Structure of Di-*n*-butyl(1,1-cyclobutanedicarboxylato)tin(IV)

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Abstract. *catena*-Dibutyltin-μ-[cyclobutanedi-carboxylato(2−)-$O,O':O'',O'''$]-tin(IV), [Sn(C_4H_9)$_2$-($C_6H_6O_4$)]$_n$, $C_{14}H_{24}O_4Sn$, M_r = 375·03, monoclinic, $P2_1/c$, a = 11·659 (8), b = 10·408 (9), c = 14·541 (9) Å, β = 105·57 (6)°, V = 1700 (2) Å^3, Z = 4, D_x = 1·466 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 1·51 mm^{-1}, $F(000)$ = 760, T = 291 (1) K, final R = 0·055 for 2478 unique observed [$F \geq 2\cdot0\sigma(F)$] diffractometer data. The coordination polyhedron around tin can be considered to be a heavily distorted octahedron, with the two C(butyl) atoms in axial positions, while the equatorial plane is formed by four O atoms of two asymmetrically chelating carboxylate groups [Sn—O(1) 2·116 (5), Sn—O(2) 2·111 (4), Sn—O(3) 2·563 (5), Sn—O(4) 2·579 (5) Å]. The two carboxylate groups of one ligand are linked to different Sn atoms and a zigzag chain is formed. No short interactions between the chains are observed.

Introduction. In the course of studies of organotin-(IV) compounds having antileukaemia properties the title compound was synthesized (Gielen, Mélotte & Willem, 1989) as a di-*n*-butyltin(IV) analogue of *cis*-diammine(1,1-cyclobutanedicarboxylato)plat-inum(II), which is in clinical use against some cancers. It therefore seemed worthwhile to determine the structure of the new diorganotin(IV) compound for reasons of comparison and to gain more structural data for later studies on structure–activity relationships, but also since rather few X-ray structure determinations of diorganotin(IV) dicarboxylates and of derivatives of 1,1-cyclobutanedicarboxylic acid are known.

Experimental. Single crystals from diethyl ether. Crystal size ~0·16 × 0·32 × 0·26 mm, $\omega/2\theta$ scan, scan speed 2·0–5·0° min^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 25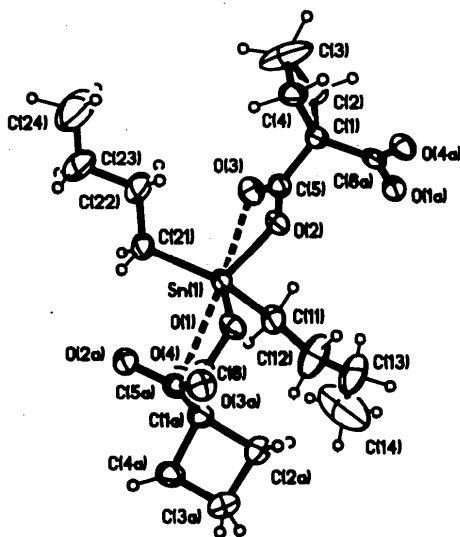 reflexions up to 2θ = 23·2°; six standard reflexions recorded every 2·5 h showed up to 14% intensity loss during data collection; 6525 reflexions measured, 1·5 $\leq \theta \leq$ 25°, −13 $\leq h \leq$ 13, 0 $\leq k \leq$ 12, −17 $\leq l \leq$ 17; after averaging (R_{int} = 0·049) 2998 unique reflexions, 2478 with $F \geq 2\cdot0\sigma(F)$; Lorentz–polarization, decay correction and absorption correction *via* ψ scans, max./min. transmission 1·00/0·67; systematic absences ($h0l$) $l = 2n + 1$, ($0k0$) $k = 2n + 1$ conform to space group $P2_1/c$; structure solution *via* direct methods, ΔF syntheses and full-matrix, least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C—H 1·08 Å); refinement on F with 2478 reflexions and 173 refined parameters; $w = 1·16/[\sigma^2(F) + (0·001F^2)]$; $V = 1·21$, $R = 0·055$, $wR = 0·053$, $(\Delta/\sigma)_{max}$ = 0·40, no extinction correction; largest peak in final ΔF map $\pm 1\cdot2$ e Å^{-3} near Sn and $\pm 0\cdot4$ e Å^{-3} in the remaining parts, atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography* (1974); programs: Enraf–Nonius *Structure Determination Package* (Frenz, 1985), *PARST* (Nardelli, 1983), *SHELX*76 (Sheldrick, 1976), *SHELXTL-Plus* (Sheldrick, 1987), *SCHAKAL*86 (Keller, 1986), *MISSYM* (Le Page, 1987).

