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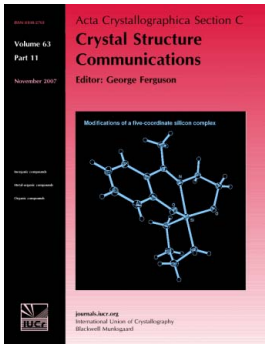

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Tetrakis(μ_2-4-aminobenzoato)di-μ_3-oxido-tetrakis[dibutyltin(IV)]

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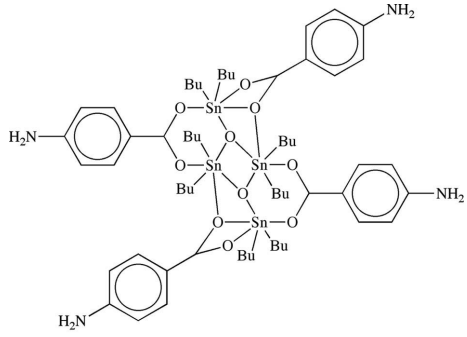
The molecule of the title compound, $[Sn_4(C_4H_9)_8(C_7H_6NO_2)_4O_2]$, lies about an inversion centre and is a tetranuclear bis(tetrabutyldicarboxylatodistannoxane) complex containing a planar Sn_4O_2 core in which two μ_3-oxide O atoms connect an Sn_2O_2 ring to two exocyclic Sn atoms. Each Sn atom has a highly distorted octahedral coordination. In the molecule, the carboxylate groups of two aminobenzoate ligands bridge the central and exocyclic Sn atoms, while two further aminobenzoate ligands have highly asymmetric bidentate chelation to the exocyclic Sn atoms plus long O···Sn interactions with the central Sn atoms. Each Sn atom is also coordinated by two pendant *n*-butyl ligands, which extend roughly perpendicular to the plane of the Sn_4O_{10} core. Only one of the four unique hydrogen-bond donor sites is involved in a classic N—H···O hydrogen bond, and the resulting supramolecular hydrogen-bonded structure is an extended two-dimensional network which lies parallel to the (100) plane and consists of a checkerboard pattern of four-connected molecular cores acting as nodes. The amine groups not involved in the hydrogen-bonding interactions have significant N—H···π interactions with neighbouring aminobenzene rings.

Comment

Bis(dicarboxylatotetraorganodistannoxanes), $\{[R_2Sn(O_2CR')]_2O\}_2$, are of interest because of their useful applications in biology and catalysis (Blair *et al.*, 1997; Petrosyan *et al.*, 1996; Ribot *et al.*, 1998; Tiekink *et al.*, 1995). We have previously reported the crystal structures of related bis(dicarboxylatotetraorganodistannoxanes) prepared from various carboxylates, *viz*. *β*-{[(*E*)-1-(2-hydroxy-3-methylphenyl)ethylidene]amino}propionate, *β*-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}propionate (Basu Baul, Masharing *et al.*, 2006), and 5-[(*E*)-2-aryl-1-diazenyl]-2-hydroxybenzoates, where aryl is 2-methoxy, 3-methyl (Basu Baul *et al.*, 2007) and 4-unsubstituted, 4-methyl, 4-chloro and 4-bromo (Basu Baul, Rynjah *et al.*, 2006). During an extension of these studies into the coordination chemistry of substituted carboxylates with organotin species, 4-aminobenzoic acid was reacted with dibutyltin(IV) oxide to form the tetranuclear title compound, $\{[Bu_2Sn(O_2CC_6H_4\text{-}p\text{-}NH_2)]_2O\}_2$ (Bu = *n*-butyl), (I), and its crystal structure is reported here.



