(6)	Sn(4)–C(42A)–C(42B)	107(1)
C(1)–C(12)–O(121)	114.8(8)	C(42A)–C(42B)–C(42C)	93(2)
C(1)–C(12)–O(122)	120.2(8)	C(42B)–C(42C)–C(42D)	100(2)
O(121)–C(12)–O(122)	125.0(8)	Sn(4)–C(43A)–C(43B)	112.3(7)
Sn(1)–O(121)–C(12)	133.6(6)	C(43A)–C(43B)–C(43C)	112(1)
C(12″)–O(122″)–Sn(2)	137.3(5)	C(43B)–C(43C)–C(43D)	112(2)
C(21)–C(2)–C(22)	115.5(8)	C(111)–N(1)–C(121)	117.2(7)
C(2)–C(21)–O(211)	118.9(8)	N(1)–C(111)–C(112)	109.2(8)
C(2)–C(21)–O(212)	118.5(8)	N(1)–C(111)–C(116)	106.7(8)
O(211)–C(21)–O(212)	122.5(8)	C(112)–C(111)–C(116)	111.5(9)
Sn(2)–O(212)–C(21)	120.0(6)	C(111)–C(112)–C(113)	109(1)
C(2)–C(22)–O(221)	118.5(8)	C(112)–C(113)–C(114)	112(1)
C(2)–C(22)–O(222)	117.0(8)	C(113)–C(114)–C(115)	111(1)
O(221)–C(22)–O(222)	124.5(8)	C(114)–C(115)–C(116)	111(1)
Sn(3)–O(221)–C(22)	136.4(6)	C(111)–C(116)–C(115)	108.3(9)
C(31)–C(3)–C(32)	114.2(7)	N(1)–C(121)–C(122)	112.0(8)
C(3)–C(31)–O(311)	116.7(7)	N(1)–C(121)–C(126)	108.1(8)
C(3)–C(31)–O(312)	118.8(8)	C(122)–C(121)–C(126)	108.7(9)
O(311)–C(31)–O(312)	124.5(8)	C(121)–C(122)–C(123)	110(1)
Sn(1)–O(311)–C(31)	138.9(6)	C(122)–C(123)–C(124)	
C(3)–C(32)–O(321)	115.3(8)	C(123)–C(124)–C(125)	111(1)
C(3)–C(32)–O(322)	122.0(8)	C(124)–C(125)–C(126)	109(1)
O(321)–C(32)–O(322)	122.7(8)	C(121)–C(126)–C(125)	112(1)
Sn(4)–O(321)–C(32)	123.2(5)	C(211)–N(2)–C(221)	117.0(8)
Sn(1)–C(11A)–C(11B)	107(1)	N(2)–C(211)–C(212)	108.5(8)
C(11A)–C(11B)–C(11C)	113(2)	N(2)–C(211)–C(216)	105.3(8)
C(11B)–C(11C)–C(11D)	118(2)	C(212)–C(211)–C(216)	110.3(9)
Sn(1)–C(12A)–C(12B)	130(1)	C(211)–C(212)–C(213)	109(1)
C(12A)–C(12B)–C(12C)	122(2)	C(212)–C(213)–C(214)	112(1)
C(12B)–C(12C)–C(12D)	117(2)	C(213)–C(214)–C(215)	110(1)
Sn(1)–C(13A)–C(13B)	138(1)	C(214)–C(215)–C(216)	110(1)
C(13A)–C(13B)–C(13C)	128(2)	C(211)–C(216)–C(215)	110(1)
C(13B)–C(13C)–C(13D)	93(2)	N(2)–C(221)–C(222)	108.2(9)
Sn(2)–C(21A)–C(21B)	116(1)	N(2)–C(221)–C(226)	105.9(8)
C(21A)–C(21B)–C(21C)	111(2)	C(222)–C(221)–C(226)	110(1)
C(21B)–C(21C)–C(21D)	106(3)	C(221)–C(222)–C(223)	106(1)
Sn(2)–C(22A)–C(22B)	121(1)	C(222)–C(223)–C(224)	108(1)
C(22A)–C(22B)–C(22C)	118(1)	C(223)–C(224)–C(225)	104(2)
C(22B)–C(22C)–C(22D)	106(2)	C(224)–C(225)–C(226)	106(1)
Sn(2)–C(23A)–C(23B)	116.5(8)	C(221)–C(226)–C(225)	112(1)
C(23A)–C(23B)–C(23C)	117(1)		

