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Structural chemistry of organotin carboxylates XV.* Diorganostannate esters of dicyclohexylammonium hydrogen oxalate. Synthesis, crystal structure and *in vitro* antitumour activity of bis(dicyclohexylammonium) bisoxalatodi-n-butylstannate and bis(dicyclohexylammonium) μ-oxalatobis(aquadi-n-butyloxalatostannate)†

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Dicyclohexylamine, oxalic acid dihydrate and di-n-butyltin oxide were reacted in 2:2:1 or 2:3:2 stoichiometries in ethanol solution to yield, respectively bis(dicyclohexylammonium) bisoxalatodi-n-butylstannate (1) and bis(dicyclohexylammonium) μ-oxalatobis(aquadi-n-butyloxalatostannate (2); the hydrate was also obtained upon recrystallization of 1 from moist acetonitrile solution. The crystal structures of the two ammonium stannates have been determined at room temperature. In 1, the tin atom in the dianion exists in a skew-trapezoidal bipyramidal geometry with the basal plane being defined by two bidentate oxalate ligands; each ligand forms asymmetric Sn–O bonds [Sn–O 2.348(4), 2.110(4) Å and 2.112(4), 2.363(4) Å]. The apical sites are occupied by the two organo groups disposed over the weaker Sn–O bonds. In 2, the two tin centres of the dianion are connected via a tetradentate oxalate ligand situated about a centre of inversion and each tin atom exists in a pentagonal bipyramidal geometry. The pentagonal plane is defined by four oxygen atoms, two from the central ligand [Sn–O 2.282(4), 2.473(4) Å] and two from a 'terminal' oxalate ligand [Sn–O 2.239(4), 2.210(4) Å], and the fifth site is occupied by a water molecule of crystallization [Sn–O 2.422(4) Å]; the apical sites are filled by the n-butyl groups. Both compounds feature extended hydrogen-bonded networks involving the oxygen atoms of the dianion and the N-bound hydrogen atoms. Crystals of 1 are monoclinic, space group $P2_1/n$, with cell dimensions $a = 13.408(3)$, $b = 22.461(4)$, $c = 13.996(2)$ Å, $\beta = 100.97(2)$ °; full-matrix least-squares refinement on 3305 reflections with $I \geqslant 2.5\sigma(I)$ converged to $R = 0.042$ and $R_w = 0.046$. Crystals of 2 are monoclinic, space group $P2_1/n$, $a = 13.729(3)$, $b = 14.694(2)$, $c = 14.889(2)$ Å, $\beta = 104.83(2)$ °; refinement on 2093 reflections converged to $R = 0.030$ and $R_w = 0.031$. The two di-n-butylstannates were screened *in vitro* against the mammary MCF-7 and WiDr colon carcinoma cell lines, and were found to be as active as cisplatin, a clinically used antineoplastic drug.

Keywords: Organotin, oxalate, structure, Mössbauer, antitumour

INTRODUCTION

We have recently reported the synthesis of triorganotin esters of dicyclohexylammonium hydrogen dicarboxylates, $[(c\text{-}C_6H_{11})_2NH_2]$-$[O_2C(CH_2)_nCO_2H]^-$ ($n = 0$–2); these esters comprise an interesting class of stannate derivatives displaying unusual structural features.[2-4] In an extension of this work with diorganotin compounds,

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we have synthesized bis(dicyclohexylammonium) bisoxalatodi-n-butylstannate (**1**) and bis(dicyclohexylammonium) μ-oxalatobis(aquadi-n-butyloxalatostannate) (**2**). Their characterization by Mössbauer spectroscopy and X-ray crystallography is reported along with some results of *in vitro* screening against MCF-7 mammary tumour and WiDr colon carcinoma cell lines.

EXPERIMENTAL

Synthesis

Dicyclohexylamine (3.62 g, 20 mmol) and oxalic acid dihydrate (2.52 g, 20 mmol) were dissolved in a small volume of hot ethanol. Di-n-butyltin oxide (2.49 g, 10 mmol) was added and the mixture heated until all of the oxide had dissolved. The product (90% yield) after recrystallization from ethanol was found to be pure bis(dicyclohexylammonium) bisoxalatodi-n-butylstannate (**1**). Analysis: Calcd for $C_{36}H_{66}N_2O_8Sn$: C, 55.89; H, 8.59; N, 3.62. Found: C, 55.60; H, 8.71; N, 3.56%. Tin-119*m* Mössbauer (78 K) parameters: isomer shift (IS) = 1.22, quadrupole splitting (QS) = 3.37, $\Gamma_1 = 0.91$, and $\Gamma_2 = 0.92$ mm s^{-1}. Infrared CO_2 bands (Nujol mull): asymmetric, 1713*m*, 1684*vs*, 1658*vs*, 1626*vs*, 1573*s*; symmetric, 1265*s* cm^{-1}.

