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Synthesis of triorganostannate esters of dicarboxylic acids. Crystal structure of bis(dicyclohexylammonium) trisoxalatotetrakis(tri-n-butylstannate) · 2 ethanol

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Abstract

Triphenyltin hydroxide has been shown to react with dicyclohexylammonium oxalate to give $[(\text{cyclo-}C_6H_{11})_2NH_2]^+$ $[(C_6H_5)_3SnOC(O)C(O)O]^-$, and to give with dicyclohexylammonium malonate $[(\text{cyclo-}C_6H_{11})_2NH_2]^+$ $\{[(C_6H_5)_3SnOC(O)CH_2C(O)O]_2H\}^-$. Bis(tri-n-butyltin) oxide afforded $2[(\text{cyclo-}C_6H_{11})_2NH_2]^+$ $\{[(n\text{-}C_4H_9)_3Sn]_4[OC(O)CH_2C(O)O]_3\}^{2-}$ on treatment with dicyclohexylammonium malonate, but with dicyclohexylammonium oxalate it yielded a stannate which crystallized with two molecules of ethanol. A low-temperature X-ray diffraction study of this ethanol-containing stannate, $2[(\text{cyclo-}C_6H_{11})_2NH_2]^+$ $[C_2H_5OH \cdot (n\text{-}C_4H_9)_3SnOC(CO_2)({=}O)(n\text{-}C_4H_9)_3SnOC({=}O)\text{–}]_2{}^{2-}$ revealed the presence of centrosymmetric chains, each consisting of four $[(n\text{-}C_4H_9)_3Sn]^+$ cations linked by three $[OC(O)C(O)]^{2-}$ anions. The chains are hydrogen bonded by $[(\text{cyclo-}C_6H_{11})_2NH_2]^+$ cations and ethanol molecules into a three-dimensional lattice. The geometry around the ethanol-coordinated (Sn–O 2.465(4) Å) terminal tin atom is essentially a *trans*-C_3SnO_2 trigonal bipyramid, but is distorted towards a C_3SnO_3 skew-trapezoidal bipyramid; the tin atom is part of a five-membered $\overline{\mathrm{Sn{-}O{-}C{-}C{-}O}}$ ring in which the O–Sn–O angle is 63.4(1)° and Sn–O distances are 2.191(3) and 2.890(3) Å. The geometry around the inner tin atom is a less distorted *trans*-C_3SnO_2 trigonal bipyramid; the four Sn–O–C–O (Sn · · · O 3.043(3) Å) atoms do not form a ring owing to the small chelate bite.

Introduction

If the chelating ability of the $[OC(O)C(O)O]^{2-}$ oxalate, previously established for its diorganotin [1,2] complexes, is preserved in the $[R_3SnOC(O)C(O)O]^-$ anion the tin atom in this hypothetical triorganostannate would be five-coordinated, in which case its geometry would be either square pyramidal [3] or *cis*-trigonal bipyramidal. Such carboxylatotriorganostannates have not previously been synthesized. In this study, the results of the synthesis of the stannate esters of oxalic and malonic acids are reported, with results of a crystallographic study of an ethanol-coordinated stannate.

Experimental

Synthesis

In an attempt to prepare $[(c\text{-}C_6H_{11})_2NH]^+$ $[(n\text{-}C_4H_9)_3SnOC(O)C(O)O]^-$ (c = cyclo) a molar equivalent of bis(tri-n-butyltin) oxide was added to a hot ethanol solution containing two molar equivalents of dicyclohexylamine and oxalic acid dihydrate. Evaporation of the solvent yielded a semi-solid material which was filtered off under suction and crystallized from ethanol to give crystals whose ^{13}C NMR spectrum indicated the presence of ethanol. The same compound was obtained in higher yield when the tin oxide/acid/amine mole ratio was changed to 1/1.5/1. It does not melt but chars over a range of temperature. Crystals suitable for X-ray diffraction were obtained from an ethanol/hexane solution. Anal. Found: C, 52.52; H, 9.26; N, 1.55. $C_{82}H_{168}N_2O_{14}Sn_4$ calcd.: C, 52.37; H, 8.94; N, 1.49%. ^{13}C NMR in $CDCl_3$: n-butyl carbons C(1) 18.3 (372.2), C(2) 27.7 (20.6), C(3) 26.9 (58.7), C(4) 13.4 ppm (– Hz); cyclohexyl carbons 24.6, 24.9, 28.7, 52.5 ppm; carboxylate carbon 165.7 ppm; ethanol carbons 18.1, 57.7 ppm. Infrared (Nujol mull): 1667, 1624, 1593 (asymmetric CO_2 stretching); 1306 (shoulder), 1293 (symmetric CO_2 stretching); 609 cm^{-1} (Sn–C stretching).

