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Tetrakis(μ_2-3-hydroxypyridine-2-carboxylato-κ^2O,N)di-$\mu_3$oxo-tetrakis[dimethyltin(IV)]

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In the crystal structure of the title centrosymmetric distannoxane, [Sn$_4$(CH$_3$)$_8$(C$_6$H$_4$NO$_3$)O$_2$], one 3-hydroxypyridine-2-carboxylate ligand chelates through N and O atoms to an Sn atom. A singly bonded carboxylate O atom coordinates weakly to another independent Sn atom [at a distance of 2.983 (4) Å], which is pseudo-chelated by the other 3-hydroxypyridine-2-carboxylate ligand [Sn···N 2.846 (4) Å]. The μ_3-binding mode of both ligands leads to a skew-trapezoidal bipyramidal geometry [C—Sn—C 136.0 (3)°] for the six-coordinate Sn atom and a trans-pentagonal bipyramidal geometry [C—Sn—C 148.9 (3)°] for the seven-coordinate Sn atom.

Comment

Bis(3-hydroxypyridyl-2-carboxylato)dimethyltin adopts a six-coordinate skew-trapezoidal bipyramidal structure, in which the dimethyltin skeleton is bent [C—Sn—C 149.4 (3)°; Tian et al., 2005]. The title distannoxane, (I), can be considered as the hydrolysis product of this compound. The structural chemistry of this class of organotin carboxylates has been reviewed (Ng et al., 1991; Tiekink, 1991, 1994).

(I)
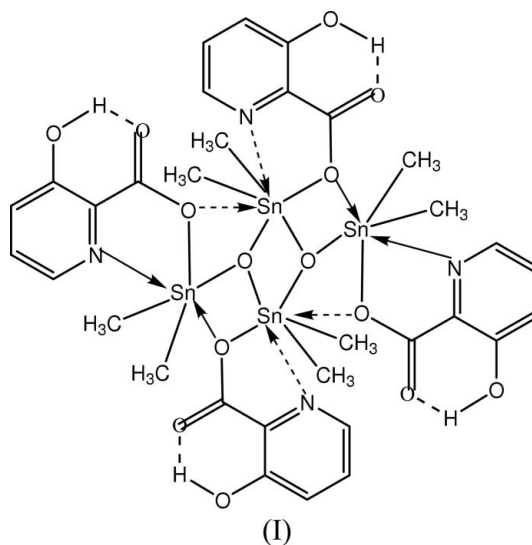
The title centrosymmetric dimer features two unique 3-hydroxypyridyl-2-carboxylate groups, both of which bridge two Sn centres through their singly bonded carboxylate O atom (the doubly bonded carbonyl O atom is not coordinated to the Sn atom, but instead is involved in intramolecular hydrogen bonding with the hydroxy group).

Atom Sn1 is seven-coordinate (Fig. 1), owing to the presence of two relatively long interactions, namely an Sn—N
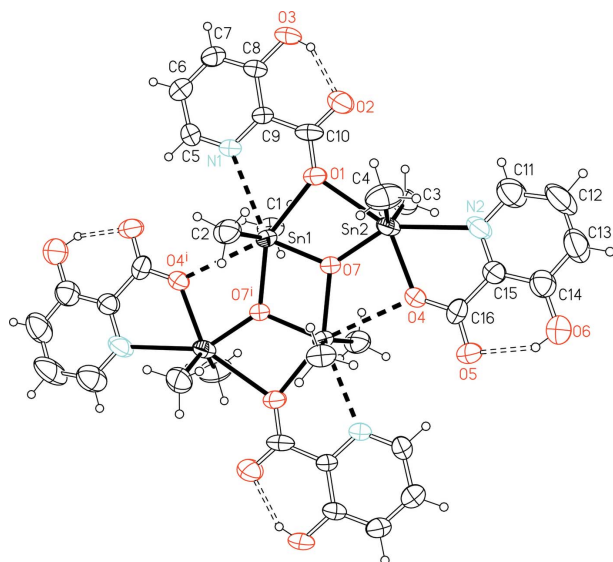
Figure 1
A plot of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii. Open dashed lines indicate hydrogen bonds. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

interaction of 2.846 (4) Å and an Sn—O interaction of 2.983 (4) Å (arising from the carboxylate that is also covalently bonded to the other unique Sn atom). The geometry can be described as a cis-C_2SnO_3 trigonal bipyramidal, distorted to a trans-C_2SnO_5 pentagonal bipyramidal because (in part) of the two longer interactions. These long interactions cause a widening of the C1—Sn1—C2 angle but are, however, not strongly coordinating enough to cause the axial atoms to adopt a linear arrangement. On the other hand, atom Sn2 is six-coordinate, with the ligand coordinating in an unambiguous chelating mode through O and N atoms.