[a] Symmetry operations: (′) $x, \frac{1}{2}+y, \frac{1}{2}-z$; (″) $1\frac{1}{2}-x, y, z-\frac{1}{2}$.

Experimental

Preparations

(a) Bis(dicyclohexylammonium)tris(malonato)tetrakis(tributylstannate) was prepared as previously described [7]. Recrystallization of the compound from ethanol afforded colorless crystals suitable for X-ray analysis.

(b) Bis(dicyclohexylammonium) hydronium bis(succinato)tributylstannate was made by mixing dicyclohexylamine (0.91 g, 5 mmol), succinic acid (1.77 g, 15 mmol), and bis(tributyltin) oxide (5.96 g, 10 mmol) in a small volume of ethanol. It was purified by recrystallization from an acetonitrile/hexane mixture. Anal. Found: C, 58.00; H, 9.90; N, 3.08. $C_{44}H_{86}N_2O_9Sn$ calc.: C, 58.36; H, 9.51; N, 3.09%. ^{13}C NMR in $CDCl_3$ [$\delta(^nJ)$]: butyl carbons C1 16.2 (363.3), C2 27.6 (19.7), C3 26.8 (66.5), C4 13.4 ppm (−Hz); cyclohexyl carbons 24.6, 24.9, 29.0, 52.5 ppm; carboxylate carbon 178.3 ppm; methylene carbon 32.7 ppm. The presence of water in the compound was indicated by the peak at *ca.* 3500 cm^{-1} in the infrared spectrum.

(c) Dicyclohexylammonium oxalatotributylstannate was made (90% yield before purification) by mixing dicyclohexylamine (3.62 g, 20 mmol), oxalic acid dihydrate (2.52 g, 20 mmol) and bis(tributyltin) oxide (5.96 g, 10 mmol) in a small volume of toluene. It was purified by recrystallization from toluene to give a gel-like product that turns to a powder when washed with hexane. Anal. Found: C, 55.90; H, 9.26; N, 2.56. $C_{26}H_{51}NO_4Sn$ calc.: C, 55.72; H, 9.17; N, 2.49%. ^{13}C NMR in $CDCl_3$ [$\delta(^nJ)$]: butyl carbons C1 19.5 (386.2), C2 27.9 (19.8), C3 27.1 (67.4), C4 13.6 ppm (−Hz); cyclohexyl carbons 24.6, 25.0, 28.7, 52.4 ppm; carboxylate carbon 166.1 ppm. ^{119m}Sn Mössbauer (78 K): *IS* 1.20, *QS* 2.69, Γ_1 0.90, Γ_2 0.92 mm s^{-1}.

Crystallography

Unique intensity data (17179) for the colorless cuboidal crystal fragment (approx. 0.55 mm) of the tris(malonato)tetrakis(tributylstannate) were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with an extended counter arm by the $\theta/2\theta$ scan mode up to $2\theta = 50°$ (monochromatic Mo-K_α radiation, λ 0.71069 Å). The 6802 $I \geq 3\sigma(I)$ reflections were corrected for absorption effects by a Gaussian procedure ($A^*_{min,max}$ 1.52, 1.58). The heavy atoms were located by vector methods and the remaining non-H atoms from difference maps; thermal parameters of all non-H atoms were refined anisotropically. Hydrogen atom parameters were kept in calculated positions. Refinement converged at $R = 5.4\%$ ($R_w = 5.1\%$). All computations were performed with the XTAL 3.0 program system devised by Hall [8]. Fractional coordinates are given in Table 1 and bond distances and angles in Table 2. Figure 1 is a plot of the asymmetric unit and Fig. 2 is a projection of the packing of the tetranuclear chain on the *bc* plane. Figure 3 shows the hydrogen bonding scheme in the tetranuclear chain.