The salt $2[(c\text{-}C_6H_{11})_2NH_2]^+$ $\{[(n\text{-}C_4H_9)_3SnOC(CH_2CO_2)(O)(n\text{-}C_4H_9)_3SnOC(O)]_2CH_2]\}^{2-}$, prepared by a similar procedure, does not contain ethanol. Anal. Found: C, 53.45; H, 9.28; N, 1.47. $C_{81}H_{162}N_2O_{12}Sn_4$ calcd.: C, 53.15; H, 8.86; N, 1.53%. ^{13}C NMR in $CDCl_3$: n-butyl carbons C(1) 16.3 (361.9), C(2) 27.6 (19.1), C(3) 26.8 (66.0), C(4) 13.4 ppm (– Hz); cyclohexyl carbons 24.8, 25.2, 29.9, 52.6 ppm; carboxylate carbon 173.0 ppm; methylene carbon 43.6 ppm.

$[(c\text{-}C_6H_{11})_2NH_2]^+$ $[(C_6H_5)_3SnOC(O)C(O)]^-$ was the only simple stannate isolated in this study when the reactants were treated in the way described, but unfortunately, recrystallization from ethanol gave only a fine powder. Anal. Found: C, 61.89; H, 6.41; N, 2.20. $C_{32}H_{39}NO_4Sn$ calcd.: C, 61.97; H, 6.29; N, 2.26%. ^{13}C NMR in $CDCl_3$: phenyl carbons C_{ipso} 144.5 (–), C_{ortho} 137.1 (49.8), C_{meta} 128.1 (64.5), C_{para} 128.9 ppm (14.7 Hz); cyclohexyl carbons 24.7, 25.0, 29.0, 53.0 ppm; carboxylate carbon 165.6 ppm.

$[(c\text{-}C_6H_{11})_2NH_2]^+$ $\{[(C_6H_5)_3SnOC(O)CH_2(O)O]_2H\}^-$ was obtained by heating an ethanol solution of triphenyltin hydroxide, dicyclohexylamine and malonic acid in a 1/1/1 molar ratio. Anal. Found: C, 60.11; H, 5.32; N, 1.05. $C_{54}H_{58}NO_8Sn_2$ calcd.: C, 59.70; H, 5.34; N, 1.30%. ^{13}C NMR in $CDCl_3$: phenyl carbons C_{ipso} 138.7 (665.3), C_{ortho} 136.6 (46.9), C_{meta} 128.6 (61.5), C_{para} 129.8 ppm (– Hz); cyclohexyl carbons 24.6, 24.9, 29.1, 52.9 ppm; carboxylate carbon 173.5 ppm; methylene carbon 43.2 ppm.

X-Ray crystallography

A crystal of the ethanol stannate with dimensions 0.42 × 0.32 × 0.18 mm was used for the X-ray measurements. Cell parameters were determined from the $\pm 2\theta$