Bis(dicyclohexylammonium) μ-oxalatobis(aquadi-n-butyloxalatostannate) (**2**) was obtained in similar yields by reacting 2:3:2 molar amounts of dicyclohexylamine, oxalic acid dihydrate and di-n-butyl oxide in ethanol solution, and was recrystallized from ethanol solution. The presence of water in the compound was indicated by a peak at around 3600 cm^{-1} in the infrared spectrum, and the analytical data could only be properly accounted for when two molecules of water were included in the formulation. Analysis: Calcd for $C_{46}H_{88}N_2O_{14}Sn_2$: C, 48.87; H, 7.84; N, 2.47. Found: C, 49.00; H, 8.04; N, 2.50%. Mössbauer parameters: IS = 1.38, QS = 4.18, $\Gamma_1 = 0.87$, and $\Gamma_2 = 0.86$ mm s^{-1}. Infrared CO_2 bands: asymmetric, 1716*vs*, 1672*vs*, 1651*vs*, 1646*vs*, 1615*vs*; symmetric, 1314*m*, 1288*m* cm^{-1}.

Crystallography

Intensity data for colourless crystals of **1** (0.21 mm × 0.52 mm × 0.17 mm) and **2** (0.08 mm × 0.40 mm × 0.40 mm) were measured at room temperature on an Enraf–Nonius CAD4*F* diffractometer fitted with Mo*K*α radiation, λ = 0.7107 Å. The ω:2θ scan technique was employed in both cases. No decomposition of either crystal occurred during its respective data collection. Both data sets were corrected for Lorentz and polarization effects as well as for absorption effects with the use of an analytical procedure. Crystal data are listed in Table 1.

Table 1 Crystal data for **1** and **2**

Compound	**1**	**2**
Formula	$C_{36}H_{66}N_2O_8Sn$	$C_{23}H_{44}NO_7Sn$
Mol. wt	773.6	565.3
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	13.408(3)	13.729(3)
b, Å	22.461(4)	14.694(2)
c, Å	13.996(2)	14.889(2)
β, deg	100.97(2)	104.83(2)
V, Å^3	4138.0	2903.6
Z	4	4
D_c (g cm^{-3})	1.242	1.293
$F(000)$	1640	1180
μ, cm^{-1}	5.93	8.26
Transmission factors (max./min.)	0.908/0.861	0.941/0.722
θ limits	1.5–22.5°	1.5–22.5°
No. of data collected	5921	5325
No. of unique data	5413	3799
No. of unique reflections used with $I \geq 2.5\sigma(I)$	3305	2093
R	0.042	0.030
k	1.00	1.96
g	0.0024	0.0004
R_w	0.046	0.031
Residual ρ_{max}, e Å^{-3}	0.54	0.34

Each structure was solved by an analysis of its Patterson synthesis and refined by a full-matrix least-squares procedure based on *F*.[5] Except for the n-butyl group involving the C(21)–C(24) atoms in **1**, all non-hydrogen atoms were refined with anisotropic thermal parameters. The disordered butyl group in **1** was refined with constrained C–C bond distances [1.52(2) Å] and isotropic thermal parameters. The N-bound hydrogen atoms in **2** were located from a difference map and included in the model; all other hydrogen atoms (except for those on the H_2O molecule in **2**) were included at their calculated positions. Weighting schemes of the form $w = k/[\sigma^2(F) + g|F|^2]$ were introduced and the refinements continued until convergence; final refinement details are listed in Table 1. The analysis of variance in each case showed no special features, indicating an appropriate weighting scheme had been employed.

Fractional atomic coordinates for **1** and **2** are given in Tables 2 and 3, respectively, and the numbering schemes for both compounds are shown in Figs 1 and 3 (all diagrams are drawn with ORTEP[6] at 25% and 15% probability ellipsoids for **1** and **2**, respectively). Scattering factors for all atoms were those as incorporated in the SHELX program.[5] Calculations were performed on a SUN4/280 computer.

For both structures, full listings of the thermal parameters, hydrogen-atom parameters, all bond distances and angles, and the observed and calculated structure factors are available on request from one of the authors (E.R.T.T.).