Crystal data: $C_{81}H_{158}N_2O_{12}Sn_4$, *MW* 1826.9, orthorhombic, *Pcab*, *a* 29.27(1), *b* 28.62(2), *c* 23.41 (2) Å, *V* 19608 Å^3, D_X 1.24 g cm^{-3}, μ 9.6 cm^{-1} for $Z = 8$.

Results and discussion

The structure of bis(dicyclohexylammonium) tris(oxalato)tetrakis(tributylstannate) bis-ethanol contains a centrosymmetric tetranuclear dianion (Fig. 4). Unlike the situation for most triorganotin mono(alkanoates) the dianion does not give rise

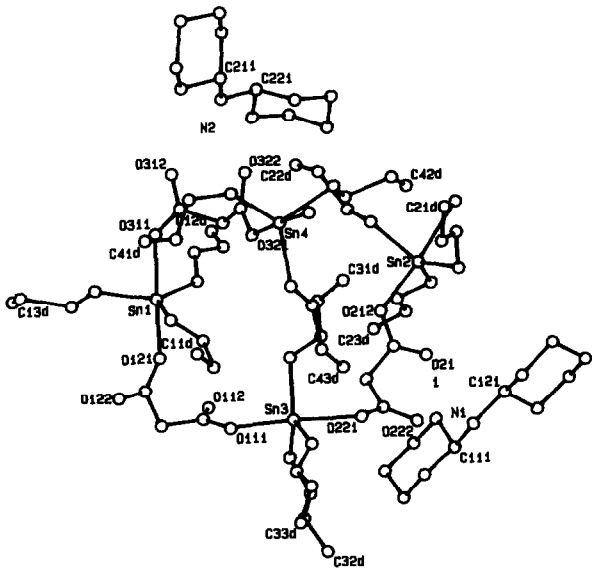

Fig. 1. The asymmetric unit of bis(dicyclohexylammonium) tris(malonato)tetrakis(tributylstannate) (hydrogen atoms not shown).

to an infinite chain in the crystal because the terminal tin atoms are coordinated by ethanol molecules [7].

The tris(malonato)tetrakis(tributylstannate) analogue (which was prepared in the same way in ethanol) also contains a neutral bis(tributyltin)dicarboxylate molecule linked to a pair of (dicarboxylato)tributylstannate anions to form a tetranuclear chain. However, in this compound, each dicyclohexylammonium cation is hydrogen bonded (N1 $\cdots$ O 2.866(9), 3.030(9); N2 $\cdots$ O 2.842(10), 3.057(10) Å) to only one malonato ligand, facilitating the formation of relatively strain-free

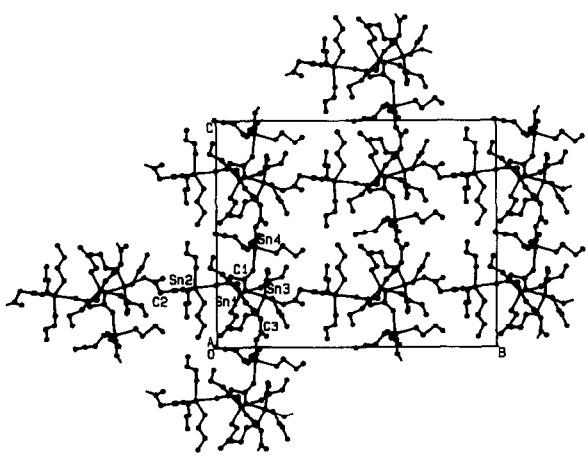

Fig. 2. Projection of the packing (asymmetric units that are related by $-x$, $-y$, $-z$ omitted) on the *bc* face showing the tris(malonato)tetrakis(tributylstannate) chains linked into rings; dicyclohexylammonium cations are omitted.