Table 1

Atomic parameters

Atom	x	y	z	U_{eq}
Sn(1)	0.09915(1)	−0.15367(2)	0.11456(1)	0.0215(2)
Sn(2)	0.25635(1)	−0.43801(2)	0.19638(1)	0.0234(2)
O(1)	0.0236(1)	−0.1042(2)	0.0310(1)	0.023(2)
O(2)	0.0736(1)	0.0210(2)	0.0541(1)	0.031(2)
O(3)	0.1758(1)	−0.1989(2)	0.2061(1)	0.027(2)
O(4)	0.2060(1)	−0.3187(2)	0.1841(1)	0.027(2)
C(1)	0.0282(2)	−0.0233(3)	0.0243(2)	0.023(2)
C(2)	0.2113(2)	−0.2598(3)	0.2190(2)	0.024(2)
C(3)	0.2657(2)	−0.2628(3)	0.2814(2)	0.025(2)
O(5)	0.3035(1)	−0.3209(2)	0.2922(1)	0.031(2)
O(6)	0.2668(1)	−0.2085(2)	0.3148(1)	0.035(2)
C(11)	0.1659(2)	−0.1369(4)	0.0951(2)	0.033(3)
C(12)	0.1478(3)	−0.1553(5)	0.0348(3)	0.056(4)
C(13)	0.2003(5)	−0.1455(9)	0.0266(5)	0.092(7)
C(14)	0.1857(5)	−0.1645(8)	−0.0313(4)	0.134(8)
C(21)	0.0579(2)	−0.2791(3)	0.1004(2)	0.027(2)
C(22)	0.0311(2)	−0.2923(4)	0.1373(2)	0.037(3)
C(23)	0.0043(3)	−0.3816(4)	0.1308(3)	0.049(4)
C(24)	−0.0228(4)	−0.3901(6)	0.1669(4)	0.069(5)
C(31)	0.0806(2)	−0.0652(4)	0.1618(2)	0.034(3)
C(32)	0.0168(3)	−0.0426(4)	0.1382(3)	0.036(3)
C(33)	0.0058(4)	0.0094(7)	0.1778(4)	0.054(4)
C(34)	−0.0575(4)	0.0324(7)	0.1533(4)	0.085(6)
C(41)	0.2466(2)	−0.5022(3)	0.2591(2)	0.034(3)
C(42) [a] (70%)	0.1889(4)	−0.4700(6)	0.2556(4)	0.030(4)
C(42′) (30%)	0.196(1)	−0.547(2)	0.248(1)	0.06(1)
C(43) (70%)	0.1793(4)	−0.5217(6)	0.2971(4)	0.046(5)
C(43′) (30%)	0.148(1)	−0.481(1)	0.2312(9)	0.05(1)
C(44) (70%)	0.1253(5)	−0.4886(7)	0.2978(5)	0.068(7)
C(44′) (30%)	0.156(1)	−0.426(2)	0.283(1)	0.09(2)
C(51)	0.1872(3)	−0.4713(4)	0.1112(3)	0.040(3)
C(52)	0.1922(3)	−0.4308(6)	0.0645(3)	0.079(4)
C(53) (60%)	0.1445(5)	−0.488(1)	0.0058(5)	0.062(3)
C(53′) (40%)	0.1452(7)	−0.439(1)	0.0029(7)	0.046(4)
C(54) (60%)	0.1529(7)	−0.454(1)	−0.0419(7)	0.087(4)
C(54′) (40%)	0.1592(9)	−0.523(2)	−0.0144(9)	0.079(6)
C(61)	0.3321(3)	−0.3813(4)	0.2020(3)	0.035(4)
C(62)	0.3247(3)	−0.2879(4)	0.1812(3)	0.056(4)
C(63) (60%)	0.3675(5)	−0.2481(7)	0.1707(5)	0.042(3)
C(63′) (40%)	0.3952(9)	−0.258(1)	0.2000(9)	0.052(4)
C(64) (60%)	0.4255(5)	−0.2366(8)	0.2286(5)	0.058(3)
C(64′) (40%)	0.3932(9)	−0.168(1)	0.1796(9)	0.084(6)
O(7)	0.3034(2)	−0.5761(3)	0.1967(2)	0.029(2)
C(4)	0.3148(3)	−0.6079(4)	0.1553(3)	0.040(3)
C(5)	0.3612(3)	−0.6777(5)	0.1797(3)	0.062(4)
N(1)	0.1156(2)	0.1866(3)	0.0889(2)	0.026(2)
C(71)	0.0661(2)	0.2469(3)	0.0767(2)	0.029(2)
C(72)	0.0427(3)	0.2190(4)	0.1132(3)	0.037(3)
C(73)	−0.0072(3)	0.2796(5)	0.1051(3)	0.051(4)
C(74)	0.0123(3)	0.3738(4)	0.1148(3)	0.054(4)
C(75)	0.0355(3)	0.4011(4)	0.782(3)	0.052(4)
C(76)	0.0857(3)	0.3415(4)	0.0868(3)	0.039(3)
C(81)	0.1499(2)	0.2039(4)	0.0609(2)	0.029(3)

Table 1 (continued)

Atom	x	y	z	U_{eq}
C(82)	0.1094(2)	0.2066(4)	−0.0030(2)	0.037(3)
C(83)	0.1466(3)	0.2182(5)	−0.0300(3)	0.052(4)
C(84)	0.1927(3)	0.1477(5)	−0.0111(3)	0.054(4)
C(85)	0.2332(3)	0.1475(5)	0.0538(3)	0.042(3)
C(86)	0.1975(2)	0.1341(4)	0.0813(2)	0.035(3)

[a] Disordered atom, percentage of occupancy given in parentheses.

values of 48 Mo-K_α radiation reflections measured at −110 °C on an Enraf–Nonius CAD-4 diffractometer. A total of 6694 independent reflections were collected at −110 °C by use of graphite-monochromated Mo-K_α radiation up to $2\theta_{max}$ 46°. Three standard reflections monitored every 2 h of X-ray exposure showed a maximum variation in intensity of about 7.5%. The intensity data were corrected for Lorentz and polarization factors, and for absorption effects (μ 9.8 cm^{-1}; max/min transmission 0.8350/0.6885). The structure was solved by the heavy-atom method

