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Structure of Tri-*n*-butyltin(IV) 1-Uracilacetate

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Abstract. (Tri-*n*-butyl)(1,2,3,4-tetrahydro-2,4-dioxo-1-pyrimidineacetato)tin(IV), $[Sn(C_4H_9)_3(C_6H_5N_2O_4)]$, $M_r = 459.15$, monoclinic, $C2/c$, $a = 18.402$ (17), $b = 16.861$ (19), $c = 16.328$ (16) Å, $\beta = 117.04$ (7)°, $V = 4512$ (8) Å^3, $Z = 8$, $D_m = 1.31$ (2), $D_x = 1.35$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.15$ mm^{-1}, $F(000) = 1888$, room temperature, $R = 0.055$ for 1540 unique observed reflections. Tri-*n*-butyltin(IV) 1-uracilacetate is a one-dimensional polymer containing Sn atoms with trigonal bipyramidal coordination. The *n*-butyl C atoms occupy the equatorial sites; one axial site contains the O atom of a monodentate acetate group [Sn—O 2.124 (5) Å]; the other contains a uracil O atom [Sn—O 2.669 (6) Å] from a different uracilacetate ligand.

Introduction. A central question in the structural chemistry of triorganotin(IV) carboxylates is whether carboxylate groups will chelate to form monomers with four-coordinate tin or give five-coordinate polymers as a result of carboxylate bridging (Amini, Ng, Fidelis, Heeg, Muchmore, van der Helm & Zuckerman, 1989). Triphenyltin(IV) arylcarboxylates are generally monomeric molecules with tetrahedral tin (Ng, Kumar Das, van Meurs, Schagen & Straver, 1989); the aryl group prefers to be conjugated to the carboxylate group and to be coplanar with it. Triorganotin(IV) alkanoates are often polymeric; each ligand links two Sn atoms *via* the carboxylate group to form a chain with five-coordinate *trans*-C_3SnO_2 units (Ng, Chen & Kumar Das, 1988). The discovery of antitumour properties (Meriem, Gielen & Willem, 1989) and the industrial importance of organotin(IV) compounds (Evans & Karpel, 1985) have stimulated our interest in this class of compound and led us to determine the structure of the title compound.

Experimental. Air-stable colourless prismatic crystals of tri-*n*-butyltin(IV) 1-uracilacetate were prepared by reaction of stoichiometric amounts of tributyltin(IV) oxide and 1-uracilacetic acid. The mixture was refluxed in toluene in vacuum. A white crystalline solid was recrystallized from toluene. Analysis calculated for $(C_4H_9)_3SnC_6H_5N_2O_4$: C 47.08, H 7.03, N 6.10%; found: C 46.98, H 6.87, N 6.21%. Space group $C2/c$ from systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. Data collected on a crystal of size 0.2 × 0.1 × 0.3 mm. D_m by flotation in $ZnSO_4$ solution. Approximate values of lattice parameters from rotation and Weissenberg patterns. Accurate lattice parameters were refined by least squares on the basis of 15 precisely centred reflections with $5 < 2\theta < 14°$ on a Syntex $P2_1$ four-circle diffractometer using Mo $K\alpha$ radiation filtered by a graphite monochromator. Intensities of 5135 unique reflections, collected in the range $0 < 2\theta < 55°$, $h = 0 \rightarrow 22$, $k = 0 \rightarrow 21$, $l = -19 \rightarrow 18$ by $\theta/2\theta$ scans, variable rate 4.9 to 29.3° min^{-1} in 2θ, background to scan-time ratio 1.0, scan width 2° plus α_1–α_2 dispersion. No significant variation in intensities of two standard reflections ($\bar{2}02$, $\bar{2}00$) measured after 98 reflections. Data reduction performed with the program *XP*21 (Pavelčik, 1987). All intensities corrected for Lorentz and polarization effects, but not for absorption or extinction. The structure was solved by the Patterson method and refined on F by the block-diagonal least-squares method using 1540 observed reflections with $I > 1.96\sigma(I)$. H atoms located at calculated positions; their coordinates and