RESULTS AND DISCUSSION

The one-pot synthesis of the two bis(dicyclohexylammonium) di-n-butylstannates was achieved in high yield by reacting dicyclohexylamine, oxalic acid dihydrate and dihydrate and di-n-butyltin oxide in the appropriate stoichiometries. The structures of **1** and **2** were probed employing tin-119*m* Mössbauer spectroscopy and X-ray crystallography.

In the Mössbauer experiment, the observed quadrupole splitting (QS) is a measure of the electric field gradient at tin nucleus, and of the asymmetry of the electrical environment in which the Mössbauer nucleus exists. With the diorganotin(IV) class of compounds, the observed QS values are generated predominantly by the organic ligands (R); these values have been successfully correlated[7] with the crystallographically determined C–Sn–C angles, the correlation being independent of the coordination number of the Sn atom:

$$|\mathrm{QS}| = 4\{\mathrm{R}\}(1 - 3\sin^2\theta\cos^2\theta)^{1/2}$$

where {R} is the partial QS for R and $\langle \mathrm{R{-}Sn{-}R} \rangle = (180 - 2\theta)^\circ$.

For the $[(n\text{-}C_4H_9)_2Sn(O_2CCO_2)_2]^{2-}$ anion, for which a doublet spectrum with a QS value of 3.37 mm s^{-1} is observed, application of this equation yields a value of 138.4° for the C–Sn–C angle. If the oxalate ligand adopts a chelating mode, as it does in the diphenyloxalatotin complexes,[8,9] the stannate would then be six-coordinate, but the calculated value for the C–Sn–C angle suggests a skew-trapezoidal bipyramidal geometry rather than a distorted octahedral geometry.[10,11]

Table 2 Fractional atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for other atoms) for $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_2Sn(O_2CCO_2)_2]$ (**1**)

Atom	*x*	*y*	*z*
Sn	24330(3)	37160(2)	23096(3)
O(1)	2698(3)	2842(2)	3244(3)
O(2)	2087(3)	1919(2)	3240(3)
O(3)	1210(3)	3138(2)	1788(3)
O(4)	414(3)	2299(2)	1976(4)
O(5)	1631(3)	4163(2)	1070(3)
O(6)	1444(3)	4975(2)	157(3)
O(7)	3197(3)	4661(2)	2256(3)
O(8)	2968(3)	5504(2)	1419(3)
C(1)	2063(5)	2441(3)	2970(4)
C(2)	1139(5)	2633(2)	2187(4)
C(3)	1862(5)	4694(3)	859(4)
C(4)	2765(5)	4988(3)	1573(4)
C(11)	3683(6)	3421(3)	1744(5)
C(12)	3529(7)	2863(4)	1121(6)
C(13)	4462(8)	2688(5)	693(8)
C(14)	4219(12)	2205(8)	−9(12)
C(21)	1921(8)	4125(4)	3484(7)
C(22)	1493(20)	3848(10)	4261(18)
C(23)	853(19)	4402(12)	4624(18)
C(24)	1512(18)	4303(13)	5536(17)
N(100)	3561(4)	1330(2)	4646(3)
C(111)	4574(5)	1323(3)	4337(5)
C(112)	4482(7)	995(4)	3394(6)
C(113)	5467(9)	993(5)	3030(7)
C(114)	5883(7)	1617(5)	2941(7)
C(115)	5979(6)	1950(5)	3895(7)
C(116)	4972(6)	1949(4)	4266(6)
C(211)	3551(5)	1574(3)	5643(4)
C(212)	3685(10)	1113(5)	6372(6)
C(213)	3611(13)	1379(5)	7375(7)
C(214)	2654(11)	1723(9)	7338(10)
C(215)	2596(11)	2208(8)	6592(9)
C(216)	2640(9)	1927(6)	5638(7)
N(200)	552(4)	1052(2)	2236(3)
C(311)	651(5)	882(3)	1227(4)
C(312)	−173(7)	1188(3)	476(5)
C(313)	−46(9)	1036(5)	−561(6)
C(314)	1024(11)	1155(5)	−710(7)
C(315)	1803(8)	860(5)	26(7)
C(316)	1707(6)	1031(3)	1091(6)
C(411)	−417(5)	917(3)	2567(5)
C(412)	−319(7)	1103(4)	3591(7)
C(413)	−1212(10)	921(7)	4046(9)
C(414)	−1459(10)	291(6)	3886(9)
C(415)	−1610(9)	118(6)	2854(8)
C(416)	−682(7)	258(3)	2443(7)