Table 2

Bond distances (Å), with e.s.d.'s in parentheses

Sn(1)–O(1)	2.247(3)	C(41)–C(42)	1.574(10)
Sn(1) ··· O(2)	3.043(3)		1.390(25)
Sn(1)–O(3)	2.364(3)	C(42)–C(43)	1.532(9)
Sn(1)–C(11)	2.139(5)		1.510(32)
Sn(1)–C(21)	2.151(5)	C(43)–C(44)	1.540(13)
Sn(1)–C(31)	2.127(4)		1.595(23)
Sn(2)–O(4)	2.191(3)	C(51)–C(52)	1.507(7)
Sn(2)–O(7)	2.465(4)	C(52)–C(53)	1.682(14)
Sn(2) ··· O(5)	2.890(3)		1.494(14)
Sn(2)–C(41)	2.139(4)	C(53)–C(54)	1.550(13)
Sn(2)–C(51)	2.149(5)		1.499(26)
Sn(2)–C(61)	2.132(6)	C(61)–C(62)	1.521(9)
C(1)–O(1)	1.272(6)	C(62)–C(63)	1.459(11)
C(1)–O(2)	1.247(6)		1.728(20)
C(1)–C(1)′ [a]	1.562(7)	C(63)–C(64)	1.535(15)
C(2)–O(3)	1.242(6)		1.488(27)
C(2)–O(4)	1.280(5)	N(1)–C(71)	1.498(6)
C(2)–C(3)	1.560(6)	N(1)–C(81)	1.511(5)
C(3)–O(5)	1.258(6)	C(71)–C(72)	1.513(5)
C(3)–O(6)	1.239(5)	C(72)–C(73)	1.540(9)
C(4)–O(7)	1.425(5)	C(73)–C(74)	1.515(10)
C(4)–C(5)	1.501(10)	C(74)–C(75)	1.508(7)
C(11)–C(12)	1.506(5)	C(75)–C(76)	1.534(9)
C(12)–C(13)	1.545(12)	C(76)–C(71)	1.519(8)
C(13)–C(14)	1.473(9)	C(81)–C(82)	1.511(6)
C(21)–C(22)	1.547(5)	C(82)–C(83)	1.544(6)
C(22)–C(23)	1.513(9)	C(83)–C(84)	1.510(10)
C(23)–C(24)	1.525(7)	C(84)–C(85)	1.530(7)
C(31)–C(32)	1.504(8)	C(85)–C(86)	1.522(6)
C(32)–C(33)	1.511(8)	C(86)–C(81)	1.524(8)
C(33)–C(34)	1.490(12)		

[a] C(1)′ is related to C(1) by a center of symmetry.