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Table 1. *Final positional parameters for non*-H *atoms* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sn(1)	2375.8 (4)	446.1 (4)	2311.6 (4)	4.66 (4)
C(1)	3175 (6)	822 (6)	1771 (8)	6.1 (8)
C(2)	3508 (6)	226 (7)	1380 (7)	8.2 (6)
C(3)	4118 (6)	624 (8)	1083 (7)	8.1 (6)
C(4)	4543 (8)	−52 (10)	914 (9)	13.6 (9)
C(5)	1480 (6)	1262 (6)	2323 (7)	6.8 (6)
C(6)	1447 (7)	2015 (7)	1860 (8)	10.2 (7)
C(7)	845 (7)	2651 (8)	1884 (8)	12.4 (8)
C(8)	1135 (9)	3016 (8)	2748 (10)	12.2 (10)
C(9)	2742 (6)	−456 (6)	3344 (6)	7.9 (6)
C(10)	1992 (11)	−943 (7)	3272 (8)	14.1 (10)
C(11)	1943 (12)	−1467 (12)	3782 (14)	18.1 (17)
C(12)	1217 (10)	−1790 (12)	3621 (12)	15.9 (14)
C(13)	1193 (4)	−118 (4)	449 (5)	3.6 (4)
C(14)	754 (4)	−750 (4)	−261 (5)	3.8 (4)
C(15)	516 (5)	−1882 (5)	526 (6)	4.5 (5)
C(16)	702 (5)	−2590 (5)	929 (6)	4.4 (5)
C(17)	1348 (5)	−3044 (4)	920 (5)	4.6 (4)
C(18)	1589 (4)	−1910 (4)	100 (5)	3.9 (4)
N(1)	928 (3)	−1561 (3)	112 (4)	3.8 (3)
N(2)	1739 (4)	−2678 (4)	479 (4)	4.9 (3)
O(1)	1649 (3)	−359 (3)	1254 (3)	4.8 (3)
O(2)	1062 (3)	570 (3)	218 (4)	5.7 (3)
O(3)	1972 (3)	−1629 (3)	−256 (4)	4.4 (3)
O(4)	1585 (3)	−3694 (4)	1264 (4)	6.1 (4)

thermal parameters were fixed. Positional and anisotropic thermal parameters for non-H atoms were refined to $R = 0.055$ and $wR = 0.057$. Atoms C(10), C(11) and C(12) possess high thermal parameters (Table 1) and the C(10)—C(11) and C(11)—C(12) bonds (Table 2) are anomalously short; examination of the ΔF map did not, however, reveal any evidence of disorder of these atoms. 226 variables, $(\Delta/\sigma)_{max}$ = 0.4, $w = 1$. Maximum and minimum heights in the final difference Fourier synthesis 0.59 and −0.48 e Å^{-3}. Scattering factors for uncharged atoms taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1984) using an M 4030 computer at the Slovak Technical University, Bratislava, Czechoslovakia.

Discussion. Positional parameters of non-H atoms and B_{eq} values are listed in Table 1,* bond lengths and angles in Table 2. The molecular structure and the atom numbering are shown in Fig. 1, the molecular packing in Fig. 2.

The structure of the title compound is polymeric with five-coordinate tin; O atoms lie in apical positions of the trigonal bipyramid. One O atom belongs to a carboxylate group and the other to the uracil

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Sn—C(1)	2.126 (14)	O(1)—C(13)	1.264 (8)
Sn—C(5)	2.154 (11)	O(2)—C(13)	1.210 (9)
Sn—C(9)	2.140 (10)	C(13)—C(14)	1.510 (10)
Sn—O(1)	2.124 (5)	C(14)—N(1)	1.472 (9)
Sn—O(4^i)	2.669 (6)	C(18)—N(1)	1.359 (11)
C(1)—C(2)	1.466 (18)	C(18)—O(3)	1.197 (12)
C(2)—C(3)	1.563 (19)	C(18)—N(2)	1.405 (10)
C(3)—C(4)	1.477 (22)	C(17)—N(2)	1.376 (13)
C(5)—C(6)	1.465 (16)	C(17)—O(4)	1.218 (9)
C(6)—C(7)	1.555 (19)	C(17)—C(16)	1.419 (13)
C(7)—C(8)	1.403 (19)	C(16)—C(15)	1.330 (12)
C(9)—C(10)	1.564 (22)	C(15)—N(1)	1.337 (13)
C(10)—C(11)	1.245 (27)	C(11)—C(12)	1.353 (29)
C(1)—Sn—C(5)	119.3 (4)	C(14)—N(1)—C(15)	121.2 (7)
C(5)—Sn—C(9)	114.5 (4)	N(1)—C(18)—O(3)	124.4 (8)
C(1)—Sn—C(9)	120.6 (5)	N(2)—C(18)—O(3)	122.4 (8)
O(1)—Sn—C(1)	98.7 (3)	N(1)—C(18)—N(2)	112.9 (8)
O(1)—Sn—C(5)	102.3 (3)	C(10)—C(11)—C(12)	121.4 (19)
O(1)—Sn—C(9)	92.4 (3)	C(17)—N(2)—C(18)	126.8 (8)
O(1)—Sn—O(4^i)	172.8 (2)	N(2)—C(17)—C(16)	113.7 (7)
O(4^i)—Sn—C(1)	80.5 (3)	N(2)—C(17)—O(4)	118.8 (9)
O(4^i)—Sn—C(5)	83.7 (3)	O(4)—C(17)—C(16)	127.4 (9)
O(4^i)—Sn—C(9)	81.6 (2)	C(15)—C(16)—C(17)	120.4 (9)
Sn—O(1)—C(13)	121.1 (5)	C(16)—C(15)—N(1)	122.5 (9)
O(1)—C(13)—O(2)	125.2 (7)	Sn—C(1)—C(2)	118.8 (8)
O(1)—C(13)—C(14)	116.3 (7)	C(1)—C(2)—C(3)	110.1 (10)
O(2)—C(13)—C(14)	118.4 (7)	C(2)—C(3)—C(4)	104.0 (11)
C(13)—C(14)—N(1)	113.5 (6)	Sn—C(5)—C(6)	113.7 (8)
C(14)—N(1)—C(18)	115.1 (7)	C(5)—C(6)—C(7)	116.6 (10)
Sn—C(9)—C(10)	111.3 (7)	C(6)—C(7)—C(8)	112.2 (12)
C(9)—C(10)—C(11)	130.7 (16)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

