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Key indicators

Single-crystal X-ray study  
 T = 298 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.010 \text{ \AA}$   
 Disorder in main residue  
 R factor = 0.039  
 wR factor = 0.114  
 Data-to-parameter ratio = 14.9

For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

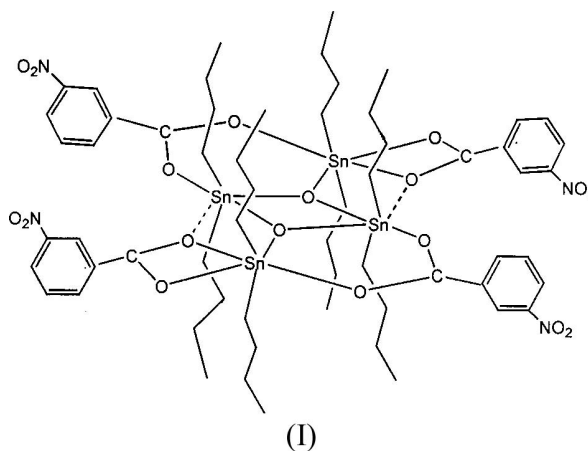
Bis( $\mu$ -3-nitrobenzoato)-1:2 $\kappa^2\text{O}:\text{O}'$ ;3:4 $\kappa^2\text{O}:\text{O}'$ -  
 bis(3-nitrobenzoato)-1 $\kappa^2\text{O},\text{O}'$ ;3 $\kappa^2\text{O},\text{O}'$ -di- $\mu_3$ -oxo-  
 1:2:4 $\kappa^3\text{O}$ ;2:3:4 $\kappa^3\text{O}$ -tetrakis[di-*n*-butyltin(IV)]

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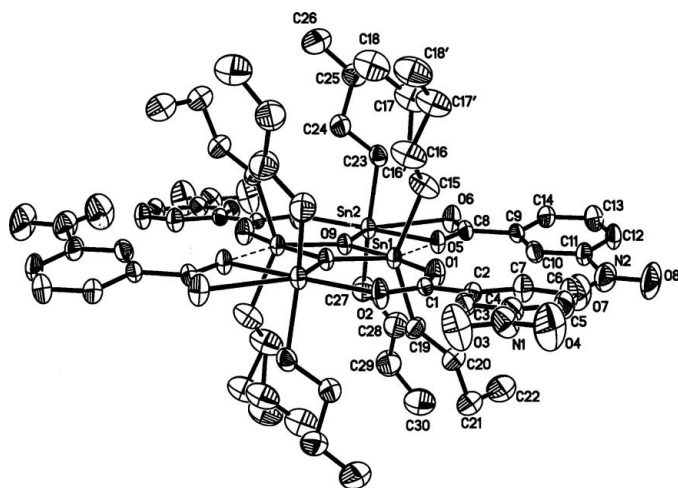
The reaction of bis(tributyltin) oxide with 3-nitrobenzoic acid yields a stable crystalline material with the composition  $[\text{Sn}_4\text{O}_2(\text{C}_4\text{H}_9)_8(\text{C}_7\text{H}_4\text{NO}_4)_4\text{O}_2]$ , which contains two bridging and two non-bridging (bidentate) 3-nitrobenzoate groups. It is a tetranuclear dimer in which there are two six-coordinate endocyclic and two six-coordinate exocyclic Sn atoms.

Comment

Fig. 1 shows that the title compound, (I), is a tetranuclear centrosymmetric dimer with a central four-membered ring defined by  $\text{Sn1}-\text{O9}-\text{Sn1}^i-\text{O9}^i$  [symmetry code: (i)  $-x + 1, -y + 1, -z$ ]. Two bridging carboxyl groups link the four Sn atoms, while the remaining two act as bidentate ligands to the exocyclic Sn atoms. Consideration of the axial angles  $\text{O1}-\text{Sn1}-\text{O9}$  and  $\text{O5}-\text{Sn2}-\text{O2}^i$  and of the Sn—O distances leads to the conclusion that the two Sn atoms are in different environments. Both Sn atoms are coordinated by two *n*-butyl groups. In particular, as can be seen from Fig. 1, two of the eight *n*-butyl groups, those coordinated to atoms Sn1 or Sn1<sup>i</sup> atoms, contain three atoms, C16, C17 or C18, which occupy two positions. In the case of the exocyclic atom Sn2, coordination is completed by atoms O5, O6, O2<sup>i</sup> and O9. For the endocyclic atom Sn1, atoms O1, O9 and O9<sup>i</sup> all coordinate at different distances, and there is a weak but significant interaction to atom O5. Thus, it may be concluded that the exocyclic atom Sn2 is best described as six-coordinate and the endocyclic atom Sn1 as pseudo-six-coordinate.