Table 3 Fractional atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for other atoms) for $[(c\text{-}C_6H_{11})_2NH_2]_2[\{(n\text{-}C_4H_9)_2Sn(O_2CCO_2)(H_2O)\}_2(O_2CCO_2)]$ (**2**)

Atom	*x*	*y*	*z*
Sn	13692(3)	−890(2)	19816(3)
O(1)	465(3)	835(2)	837(3)
O(2)	466(3)	−985(3)	616(3)
O(3)	2415(3)	−240(2)	3399(3)
O(4)	3466(3)	519(3)	4531(3)
O(5)	1715(3)	1295(3)	2556(3)
O(6)	2723(4)	2098(3)	3679(4)
O(7)	1745(4)	−1676(3)	2357(4)
C(1)	2(5)	521(4)	57(6)
C(2)	2795(5)	486(4)	3809(5)
C(3)	2374(5)	1385(4)	3318(5)
C(11)	36(6)	−282(6)	2433(6)
C(12)	61(9)	−606(12)	3307(10)
C(13)	−946(11)	−741(14)	3537(10)
C(14)	−893(14)	−1232(20)	4315(14)
C(21)	2606(5)	−22(7)	1388(5)
C(22)	2549(8)	−131(10)	458(8)
C(23)	3484(8)	−14(10)	105(8)
C(24)	3376(13)	−326(13)	−836(13)
N(100)	4755(3)	2054(3)	5038(3)
C(111)	5673(5)	1689(4)	4793(5)
C(112)	5443(6)	1614(5)	3751(5)
C(113)	6351(9)	1280(6)	3434(8)
C(114)	7261(8)	1871(7)	3832(8)
C(115)	7499(6)	1946(6)	4864(7)
C(116)	6586(5)	2299(5)	5163(5)
C(211)	4793(5)	2127(3)	6058(4)
C(212)	4994(5)	1208(4)	6546(5)
C(213)	4952(6)	1300(6)	7565(5)
C(214)	3941(7)	1709(6)	7619(6)
C(215)	3759(7)	2607(6)	7133(6)
C(216)	3792(5)	2517(5)	6127(5)

A sharp doublet (line-width = 0.86, 0.87 mm s^{-1}) is observed in the Mössbauer spectrum of **2**. On the assumption that the two tin sites in the stannate are equivalent, a *trans*-C_2SnO_5 pentagonal bipyramidal geometry can be assigned, by analogy to the diphenyloxalatotin complexes.[8,9] The large QS of 4.18 mm s^{-1} suggests a near-linear C–Sn–C skeleton.

The molecular structure of the anion in **1**, $[(n\text{-}C_4H_9)_2Sn(O_2CCO_2)_2]^{2-}$, is shown in Fig. 1; selected interatomic bond distances and angles are listed in Table 4. The tin atom in the dianion is coordinated by two doubly deprotonated oxalate anions which define a basal plane. The two remaining sites about the tin atom are occupied by n-butyl groups. The O(1), O(3), O(5) and O(7) atoms lie 0.068(4), −0.097(4), 0.105(4) and −0.070(4) Å, respectively, out of the least-squares plane calculated through these atoms, and the tin atom lies 0.0024(4) Å out of this plane in the direction of the C(21) atom. The oxalate ligands form dissimilar bonds to the tin atom, i.e. Sn–O(1) 2.348(4), Sn–O(3) 2.110(4) and Sn–O(5) 2.112(4), Sn–O(7) 2.363(4) Å: the two organo-groups are disposed over the two longer Sn–O bonds defining a C(11)–Sn–C(21) angle of 146.7(3) °. The coordination geometry about the tin atom is best described as being based on a skew-trapezoidal bipyramid. Within the basal plane, the O(3)–Sn–O(5) angle is 76.5(2) ° and the O(1)–Sn–O(7) angle is 138.4(1) °, consistent with the above description of the tin atom coordination geometry.

That the oxalate ligands adopt a *cis*-arrangement in their coordination to the tin atom is reflected in the C–O bond distances, i.e. the exocyclic C–O bond distances are indicative of normal C═O bonds and the two C–C bond distances are consistent with normal C—C single bonds.