Table 3

Bond angles, with e.s.d.'s in parentheses

O(1)–Sn(1)–O(3)	175.5(1)	C(2)–C(3)–O(5)	116.2(3)
O(1)–Sn(1)–C(11)	96.2(1)	C(2)–C(3)–O(6)	116.7(4)
O(1)–Sn(1)–C(21)	91.4(1)	O(5)–C(3)–O(6)	127.1(4)
O(1)–Sn(1)–C(31)	92.6(1)	O(7)–C(4)–C(5)	111.3(4)
O(3)–Sn(1)–C(11)	87.0(1)	C(11)–C(12)–C(13)	111.5(6)
O(3)–Sn(1)–C(21)	89.9(1)	C(12)–C(13)–C(14)	114.1(9)
O(3)–Sn(1)–C(31)	82.9(2)	C(21)–C(22)–C(23	113.3(4)
C(11)–Sn(1)–C(21)	118.5(2)	C(22)–C(23)–C(24)	111.1(5)
C(11)–Sn(1)–C(31)	125.5(2)	C(31)–C(32)–C(33)	114.9(5)
C(21)–Sn(1)–C(31)	114.8(2)	C(32)–C(33)–C(34)	114.1(6)
O(4)–Sn(2)–O(7)	172.3(1)	C(41)–C(42)–C(43)	110.1(6)
O(4)–Sn(2)–O(5)	63.4(1)		108.0(17)
O(4)–Sn(2)–C(41)	100.4(1)	C(42)–C(43)–C(44)	111.9(7)
O(4)–Sn(2)–C(51)	86.1(2)		113.2(17)
O(4)–Sn(2)–C(61)	98.6(2)	C(51)–C(52)–C(53)	104.6(7)
O(5)–Sn(2)–O(7)	124.3(1)		123.3(8)
O(5)–Sn(2)–C(41)	73.6(1)	C(52)–C(53)–C(54)	106.0(10)
O(5)–Sn(2)–C(51)	149.4(2)		103.7(13)
O(5)–Sn(2)–C(61)	75.4(1)	C(61)–C(62)–C(63)	121.0(7)
O(7)–Sn(2)–C(41)	83.4(1)		103.5(8)
O(7)–Sn(2)–C(51)	86.3(2)	C(62)–C(63)–C(64)	107.4(6)
O(7)–Sn(2)–C(61)	83.6(2)		108.6(14)
C(41)–Sn(2)–C(51)	112.5(2)	C(71)–N(1)–C(81)	118.8(4)
C(41)–Sn(2)–C(61)	130.8(2)	N(1)–C(71)–C(72)	107.7(4)
C(51)–Sn(2)–C(61)	113.8(2)	N(1)–C(71)–C(76)	112.0(4)
Sn(1)–O(1)–C(1)	112.2(3)	C(72)–C(71)–C(76)	111.8(3)
Sn(1)–O(3)–C(2)	128.5(2)	C(71)–C(72)–C(73)	111.4(4)
Sn(2)–O(4)–C(2)	131.6(3)	C(72)–C(73)–C(74)	111.3(5)
Sn(2)–O(7)–C(4)	128.5(3)	C(73)–C(74)–C(75)	111.7(4)
Sn(1)–C(11)–C(12)	116.3(4)	C(74)–C(75)–C(76)	111.7(5)
Sn(1)–C(21)–C(22)	111.7(3)	C(75)–C(76)–C(71)	110.8(5)
Sn(1)–C(31)–C(32)	117.5(3)	N(1)–C(81)–C(82)	111.0(4)
Sn(2)–C(41)–C(42)	110.3(4)	N(1)–C(81)–C(86)	107.6(4)
	125.1(7)	C(82)–C(81)–C(86)	112.9(4)
Sn(2)–C(51)–C(52)	115.6(5)	C(81)–C(82)–C(83)	109.4(4)
Sn(2)–C(61)–C(62)	115.6(4)	C(82)–C(83)–C(84)	111.5(5)
O(1)–C(1)–O(2)	124.9(4)	C(83)–C(84)–C(85)	110.1(5)
O(1)–C(1)–C(1)′	116.8(4)	C(84)–C(85)–C(86)	110.8(5)
O(2)–C(1)–C(1)′	118.3(4)	C(85)–C(86)–C(81)	109.9(4)
O(3)–C(2)–O(4)	123.8(4)		
O(3)–C(2)–C(3)	117.4(3)		
O(4)–C(2)–C(3)	118.8(4)		

and refined by a full-matrix least-squares routine to a final R factor of 0.042 (R_w 0.053; S 3.5; shift/$\sigma_{\max}$ 0.35) for 6033 observed reflections obeying $I > 2\sigma(I)$. All three butane chains attached to the Sn(2) atom (7 atoms in all) were found to be disordered. The occupancy factors for the disordered atoms were found from the peak heights in the difference-Fourier map and subsequent refinement, and the drawings show the higher-occupancy atoms sites only. Out of the 84 H-atoms only 46 could be located from the difference map (including the hydroxylic and the two ammonium atoms). These H-atoms were refined isotropically. The atomic coordi-