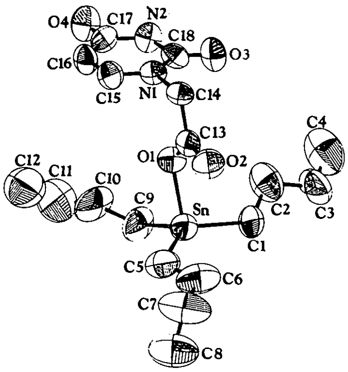

Fig. 1. Molecular structure of the title compound. The Sn—O(4) bond is not shown.

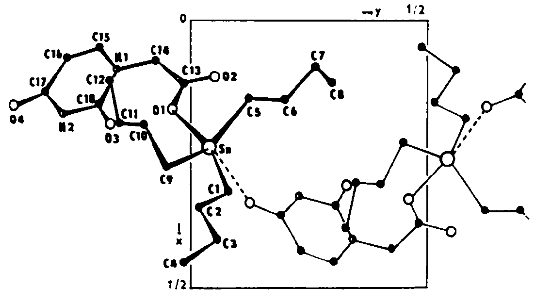

Fig. 2. Molecular packing in the crystal structure of the title compound in the (001) plane. For clarity only two molecules are depicted.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and C—H bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54546 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0200]

group of a neighbouring ligand. The chain is built by repetition of tributyltin(IV) 1-uracilacetate units along twofold screw axes. The carboxylate group bonds to tin through only one O atom [Sn—O(1) 2.124 (5) Å] and is monodentate. The Sn—O(4^{i}) bond [2.669 (6) Å] involving the uracil group is significantly shorter than the sum of the appropriate van der Waals radii (3.70 Å). Bridging by a uracil O atom is probably sterically less demanding than bridging by a carbonyl O atom. The difference in length between the Sn—O(acyl) and Sn—O(uracil) bonds is greater than 0.22 Å, the difference found in triphenyltin(IV) 8-quinolyloxyacetate hydrate (Kumar Das, Chen, Ng & Mak, 1987) where the molecules are linked by hydrogen bonding through coordinated water molecules. In a triphenyltin(IV) 3-pyridinecarboxylate (Ng, Kumar Das, van Meurs, Schagen & Straver, 1989) the corresponding difference is 0.431 Å and molecules are linked by intermolecular Sn←:N bridges.

The three C atoms C(1), C(5) and C(9) define the equatorial plane of the trigonal bipyramid, with the Sn atom located 0.292 (2) Å above this plane. The Sn—C distances are 2.126 (14), 2.154 (11) and 2.140 (10) Å and the sum of the C—Sn—C angles is 354.4 (13)°. The O—Sn—O skeleton is nearly linear [172.8 (2)°]; similar angles in polymeric triorganotin(IV) carboxylates range from 170 to 174°.

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Synthesis and Structure of 3-Fluorenyl-3-cobalta-1,2-dicarba-*closo*-nonaborane(11), 3-(η^5-$C_{13}H_9$)-3,1,2-*closo*-$CoC_2B_9H_{11}$

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Abstract. $C_{15}H_{20}B_9Co$, $M_r = 356.55$, orthorhombic, $P2_12_12_1$, $a = 8.759$ (3), $b = 13.037$ (3), $c = 15.366$ (4) Å, $V = 1754.7$ (8) Å^3, $Z = 4$, $D_x = 1.349$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.94$ mm^{-1}, $F(000) = 728$, $T = 291$ (1) K, $R = 0.0793$ for 1930 independent observed reflections. The (staggered) conformation of the fluorenyl ligand relative to the metal-bonded C_2B_3 face of the carbaborane is such that one pair of junction C atoms is *trans* to a B—B connectivity, the other being *trans* to a B—C connectivity. This conformation is shown to be the optimum by analysis of the results from molecular orbital calculations on a model compound.

Introduction. The synthesis and structural properties of carbametallaboranes in which the indenyl ligand (C_9H_7) is η^5-bonded (exopolyhedrally) to the cluster metal atom are of interest since (i) electronically controlled conformational possibilities exist that are not possible in analogous cyclopentadienyl carbametallaboranes and (ii) slipping distortions are well known both in carbametallaboranes and in indenyl transition-metal compounds separately, and it is instructive to devise molecules in which either or both distortions are present, possibly in competition.

To these ends we have already reported the compound 3-(η^5-C_9H_7)-3,1,2-*closo*-$CoC_2B_9H_{11}$ and its 1e$^-$ and 2e$^-$ reduced forms (Smith & Welch, 1986). The conformation of, and slipping distortions in, the neutral compound are rationalized (*via* frontier molecular orbital analysis) in terms of the influence of the six-carbon ring fused to the side of the η^5-

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