In many respects the structure found for the dianion in **1** resembles those found for the monomeric compounds of the general formula $[R_2Sn(O_2CR')_2]$, in which the tin atoms exist in similar coordination geometries.[12] Further, the monomeric structure found here for the dianion

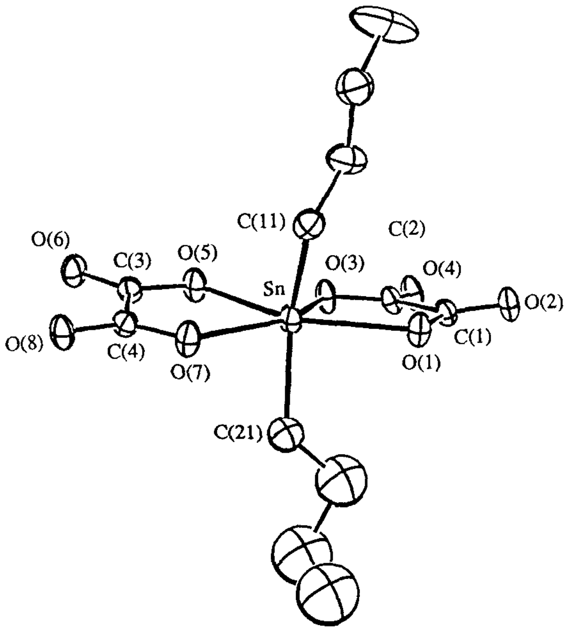

Figure 1 Molecular structure of the dianion in $[(c\text{-}C_6H_{11})_2NH_2]_2[(n\text{-}C_4H_9)_2Sn(O_2CCO_2)_2]$ (**1**) showing the numbering scheme employed.

Table 4 Selected bond distances (Å) and angles (deg.) for $[(c\text{-}C_6H_{11})_2NH_2]_2[(n\text{-}C_4H_9)_2Sn(O_2CCO_2)_2]$ (**1**)

Atoms	Distance	Atoms	Distance
Sn-O(1)	2.348(4)	Sn-O(3)	2.110(4)
Sn-O(5)	2.112(4)	Sn-O(7)	2.363(4)
Sn-C(11)	2.092(8)	Sn-C(21)	2.11(1)
O(1)-C(1)	1.249(7)	O(2)-C(1)	1.232(7)
O(3)-C(2)	1.277(7)	O(4)-C(2)	1.219(7)
O(5)-C(3)	1.282(7)	O(6)-C(3)	1.211(7)
O(7)-C(4)	1.258(7)	O(8)-C(4)	1.219(4)
C(1)-C(2)	1.551(8)	C(3)-C(4)	1.562(8)
Atoms	**Angle**	**Atoms**	**Angle**
O(1)-Sn-O(3)	72.8(1)	O(1)-Sn-O(5)	148.6(1)
O(1)-Sn-O(7)	138.4(1)	O(1)-Sn-C(11)	84.2(2)
O(1)-Sn-C(21)	88.1(3)	O(3)-Sn-O(5)	76.5(2)
O(3)-Sn-O(7)	148.7(1)	O(3)-Sn-C(11)	107.4(2)
O(3)-Sn-C(21)	101.0(3)	O(5)-Sn-O(7)	72.8(1)
O(5)-Sn-C(11)	99.1(2)	O(5)-Sn-C(21)	104.1(3)
O(7)-Sn-C(11)	83.6(2)	O(7)-Sn-C(21)	80.9(3)
C(11)-Sn-C(21)	146.7(3)	Sn-O(1)-C(1)	114.2(3)
Sn-O(3)-C(2)	120.9(3)	Sn-O(5)-C(3)	121.6(3)
Sn-O(7)-C(4)	114.2(4)	O(1)-C(1)-O(2)	128.1(5)
O(1)-C(1)-C(2)	115.0(5)	O(2)-C(1)-C(2)	116.9(5)
O(3)-C(2)-O(4)	124.4(5)	O(3)-C(2)-C(1)	116.1(5)
O(4)-C(2)-C(1)	119.5(5)	O(5)-C(3)-O(6)	125.3(5)
O(5)-C(3)-C(4)	116.0(5)	O(6)-C(3)-C(4)	118.7(5)
O(7)-C(4)-O(8)	127.2(5)	O(7)-C(4)-C(3)	115.3(5)
O(8)-C(4)-C(3)	117.5(5)		

contrasts with the polymeric structures found for other diorganotin species with dicarboxylate ligands.[3, 12]