A comparison between the structure of (I) and those of the amino-, *ortho*-methoxy- or *ortho*-nitrobenzoatodistannoxanes published previously (Narula *et al.*, 1992; Chandrasekhar *et al.*, 1988), reveal that endocyclic Sn atoms in all types of compounds are six-coordinate, while the exocyclic Sn atoms



**Figure 1**

The structure of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Dashed lines indicate the weak interactions between atoms Sn1 and O5. Unlabelled atoms are related to labelled atoms by the symmetry operation  $(-x + 1, -y + 1, -z)$ .

are five-coordinate in the *o*-nitrobenzoato- and six-coordinate in the amino-, *o*-methoxy- or *m*-nitrobenzoatostannoxanes. The existence of such six- and five-coordinate Sn atoms has also been shown by X-ray analysis (Graziani *et al.*, 1977; Valle *et al.*, 1984) in tetra-*n*-butyl bis(tri- or bis(dichloroacetoxy)distanoxanes. A close scrutiny of the available structural data for diorganostannoxanes (Graziani *et al.*, 1977; Valle *et al.*, 1984; Chow, 1971; Chandrasekhar *et al.*, 1988; Narula *et al.*, 1988) reveals that the choice between five- and six-coordinated exocyclic Sn atoms in this type of compound may depend upon the electronic effects of the substituents in the carboxyl ligands. This is supported by similar observations on triphenyltin benzoates (Molloy *et al.*, 1988). Interestingly, the electronegative ligands influence the bonding characteristics of non-bridging but not those of bridging carboxyl groups.

## Experimental

*meta*-Nitrobenzoic acid (1 mmol) was added to a benzene suspension (30 ml) of bis(tributyltin) oxide (1 mmol) and the mixture was stirred and heated at reflux for 6 h. The clear solution obtained after filtration was evaporated *in vacuo* to give a solid, which was then recrystallized from dichloromethane–hexane (yield 86.1%). Colourless crystals of (I) suitable for X-ray diffraction were obtained (m.p. 388 K). Elemental analysis, calculated for  $C_{60}H_{88}N_4O_{18}Sn_4$ : C 44.22, H 5.41, N 3.44%; found: C 44.25, H 5.33, N 3.51%.

### Crystal data

$[Sn_4O_2(C_4H_9)_8(C_7H_4NO_4)_4O_2]$   
 $M_r = 1628.10$   
 Monoclinic,  $P2_1/c$   
 $a = 11.7885$  (13) Å  
 $b = 11.6149$  (13) Å  
 $c = 25.301$  (3) Å  
 $\beta = 94.903$  (2)°  
 $V = 3451.6$  (7) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.567$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5842 reflections  
 $\theta = 2.4$ – $27.0^\circ$   
 $\mu = 1.50$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 Block, colourless  
 $0.41 \times 0.35 \times 0.29$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{min} = 0.579$ ,  $T_{max} = 0.671$   
 17627 measured reflections

6064 independent reflections  
 4273 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.035$   
 $\theta_{max} = 25.0^\circ$   
 $h = -13 \rightarrow 14$   
 $k = -13 \rightarrow 13$   
 $l = -30 \rightarrow 19$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.114$   
 $S = 1.00$   
 6064 reflections  
 408 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 4.7483P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.79$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.56$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Sn1—O9 <sup>i</sup>	2.031 (3)	Sn2—O9	2.034 (3)
Sn1—C15	2.112 (7)	Sn2—C23	2.113 (6)
Sn1—C19	2.125 (6)	Sn2—C27	2.129 (7)
Sn1—O9	2.195 (4)	Sn2—O5	2.188 (4)
Sn1—O1	2.240 (4)	Sn2—O2 <sup>i</sup>	2.275 (4)
Sn1—O5	3.011 (4)	Sn2—O6	2.746 (4)
O9 <sup>i</sup> —Sn1—C15	109.7 (3)	O9—Sn2—C23	105.6 (2)
O9 <sup>i</sup> —Sn1—C19	112.3 (2)	O9—Sn2—C27	107.2 (3)
C15—Sn1—C19	137.9 (3)	C23—Sn2—C27	146.4 (3)
O9 <sup>i</sup> —Sn1—O9	76.70 (15)	O9—Sn2—O5	84.08 (14)
C15—Sn1—O9	96.7 (3)	C23—Sn2—O5	93.1 (2)
C19—Sn1—O9	94.3 (2)	C27—Sn2—O5	97.4 (2)
O9 <sup>i</sup> —Sn1—O1	92.16 (15)	O9—Sn2—O2 <sup>i</sup>	93.63 (15)
C15—Sn1—O1	86.7 (3)	C23—Sn2—O2 <sup>i</sup>	87.7 (2)
C19—Sn1—O1	90.1 (2)	C27—Sn2—O2 <sup>i</sup>	83.2 (2)
O9—Sn1—O1	168.86 (15)	O5—Sn2—O2 <sup>i</sup>	177.70 (15)
O9 <sup>i</sup> —Sn1—O5	140.27 (12)	O9—Sn2—O6	135.69 (14)
C15—Sn1—O5	75.3 (2)	C23—Sn2—O6	76.8 (2)

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

H atoms were positioned geometrically and treated as riding on their parent atoms, with aromatic C—H distances of 0.93 Å, methylene C—H distances of 0.97 Å and methyl C—H distances of 0.96 Å. The  $U_{iso}(H)$  values were set at  $1.5U_{eq}(C)$  for the methyl H atoms and at  $1.2U_{eq}(C)$  for the other H atoms.

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

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