Discussion. Part of the crystal structure of the title compound and the numbering scheme are shown in Fig. 1 and the unit cell in a stereoview in Fig. 2. Positional parameters and the equivalent values of the anisotropic temperature factors for the non-H atoms are given in Table 1,* bond lengths, bond angles, least-squares planes and dihedral angles are given in Table 2.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn(1)	0·06007 (4)	0·38495 (3)	0·64860 (3)	67
O(1)	−0·0763 (4)	0·4784 (4)	0·6942 (3)	80
O(2)	0·0899 (3)	0·2888 (4)	0·7807 (3)	73
O(3)	0·2272 (4)	0·2221 (5)	0·7131 (3)	95
O(4)	−0·0913 (4)	0·5465 (4)	0·5497 (3)	87
C(1)	0·2251 (5)	0·1331 (5)	0·8666 (5)	77
C(2)	0·3416 (6)	0·0578 (8)	0·8696 (7)	107
C(3)	0·4033 (9)	0·145 (1)	0·949 (1)	248
C(4)	0·2941 (6)	0·2095 (7)	0·9566 (5)	100
C(5)	0·1797 (5)	0·2173 (6)	0·7805 (4)	74
C(6)	−0·1249 (5)	0·5504 (6)	0·6228 (4)	72
C(11)	−0·0233 (7)	0·2378 (7)	0·5548 (5)	97
C(21)	0·1901 (6)	0·5315 (7)	0·6719 (5)	100
C(12)	−0·141 (1)	0·205 (1)	0·5547 (9)	181
C(22)	0·2896 (8)	0·5228 (9)	0·7551 (7)	141
C(13)	−0·190 (1)	0·085 (1)	0·4969 (9)	173
C(23)	0·380 (1)	0·632 (1)	0·768 (1)	181
C(14)	−0·229 (2)	0·086 (2)	0·416 (1)	415
C(24)	0·474 (2)	0·620 (2)	0·845 (1)	277

Table 2. Bond distances (Å), bond angles (°), least-squares planes, dihedral angles (°) and selected distances (Å) from planes

O(1)—Sn(1)	2·116 (5)	C(4)—C(1)	1·558 (9)
O(2)—Sn(1)	2·111 (4)	C(5)—C(1)	1·503 (9)
O(3)—Sn(1)	2·563 (5)	C(6)—C(1^i)	1·492 (9)
O(4)—Sn(1)	2·579 (5)	C(3)—C(2)	1·495 (18)
C(11)—Sn(1)	2·107 (7)	C(4)—C(3)	1·469 (15)
C(21)—Sn(1)	2·112 (7)	C(12)—C(11)	1·416 (16)
C(6)—O(1)	1·283 (7)	C(22)—C(21)	1·437 (11)
C(5)—O(2)	1·284 (8)	C(13)—C(12)	1·528 (13)
C(5)—O(3)	1·250 (9)	C(23)—C(22)	1·524 (16)
C(6)—O(4)	1·228 (7)	C(14)—C(13)	1·138 (24)
C(2)—C(1)	1·558 (10)	C(24)—C(23)	1·344 (19)

O(2)—Sn(1)—O(1)	83·5 (2)	C(5)—C(1)—C(2)	115·2 (7)
O(3)—Sn(1)—O(1)	138·6 (2)	C(5)—C(1)—C(4)	112·9 (5)
O(3)—Sn(1)—O(2)	55·2 (2)	C(4)—C(1)—C(6^i)	116·7 (5)
O(4)—Sn(1)—O(1)	54·3 (2)	C(2)—C(1)—C(6^i)	114·1 (5)
O(4)—Sn(1)—O(2)	137·6 (2)	C(5)—C(1)—C(6^i)	108·2 (4)
O(4)—Sn(1)—O(3)	167·1 (2)	C(3)—C(2)—C(1)	87·2 (6)
C(11)—Sn(1)—O(1)	106·4 (3)	C(4)—C(3)—C(2)	95·1 (6)
C(11)—Sn(1)—O(2)	100·3 (2)	C(3)—C(4)—C(1)	88·1 (7)
C(11)—Sn(1)—O(3)	86·0 (2)	O(3)—C(5)—O(2)	120·8 (6)
C(11)—Sn(1)—O(4)	89·1 (2)	C(1)—C(5)—O(2)	116·1 (6)
C(21)—Sn(1)—O(1)	100·6 (3)	C(1)—C(5)—O(3)	123·0 (6)
C(21)—Sn(1)—O(2)	105·1 (2)	O(4)—C(6)—O(1)	120·5 (6)
C(21)—Sn(1)—O(3)	88·7 (2)	C(1)—C(6^i)—O(4^i)	123·3 (5)
C(21)—Sn(1)—O(4)	88·4 (2)	C(1)—C(6^i)—O(1^i)	116·2 (4)
C(21)—Sn(1)—C(11)	144·6 (3)	C(12)—C(11)—Sn(1)	116·9 (6)
C(6)—O(1)—Sn(1)	102·7 (4)	C(22)—C(21)—Sn(1)	118·2 (6)
C(5)—O(2)—Sn(1)	102·0 (4)	C(13)—C(12)—C(11)	114·3 (10)
C(5)—O(3)—Sn(1)	82·0 (4)	C(23)—C(22)—C(21)	115·5 (9)
C(6)—O(4)—Sn(1)	82·4 (4)	C(14)—C(13)—C(12)	123·4 (17)
C(4)—C(1)—C(2)	89·1 (5)	C(24)—C(23)—C(22)	114·6 (12)

Symmetry code: (i) $-x$, $0.5 + y$, $1.5 - z$.