As would be expected, there are significant interionic contacts in the crystal lattice involving the non-coordinated oxygen atoms of the dianion and the N-bound hydrogen atoms. A [001] projection of the unit cell of **1** is shown in Fig. 2(a) and a view of the immediate environment of the dianion is shown in Fig. 2(b). Each dianion is associated with four symmetry-related $[(c\text{-}C_6H_{11})_2NH_2]^+$ cations, each one of which forms a hydrogen bond to one exocyclic oxygen atom. These contacts are O(2)···H(1na) 1.88(1) Å, N(100)—H(1na)···O(2), 171(1) °; O(4)···H(2na) 1.91(1) Å, N(200)—H(2na)···O(4), 157(1) °; O(6)···H(1nb)′ 2.17(1), N(100)′—H(1nb)′···O(6), 152(1) °; and O(8)···H(2nb)′ 1.79(1) Å, N(200)′—H(2nb)′···O(8), 175(1) °. The primed atoms are each related by the symmetry operation: $0.5-x$, $-0.5+y$, $0.5-z$. The weaker interaction involving the H(1nb)′ atom is explained in terms of a second, but weaker, contact of this atom to the O(8) atom of 2.25(1) Å, and N(100)′-H(1nb)′-O(8) 129(1) °. A consequence of this hydrogen-bonding scheme is that each cation bridges two independent anions.

The structure of the anion in **2**, $[\{(n\text{-}C_4H_9)_2Sn(O_2CCO_2)(H_2O)\}_2(O_2CCO_2)]^{2-}$, is shown in Fig. 3. The dinuclear species is disposed about a crystallographic centre of inversion situated midway between the C(1)–C(1)′ bond of the central oxalate ligand. The coordination geometry about each tin atom is distorted pentagonal bipyramidal. The basal plane is defined by five oxygen atoms, two from each of two oxalate ligands and one from a coordinated water molecule [Sn–O(7) 2.422(4) Å]. The apical positions are occupied by the two n-butyl groups which form an angle C(11)–Sn–C(21) of 172.2(3) °. The O(1), O(2), O(3), O(5) and O(7) atoms lie −0.054(4), 0.123(4), −0.161(4), 0.141(4) and −0.031(4) Å, respectively, out of the least-squares plane

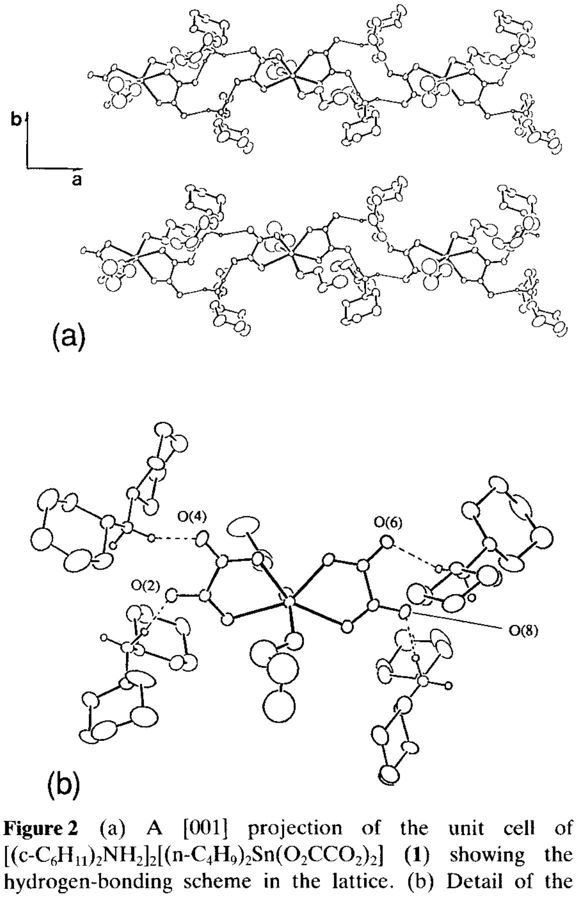

Figure 2 (a) A [001] projection of the unit cell of $[(c\text{-}C_6H_{11})_2NH_2]_2[(n\text{-}C_4H_9)_2Sn(O_2CCO_2)_2]$ (**1**) showing the hydrogen-bonding scheme in the lattice. (b) Detail of the immediate environment about the anion.

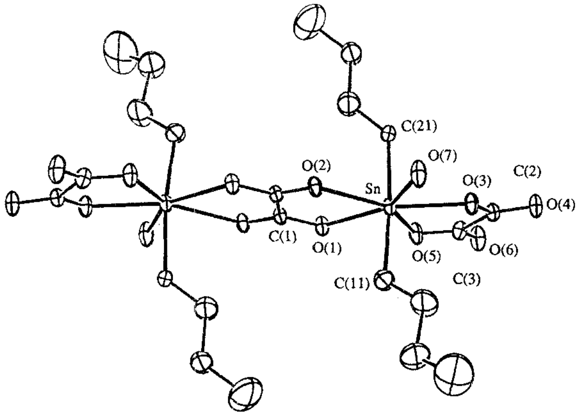

Figure 3 Molecular structure of the dimeric dianion in $[(c\text{-}C_6H_{11})_2NH_2]_2[\{(n\text{-}C_4H_9)_2Sn(O_2CCO_2)(H_2O)\}_2(O_2CCO_2)]]$ (**2**) showing the numbering scheme employed.

through these atoms. The tin atom lies −0.0351(4) Å out of the plane in the direction of the C(21) atom. The O–Sn–O angles defining the pentagonal plane lie in the narrow range 68.9(1) to 76.3(1) ° (Table 5).