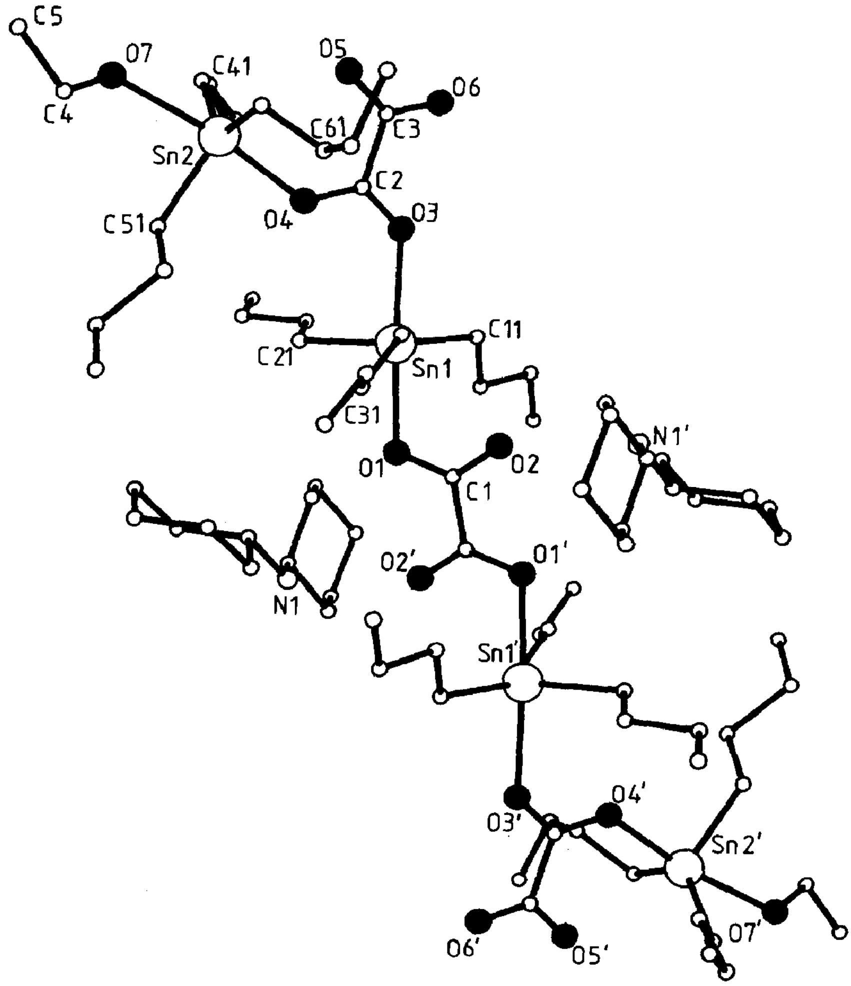

Fig. 1. Structure of bis(dicyclohexylammonium) trisoxalatotetrakis(tri-n-butylstannate)·2 ethanol, $2[(c\text{-}C_6H_{11})_2NH_2]^+$ $[C_2H_5OH\cdot(n\text{-}C_4H_9)_3SnO(CO_2)(O)(n\text{-}C_4H_9)_3SnOC(O)\text{-}]_2{}^{2-}$. Dark circles represent oxygen atoms.

nates are listed in Table 1, bond distances in Table 2 and bond angles in Table 3. The structure of the compound is depicted in Figures 1 to 4.

Crystal data: $C_{82}H_{168}N_2O_{12}Sn_4$, M 1881.0, monoclinic, $C2/c$ a 26.745(10), b 15.370 (2), c 27.814(11) Å, β 122.28(7)°; V 9666.4 Å^3, D_{calcd} 1.292 g cm^{-3} for $Z = 4$.

Results and discussion

The $[R_3SnOC(O)\ (CH_2)_xC(O)O]^-$ anion, trapped as its dicyclohexylammonium salt, was the expected product of the reaction between bis(tri-n-butyltin) oxide (or triphenyltin hydroxide) and oxalic acid ($x = 0$) ($x = 1$ for malonic acid) in the presence of dicyclohexylamine, but was obtained only from the reaction between triphenyltin hydroxide and oxalic acid. When malonic acid was used in place of

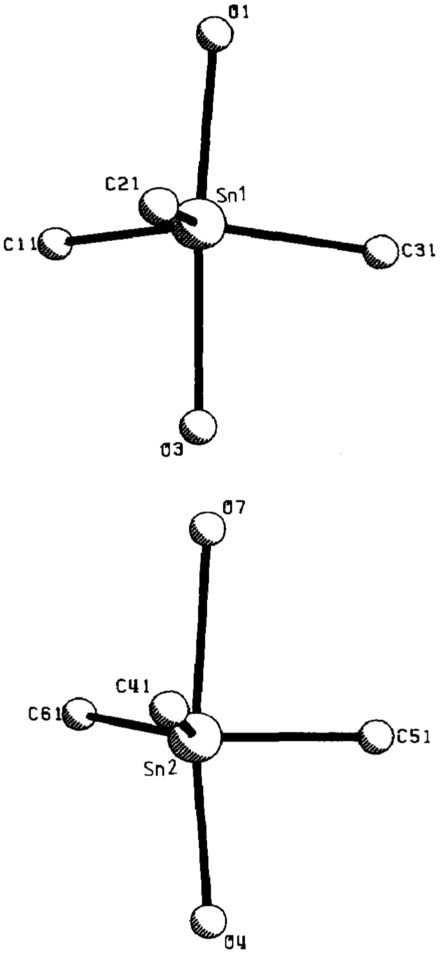

Fig. 2. Trigonal bipyramidal geometry of Sn(1) (a) and Sn(2) (b) atoms.

oxalic acid, triphenyltin hydroxide surprisingly yielded the dinuclear anion, $\{[(C_6H_5)_3SnOC(O)CH_2C(O)O]_2H\}^-$. More interestingly, when treated with malonic acid, bis(tri-n-butyltin) oxide gave a tetranuclear dianionic compound that can be regarded as an adduct made up of one molecule of bis(tri-n-butyltin) malonate, $[(n\text{-}C_4H_9)_3SnOC(O)]_2CH_2$, and two malonatotri-n-butylstannate, $[(n\text{-}C_4H_9)_3SnOC(O)CH_2C(O)O]^-$, anions. When oxalic acid was used in place of malonic acid, the trisoxalatotetrakis(tri-n-butylstannate) dianion, isolated as the bis(dicyclohexylammonium) salt, was found to contain two molecules of ethanol. The results of the preparations are depicted in 1–4.