The structure of (I) is similar to that of the tetrabutyl-distannoxane analogue of picolinic acid, which has been described in detail (Parulekar *et al.*, 1989).

Experimental

The reaction was carried out under a nitrogen atmosphere. 3-Hydroxy-2-pyridylcarboxylic acid (0.139 g, 1 mmol) and dimethyltin oxide (0.165 g, 1 mmol) were refluxed in benzene (40 ml) for 12 h. The solvent was removed and the product recrystallized from a dichloromethane–hexane mixture (1:1 *v/v*) to yield colourless crystals in nearly quantitative yield (m.p. 433 K). CHN elemental analysis, found: C 31.60, H 3.64, N 4.62%; calculated for $C_{32}H_{44}N_4O_{16}Sn_4$: C 31.62, H 3.65, N 4.61%.

Crystal data

$[Sn_4(CH_3)_8(C_6H_4NO_3)O_2]$	$Z = 1$
$M_r = 1179.44$	$D_x = 1.867$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.395$ (1) Å	Cell parameters from 3297
$b = 10.055$ (1) Å	reflections
$c = 13.157$ (2) Å	$\theta = 2.5$–28.0°
$\alpha = 89.336$ (2)°	$\mu = 2.42$ mm^{-1}
$\beta = 82.842$ (2)°	$T = 295$ (2) K
$\gamma = 72.231$ (1)°	Block, colourless
$V = 1049.0$ (2) Å^3	0.45 × 0.37 × 0.23 mm

Data collection

Siemens SMART CCD area-detector diffractometer	4646 independent reflections
	3460 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SADABS*; Sheldrick, 1996)	$h = -10 \rightarrow 10$
$T_{min} = 0.337$, $T_{max} = 0.576$	$k = -13 \rightarrow 12$
6588 measured reflections	$l = -17 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 0.3682P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
4646 reflections	$\Delta\rho_{max} = 1.39$ e Å^{-3}
248 parameters	$\Delta\rho_{min} = -0.89$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Sn1—C1	2.104 (6)	Sn2—C3	2.107 (5)
Sn1—C2	2.099 (6)	Sn2—C4	2.108 (6)
Sn1—N1	2.846 (4)	Sn2—N2	2.576 (5)
Sn1—O1	2.314 (4)	Sn2—O1	2.557 (5)
Sn1—O4^i	2.983 (4)	Sn2—O4	2.152 (4)
Sn1—O7	2.050 (3)	Sn2—O7	2.012 (3)
Sn1—O7^i	2.154 (3)		
C1—Sn1—C2	148.9 (3)	O4^i—Sn1—O7	133.5 (1)
C1—Sn1—N1	76.9 (2)	O4^i—Sn1—O7^i	58.9 (1)
C1—Sn1—O1	93.3 (2)	O7—Sn1—O7^i	74.6 (2)
C1—Sn1—O4^i	80.8 (2)	C3—Sn2—C4	136.0 (3)
C1—Sn1—O7	104.6 (2)	C3—Sn2—N2	85.9 (2)
C1—Sn1—O7^i	94.3 (2)	C3—Sn2—O1	83.7 (2)
C2—Sn1—N1	79.5 (2)	C3—Sn2—O4	108.6 (2)
C2—Sn1—O1	93.5 (2)	C3—Sn2—O7	104.7 (2)
C2—Sn1—O4^i	80.0 (2)	C4—Sn2—N2	84.5 (3)
C2—Sn1—O7^i	96.4 (2)	C4—Sn2—O1	81.3 (2)
C2—Sn1—O7	106.3 (2)	C4—Sn2—O4	107.1 (2)
N1—Sn1—O1	62.3 (1)	C4—Sn2—O7	107.2 (3)
N1—Sn1—O4^i	91.9 (1)	N2—Sn2—O1	146.6 (1)
N1—Sn1—O7	134.6 (1)	N2—Sn2—O4	67.6 (1)
N1—Sn1—O7^i	150.7 (1)	N2—Sn2—O7	145.8 (1)
O1—Sn1—O4^i	154.2 (1)	O1—Sn2—O4	145.7 (1)
O1—Sn1—O7	72.3 (1)	O1—Sn2—O7	67.7 (1)
O1—Sn1—O7^i	146.9 (1)	O4—Sn2—O7	78.2 (1)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3O$\cdots$O2	0.82	1.84	2.561 (6)	146
O6—H6O$\cdots$O5	0.82	1.95	2.579 (6)	133

All H atoms were positioned geometrically, with C—H$_{methyl}$ = 0.96, C—H$_{pyridyl}$ = 0.93 and O—H = 0.82 Å, and were included in the refinement in the riding-model approximation, with U_{iso}(H) = $1.2U_{eq}$(C,O). The final difference Fourier map had a large peak 2.9 Å from O2. Attempts to refine the peak as a water molecule were unsuccessful.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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