(I)

The molecular structure of (I) is shown in Fig. 1. The molecule lies about an inversion centre and is a tetranuclear bis(tetrabutyldicarboxylatodistannoxane) complex containing a planar Sn_4O_2 core, in which two μ_3-oxide O atoms connect an Sn_2O_2 ring (endocyclic Sn atoms) to two exocyclic Sn atoms to give an $R_8Sn_4O_2$ central unit. The central Sn2···Sn2($-x+1$, $-y$, $-z+1$) contact is 3.3140 (2) Å, while the two unique *exo*-Sn···*endo*-Sn distances are 3.6334 (2) and 3.7660 (2) Å. Two symmetry-related aminobenzoate ligands each bridge one endocyclic to one exocyclic Sn centre *via* the two carboxylate O atoms, with the Sn—O distances being quite similar (Table 1). Two additional aminobenzoate ligands each have highly asymmetric bidentate chelation *via* the two carboxylate O atoms to an exocyclic Sn atom, with the longer Sn1···O5 interactions being quite long [2.9053 (18) Å]. Additionally, the other carboxylate O atom in each of these ligands coordinates *via* a second long Sn2···O4($1-x$, $-y$, $1-z$) bond [2.7841 (17) Å] to an endocyclic Sn atom. Each Sn atom is also coordinated by two pendant Bu ligands, which subtend angles of about 140° at their parent Sn atoms. If the longer Sn···O distances are considered as part of the primary coordination

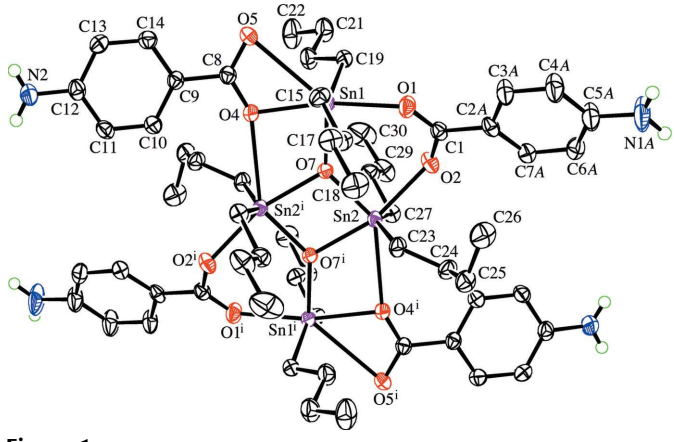


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Only one conformation of the disordered aminobenzene ring is shown. H atoms bonded to C atoms have been omitted for clarity. [Symmetry code: (i) $-x+1$, $-y$, $-z+1$.]

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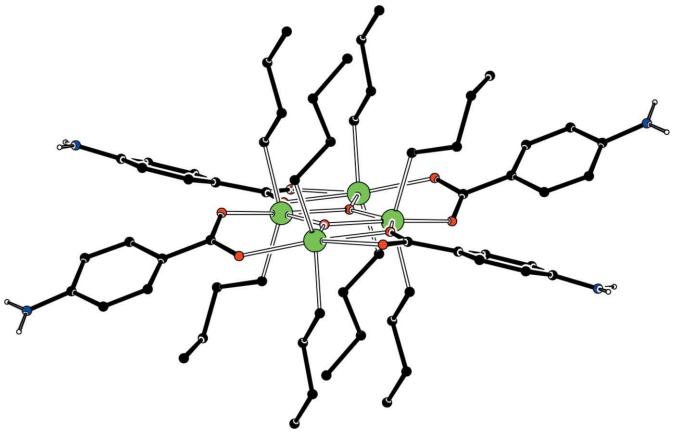

Figure 2
The disposition of the pendant *n*-butyl ligands perpendicular to the plane of the Sn_4O_{10} core and the carboxylate ligands in the molecule of (I). H atoms bonded to C atoms have been omitted for clarity and only one of the arrangements of the disordered aminobenzene ring is shown.

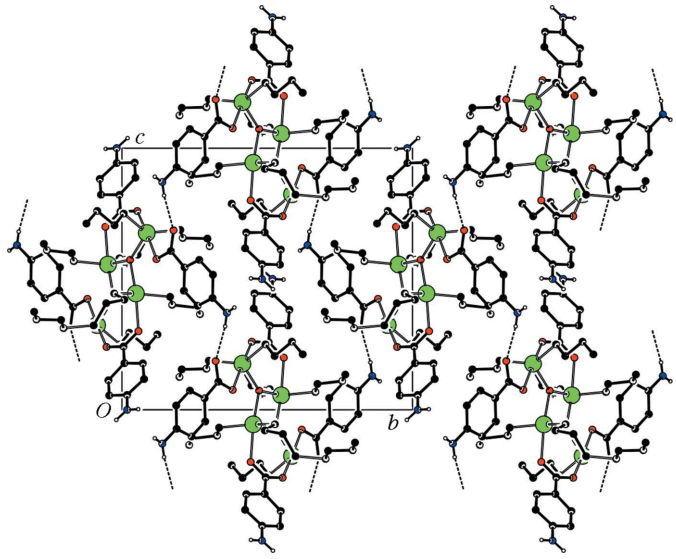

Figure 3
The supramolecular hydrogen-bonded layer in the structure of (I). H atoms bonded to C atoms have been omitted for clarity and only one of the arrangements of the disordered aminobenzene ring is shown.