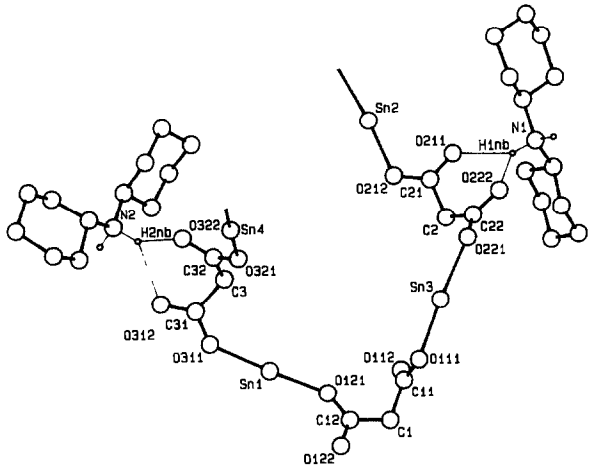

Fig. 3. The hydrogen bonding system that gives rise to the six-membered rings in the tris(malonato)tetrakis(tributylstannate) ion; ammonium hydrogens are shown but butyl groups omitted.

six-membered rings. Additional hydrogen-bonding interactions of the type present in the oxalato stannate case, are not present in this case. The absence of such interactions presumably frees the central malonate ligand to coordinate (Sn2 ← O122′ 2.473(6), Sn4 ← O112″ 2.443(7) Å) to the tin atoms of neighboring asymmetric units (′: $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; ″: $1\frac{1}{2}-x$, y, $z-\frac{1}{2}$), thereby giving rise to a three-dimensional network structure (Figs. 2 and 5).

In the tris(malonato)tetrakis(tributylstannate), the four tin atoms have the common *trans*-trigonal bipyramidal geometry. Although the Sn1 and Sn3 atoms can be considered to bear a formal negative charge, their bonds to oxygen are

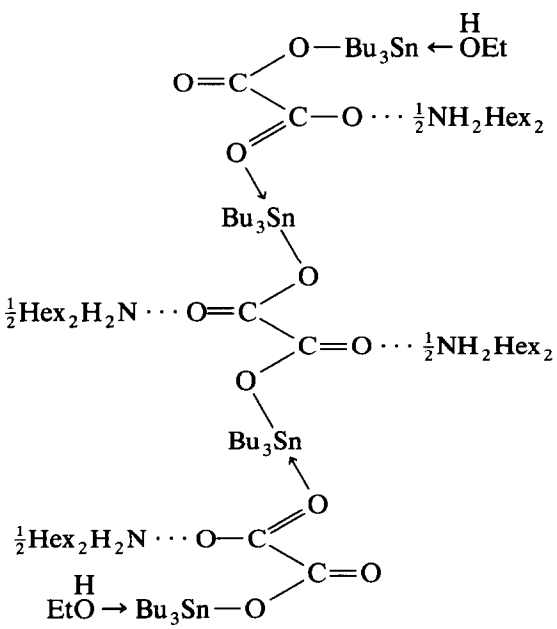

Fig. 4. Structure of bis(dicyclohexylammonium) tris(oxalato)tetrakis(tributylstannate)·2ethanol.