Least-squares planes and dihedral angles

No.	Plane through atoms	Equation of the plane (x along **a**; y in the plane **ab**; z along **c***)
1	O(1),O(2),O(3),O(4)	$-0.534x - 0.7399y - 0.409z$ $= -5.68$ (2) Å
2	Sn(1),O(1),C(6),O(4)	$-0.551x - 0.749y - 0.368z$ $= -5.33$ (3) Å
3	Sn(1),O(2),C(5),O(3)	$-0.504x - 0.738y - 0.448z$ $= -6.11$ (2) Å
4	C(1),C(2),C(3),C(4)	$0.392x + 0.693y - 0.605z$ $= -6.70$ (6) Å

Dihedral angles: 1,2 2·6(2)°; 1,3 2·9(2)°; 1,4 118·3(3)°; 2,3 5·4(2)°; 2,4 120·8(3)°, 3,4 115·9(3)°

Distances of selected atoms from planes

Atom	Plane	Distance
Sn(1)	1	0·021 (2)
C(1)	4	0·014 (7)
C(2)	4	−0·027 (9)
C(3)	4	0·09 (2)
C(4)	4	−0·021 (8)

Fig. 1. View (*SHELXTL-Plus*) of part of the crystal structure, showing the atom-numbering scheme. 'a' corresponds to the symmetry operation ($-x$, $0.5 + y$, $1.5 - z$).
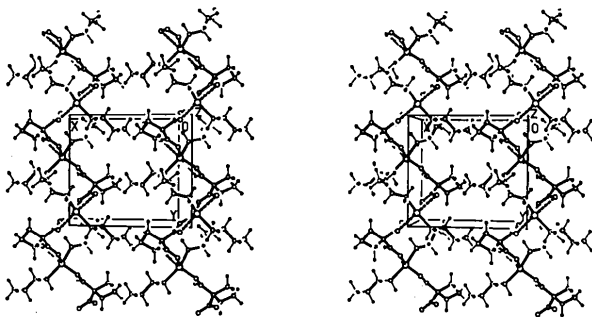
Fig. 2. Stereoscopic view (*SCHAKAL86*) of chains running through the unit cell along the **b** direction (**a** horizontal). The butyl groups and the H atoms are omitted for clarity.

The coordination polyhedron around tin can be considered to be a heavily distorted octahedron, with two C(butyl) atoms in axial and O(1), O(2), O(3) and O(4) in equatorial positions. The bond distances Sn—O(3) and Sn—O(4) [mean: 2·571 (5) Å] are appreciably shorter than the sum of the appropriate

van der Waals radii of 3·79 Å (Bondi, 1964) and indicate the bidentate chelating nature of the carboxylate groups of the ligand. The relatively small value of the angle O(1)—Sn(1)—O(2) of 83·5 (2)° and the large value of O(3)—Sn(1)—O(4) of 167·1 (2)° could be caused by lattice effects. Each ligand links two Sn centers *via* the carboxylate groups to form a zigzag chain. This type of chain formation is unusual and is possibly caused by the substitution pattern of two carboxylate groups on one C atom of the ligand.

The cyclobutane ring is nearly planar. The displacement parameters U_{ik} of C(3) point to strong 'vibration' ($r_{max}/r_{min} = 8·1$) perpendicular to the plane of the ring; the fact that the atoms C(2) and C(4) which are bound to C(3) show normal temperature factors ($r_{max}/r_{min} = 2·2$ and 2·4) indicates orientational disorder (dynamic puckering) for the position C(3) as has been found in *cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II) (Beagley, Cruickshank, McAuliffe, Pritchard, Zaki, Beddoes, Cernik & Mills, 1985). Distances between the chains smaller than the sum of the van der Waals radii do not exist.

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Structure of Bis(glycinato-κN,κO)(2,2'-bipyridyl-κ²N,N')nickel(II) 5·5-Hydrate

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Abstract. [Ni(C₂H₄NO₂)₂(C₁₀H₈N₂)].5·5H₂O, orthorhombic, $Fdd2$, $a = 28·181$ (4), $b = 40·267$ (7), $c = 7·461$ (2) Å, $V = 8466$ (3) Å³, $F(000) = 3888$, $M_r = 462·1$, $Z = 16$, $D_m = 1·430$, $D_x = 1·450$ Mg m⁻³, graphite-monochromated Mo $K\bar{\alpha}$ radiation, $\lambda = 0·71069$ Å, $T = 298$ K. The structure was solved by the heavy-atom method and refined to $R = 0·040$, $wR = 0·049$, for 2469 significant independent reflexions. The coordination about the Ni atom is a distorted octahedron in which the two Ni—N(gly) distances differ significantly, 2·065 (4) and 2·145 (5) Å. The crystal structure contains an extended network of hydrogen bonds involving water–O(gly), water–N(gly), and water–water interactions.