$$2(Bu_3Sn)_2O + 3(CO_2H)_2 + 2(c\text{-}C_6H_{11})_2NH + 2EtOH \xrightarrow{-2H_2O}$$

$$2(c\text{-}C_6H_{11})_2NH_2{}^+[(Bu_3Sn)_4(C_2O_4)_3 \cdot 2EtOH]^{2-} \qquad (1)$$

$$2(Bu_3Sn)_2O + 3CH_2(CO_2H)_2 + 2(c\text{-}C_6H_{11})_2NH \xrightarrow{-2H_2O}$$

$$2(c\text{-}C_6H_{11})_2NH_2{}^+[(Bu_3Sn)_4(C_3H_2O_4)_3]^{2-} \qquad (2)$$

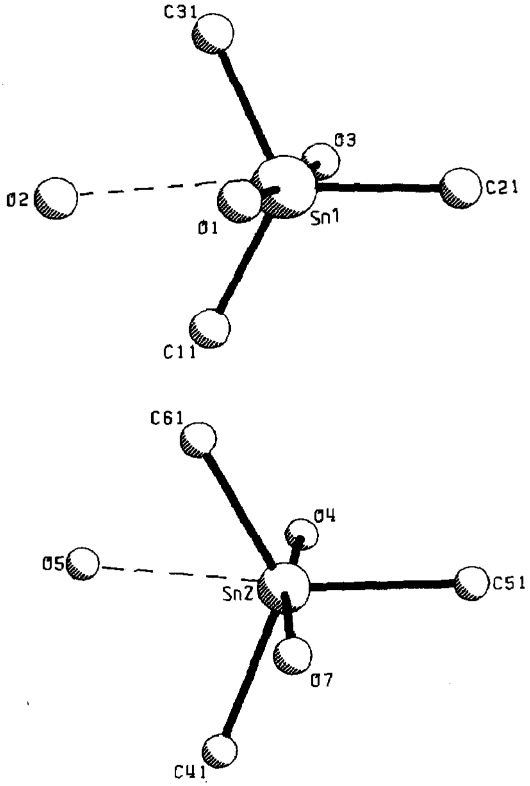

Fig. 3. Skew-trapezoidal bipyramidal geometry of Sn(1) and Sn(2) atoms.

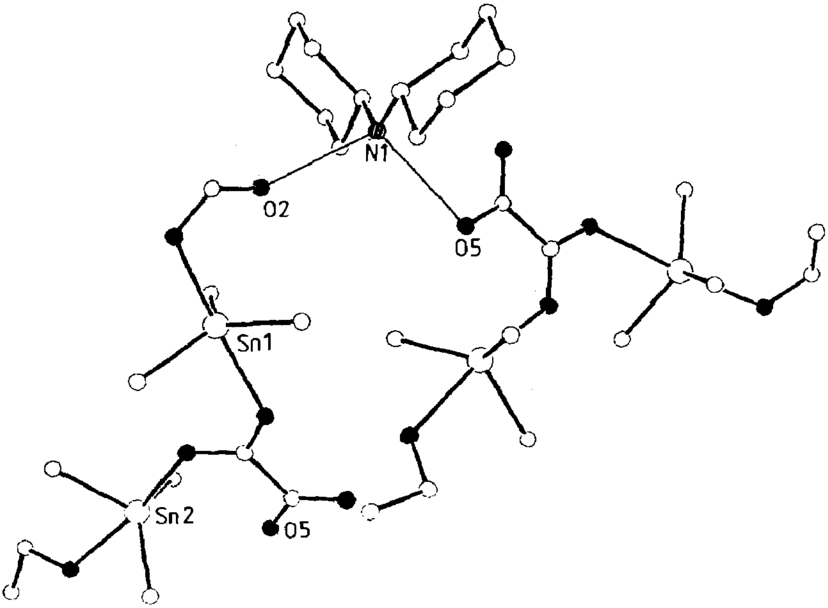

Fig. 4. Hydrogen bonds between the dicyclohexylammonium and oxalate groups.