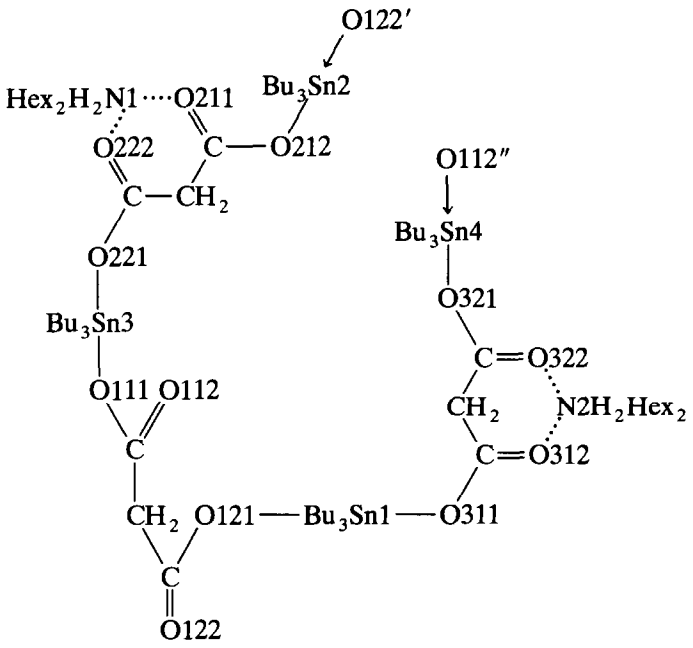

Fig. 5. Schematic representation of the asymmetric unit of bis(dicyclohexylammonium) tris(malonato)tetrakis(tributylstannate). Symmetry transformations: (′) $x, \frac{1}{2}+y, \frac{1}{2}-z$; (″) $1\frac{1}{2}-x, y, z-\frac{1}{2}$.

covalent and similar in length; for Sn1 the two tin–oxygen distances are 2.218(6) and 2.304(6) Å, and for Sn3 the distances are 2.185(6) and 2.321(6) Å. These values agree well with that of 2.214(2) Å for the tin–oxygen bond distance in the succinatotriphenylstannate polyanion; in the latter the tin atom lies on a crystallographic two-fold axis which also passes through the centre of the bond joining the methylene carbons of the succinato ligand [6]. This 2.214(2) Å distance can be considered as representative of the tin–oxygen distance in negatively-charged five-coordinate triorganostannates. The tin–oxygen bond distances in the 2,6-pyridinedicarboxylatotributylstannate polyanion (2.26(1), 2.31(1) Å [1]) and in the bis(2,6-xylyloxy)trimethylstannate (2.212(7), 2.225(7) Å [9]) are only marginally different. For the tris(malonato)tetrakis(tributylstannate) species, both short and long tin–oxygen distances are observed for the Sn2 and Sn4 atoms, the longer bonds within the pair of values for the Sn2 (2.169(6), 2.473(6) Å) and Sn4 (2.151(7), 2.443(7) Å) being clearly of the dative type.

A compound tentatively identified as bis(dicyclohexylammonium) hydronium bis(succinato)tributylstannate was obtained from succinic acid, dicyclohexylamine, and bis(tributyltin) oxide in ethanol. A non-crystallizable oil was obtained in the case of glutaric acid, and from adipic acid, bis(tributyltin)adipate was obtained.

For the reaction between bis(tributyltin) oxide and malonic acid the use of either a primary amine (*e.g.*, trishydroxymethylmethylamine) or a tertiary amine (*e.g.*, diethylethanolamine) in place of dicyclohexylamine led to formation of bis(tributyltin)malonate; the observations suggest that a secondary amine is crucial in stabilizing the structure. The choice of solvent also appears to influence the product. Thus, the reaction between dicyclohexylammonium hydrogen oxalate and bis(tributyltin) oxide in toluene as solvent gave the desired simple stannate,

dicyclohexylammonium oxalatotributylstannate. From the magnitude of the ^{119m}Sn Mössbauer quadrupole splitting of this oxalatotributylstannate, the geometry at tin is judged to be *cis*-C_3SnO_2 trigonal bipyramidal, which requires the oxalato ligand to chelate to the metal.

Acknowledgments

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