There are two independent oxalate ligands in the structure. The first employs two oxygen atoms in coordination with the tin atom forming slightly different Sn–O bond distances [Sn–O(3) 2.239(4) and Sn–O(5) 2.210(4) Å] and subtends an O(3)–Sn–O(5) angle of 72.8(1) °; cf. an ideal angle of 72 ° in a regular pentagonal plane. This oxalate ligand adopts a flat, *cis* arrangement, as found for the dianion in **1**. The two exocyclic C=O bond distances are significantly shorter than the two endocyclic C–O bond distances. The second oxalate ligand coordinates two tin atoms employing all four oxygen atoms, i.e. two oxygen atoms per tin atom, but forms inequivalent Sn–O bonds, Sn–O(1) 2.282(4), Sn–O(2) 2.473(4) Å and O(1)–Sn–O(2) 68.9(1) °. This inequivalence is reflected in the associated C–O bond distances. The O(1)–C(1) bond distance of 1.261(7) Å appears to be longer than 1.246(7) Å, the distance found for the C(1)′–O(2) bond distance, although the errors associated with these parameters are relatively high. The trend in C–O bond distances is consistent, however, with both the trends in the Sn–O bond distances and a *trans* planar arrangement of the oxalate dianion.

Similar pentagonal bipyramidal geometries about diorganotin centres have been observed previously[12] in the structures of monomeric $[(CH_3)_2Sn(O_2CCH_3)_3]^-$,[13] polymeric $[(CH_3)_2Sn(O_2CC_6H_4N\text{-}o)_2]$[14] and in the closely related aquo species, dimeric $[(CH_3)_2Sn((O_2C)_2C_5H_3N)(OH_2)]_2$[15] and polymeric $[(C_6H_5)_2Sn((O_2C)_2C_5H_3N)(OH_2)]_n$.[16]

The hydrogen-bonding scheme found in the lattice of **2** resembles that described for **1**. The dianion in **2** forms significant hydrogen-bonding contacts in the crystal lattice as shown in the [001] projection of the unit cell contents in Fig. 4. The contacts are: O(2)···H(a10)″ 1.98(1) Å, N(100)—H(a10)···O(2)″, 176(1) °; (symmetry operation: $0.5-x$, $0.5+y$, $0.5-z$) and O(4)···H(a11) 1.90(1) Å and N(100)—H(a11)···O(4), 153(1) °. As in **1**, the cation bridges two symmetry-related dimeric units. Significantly, the coordinated water molecule in **2** does not form appreciable intermolecular contacts.

Table 5 Selected bond distances (Å) and angles (deg.) for $[(c\text{-}C_6H_{11})_2NH_2]_2[\{(n\text{-}C_4H_9)_2Sn(O_2CCO_2)(H_2O)\}_2(O_2CCO_2)]$ (**2**)