$$Ph_3SnOH + (CO_2H)_2 + (c\text{-}C_6H_{11})_2NH \xrightarrow{-H_2O} (c\text{-}C_6H_{11})_2NH_2{}^+[Ph_3SnO_2CCO_2]^- \tag{3}$$

$$2Ph_3SnOH + 2CH_2(CO_2H)_2 + (c\text{-}C_6H_{11})_2NH \xrightarrow{-H_2O}$$

$$(c\text{-}C_6H_{11})_2NH_2{}^+[(Ph_3SnO_2CCH_2CO_2)_2H]^- \tag{4}$$

The crystal structure of the ethanol adduct $2[(c\text{-}C_6H_{11})_2NH_2]^+$ $[C_2H_5OH \cdot (n\text{-}C_4H_9)_3SnOC(CO_2)(=O)(n\text{-}C_4H_9)_3SnOC(=O)C(=O)Sn(n\text{-}C_4H_9)_3C(=O)(CO_2)OSn\text{-}(n\text{-}C_4H_9)_3 \cdot HOC_2H_5]^{2-}$ is depicted in Fig. 1. and the geometry of the inner Sn(1) and terminal Sn(2) tin atoms in Fig. 2(a) and 2(b), respectively. The centrosymmetric dianion consists of four tri-n-butyltin units linked through three oxalate groups into a tetranuclear chain. The Sn(1) and Sn(2) atoms are bridged by the –O–C=O: moiety of one oxalate (Sn–O 2.191(3) Å, Sn←O 2.364(3) Å), the other half of which is chelated to the Sn(2) atom through O(5) end (Sn–O 2.890(3) Å). The Sn(1) atom is covalently bonded to the ester O(1) oxygen atom (Sn–O 2.247(3) Å) of the central oxalate in a *trans*-Sn–OC(O)–C′(O′)O′–Sn′ arrangement for the carbon–carbon bond, along which lies the center of symmetry. The other O(2) oxygen atom of this oxalate is hydrogen bonded (N ··· O(2) 2.740(3) Å) to the dicyclohexylammonium cation, which in turn is bonded to the O(5) (N ··· O(5) 2.826(3) Å) oxygen atom of an adjacent chain (symmetry transformation: $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) to give a three-dimensional network. The ethanolic hydrogen atom forms a short intermolecular hydrogen bond with the O(6)′ (2.671(4) Å) oxygen atom (symmetry transformation: $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} + z$).

The Sn(1) atom is five-coordinate in a *trans*-trigonal bipyramidal geometry in which the *trans* angle is 175.5(1)°; this geometry is common for triorganotin carboxylates [4]. The Sn(1) atom is displaced out of the equatorial plane in direction of the axial ligand by 0.130 Å. The O(2) atom approaches the Sn(1) atom at 3.043(3) Å, but this distance is not regarded as representing bonding, since the C(1)–O(1)–O(2)–Sn(1) atoms would then form a four-membered ring with an implausibly small angle (47.0(1)°) at tin (Fig. 3(a)).

If the long Sn(2)–O(5) distance is not regarded as corresponding to a bond, the geometry of the Sn(2) atom is distorted trigonal bipyramidal (Fig. 2(b)), with the datively-bonded ethanolic O(7) and covalently-bonded oxalate O(4) atoms apical (*trans* angle 172.3(10)°), and the tin atom displaced out of the equatorial plane by 0.213 Å. However, the distortion is severe, and the C–Sn(2)–C angle nearest to the O(5) atom is opened from the sp^2 angle of 120 to 130.8(2)°, whereas the other two angles are compressed to 112.5(2) and 113.8(2)°. The O(5), O(4), C(51) and O(7) atoms comprise an approximate trapezoidal plane around the Sn(2) atom, and the trapezoid plane is inclined at 89.8° to the C(41)–Sn(2)–C(61) plane. Although it is somewhat long, it may not be inappropriate to suggest that the Sn(2)–O(5) distance (2.890(3) Å) corresponds to a dative bond, since it is only slightly longer than the bonds in the six-coordinate chlorooxinate (2.847(4) Å [5]) and seven-coordinated bis(dimethyldithiocarbamate) (2.751(5) Å [6]) derivatives of bis(2-carbomethoxyethyl)tin. If this interpretation is valid, the Sn(2) atom then becomes six-coordinate, and its geometry must be interpreted as a skew-trapezoidal bipyramid, a geometry that found in several diorganotin bischelates [7] and occasionally in diorganotin monochelates [8]. The oxalate bite angle (63.4(1)°) is smaller than the angles in the diorganotin oxalates. The tin–oxygen bond of 2.465(4) Å is slightly longer than the 2.394(8) Å bond in triphenyltin saccharin·ethanol [8].

The $^{119}Sn-^{13}C$ one-bond coupling constant of 372.2 Hz in chloroform solution is in a range characteristic of four-coordinate tri-n-butyltin compounds [9], and implies that the ethanol molecule is no longer attached to the tin atom. The observation of only one carboxylate and one set of n-butyl resonances is also consistent with a dissociation on the NMR timescale of the tetranuclear dianion into four equilibrating tri-n-butyltin species. Only one set of tin–carbon and one set of carboxylate signals were observed in the spectrum of each of the other three compounds.

Acknowledgements

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