Atoms	Distance	Atoms	Distance
Sn–O(1)	2.282(4)	Sn–O(2)	2.473(4)
Sn–O(3)	2.239(4)	Sn–O(5)	2.210(4)
Sn–O(7)	2.422(4)	Sn–C(11)	2.123(9)
Sn–C(21)	2.108(8)	O(1)–C(1)	1.261(7)
O(2)–C(1)′[a]	1:246(7)	O(3)–C(2)	1.273(7)
O(4)–C(2)	1.224(7)	O(5)–C(3)	1.264(8)
O(6)–C(3)	1.218(7)	C(1)–C(1)′	1.54(1)
C(2)–C(3)	1.549(8)		
Atoms	**Angle**	**Atoms**	**Angle**
O(1)–Sn–O(2)	68.9(1)	O(1)–Sn–O(3)	149.1(1)
O(1)–Sn–O(5)	76.3(1)	O(1)–Sn–O(7)	142.0(2)
O(1)–Sn–C(11)	88.1(3)	O(1)–Sn–C(21)	90.1(2)
O(2)–Sn–O(3)	142.0(1)	O(2)–Sn–O(5)	145.2(1)
O(2)–Sn–O(7)	73.1(1)	O(2)–Sn–C(11)	84.1(3)
O(2)–Sn–C(21)	88.2(2)	O(3)–Sn–O(5)	72.8(1)
O(3)–Sn–O(7)	68.9(1)	O(3)–Sn–C(11)	94.9(3)
O(3)–Sn–C(2)	90.5(2)	O(5)–Sn–O(7)	141.7(2)
O(5)–Sn–C(11)	96.8(3)	O(5)–Sn–C(21)	90.2(3)
O(7)–Sn–C(11)	87.0(3)	O(7)–Sn–C(21)	89.7(3)
C(11)–Sn–C(21)	172.2(3)	Sn–O(1)–C(1)	121.4(4)
Sn–O(2)–C(1)′	114.6(4)	Sn–O(3)–C(2)	117.0(4)
Sn–O(5)–C(3)	118.5(4)	O(1)–C(1)–O(2)′	125.1(4)
O(1)–C(1)–C(1)′	117.0(4)	O(2)′–C(1)–C(1)′	118.0(4)
O(3)–C(2)–O(4)	125.3(5)	O(3)–C(2)–C(3)	115.5(5)
O(4)–C(2)–C(3)	119.1(5)	O(5)–C(3)–O(6)	126.6(1)
O(5)–C(3)–C(2)	115.4(5)	O(6)–C(3)–C(2)	117.9(6)

[a] Primed atoms are related by a crystallographic centre of inversion.

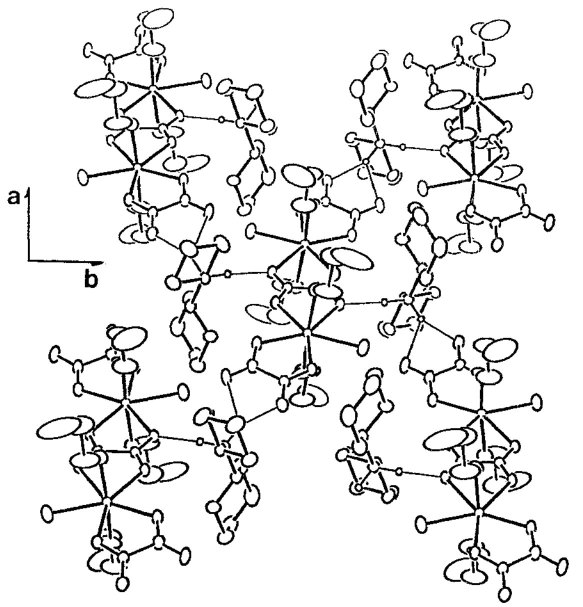

Figure 4 A [001] projection of the unit cell of $[(c\text{-}C_6H_{11})_2NH_2]_2[\{(n\text{-}C_4H_9)_2Sn(O_2CCO_2)(H_2O)\}_2(O_2CCO_2)]$ (**2**) showing the hydrogen-bonding scheme in the lattice.

ANTITUMOUR SCREENING RESULTS

Diorganotin compounds are possible antitumour compounds, and the di-n-butyl derivatives are of low mammalian toxicity. In tests conducted *in vivo* against mammary (MCF-7) and colon carcinoma (WiDr) cell lines (using an automated *in vitro* technique[17]) several di-n-butyl compounds have proved to be more effective than cisplatin, *cis*-$[(NH_3)_2PtCl_2]$. Thus, relative to ID_{50} values of 850 with MCF-7 and 624 with WiDr for cisplatin, di-n-butyltin di-*o*-aminobenzoate is more efficient (MCF-7 = 60, WiDr = 259), although less so when its amino hydrogen is replaced by larger groups (acetyl: MCF-7 = 125, WiDr = 787; phenyl: MCF-7 = 138, WiDr = 819). The tetranuclear distannoxanes, $\{[(n\text{-}C_4H_9)_2Sn(O_2CR)]_2O\}_2$, which are the partial hydrolysis products of the corresponding diorganotin dicarboxylates, have also been shown to be effective against both these cell lines, with ID_{50} values ranging from 44 to 72 for MCF-7 and 122 to 454 for WiDr. The ID_{50} values obtained for **1** and **2** and listed in Table 6 compare favourably with the above values.

Table 6 ID_{50} values ($ng\ cm^{-3}$) for dibutylstannates and other antineoplastic compounds

Compound	MCF-7	WiDr
1	76	323
2	95	353
Cisplatin	850	624
Mitomycin C	3	17

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