environment, each Sn atom has a highly distorted octahedral coordination, with some of the distortion arising from bite-angle constraints. Alternatively, ignoring Sn···O distances greater than 2.3 Å yields a distorted trigonal–bipyramidal geometry about each Sn atom, with, in each case, the Bu ligands occupying equatorial positions.

The Sn_4O_{10} core of the molecule forms an essentially planar system, although the six-membered ring formed by Sn1, Sn2, the μ_3-oxide atom O7 and the bridging carboxylate group is somewhat twisted towards a screw boat form, forcing atoms O1 and O2 out of the plane of the remainder of the core atoms by 0.323 (2) and −0.505 (2) Å, respectively. The aminobenzene rings are slightly tilted out of the plane of the Sn_4O_{10} core, with dihedral angles between the benzene ring planes and core plane in the range 12.8 (3)–24.6 (2)° (the presented range includes both disordered conformations of one aminobenzoate ligand). Nonetheless, the Sn_4O_{10} core and associated carboxylate ligands can be considered as a fairly planar entity, with the pendant Bu ligands extending roughly perpendicular to this plane (Fig. 2).

The aminobenzene moiety of the aminobenzoate ligand containing atoms O1 and O2 is disordered over two conformations. The major conformation is present in approximately 59% of the molecules.

The structures of many dimeric dicarboxylatotetraorganodistannoxanes are known and have been reviewed (Tiekink, 1991, 1994). Five predominant patterns of carboxylate ligand coordination about the Sn_4O_2 core seem to recur, but by far the most common motif is the centrosymmetric variant displayed by compound (I). The Cambridge Structural Database (Version 5.30, update 4 of September 2009; Allen, 2002) contains entries for 135 structures displaying the same basic coordination motif as (I). In structures of this type, the Sn coordination geometry, as well as the distribution of Sn—O distances, is usually much the same.

Although two symmetry-independent amine groups offering four potential hydrogen-bond donor sites are present in the molecule of (I), only one of these is involved in a classic N—H···O hydrogen bond (Table 2). This intermolecular interaction is with a carboxylate O atom in the same carboxylate ligand of a neighbouring tetranuclear molecule related by a *c*-glide operation, and serves to link the molecules into extended zigzag chains which run parallel to the [001] direction (Fig. 3) and can be described by a graph-set motif of *C*(8) [see Bernstein *et al.* (1995) for a description of graph-set motifs]. The path of this motif involves only the atoms of a single unique carboxylate ligand. As the molecule lies about an inversion centre, each molecule accepts and donates two of these hydrogen bonds, so that both sides of the molecule are involved in two antiparallel adjacent chains. A consequence of this is that the same hydrogen-bonding interactions also yield further zigzag chains which run *via* the core of each molecule parallel to [010] and which can be described by a graph-set motif of *C*(14). Effectively, the core of each molecule cross-links two adjacent [001] chains, and neighbouring molecules in each such chain crosslink different chains, resulting in a checkerboard pattern of four-connected molecular cores acting as nodes between the chains (Fig. 3). The overall supramolecular hydrogen-bonded structure arising out of these interactions is thus an extended two-dimensional network which lies parallel to the (100) plane. The hydrogen-bonded ring motif within each of the checkerboard squares is $R_4^4(22)$.

There are no significant π–π interactions in the structure of (I), but one unique N—H···π interaction is present between the amine group not involved in the hydrogen-bonding interactions described above and the aminobenzene ring defined by atoms C9–C14 (centroid *Cg*1) in a neighbouring molecule [N1*B*···*Cg*1^{i} = 3.706 (10) Å, H13···*Cg*1^{i} = 2.84 Å, H13···ring plane = 2.67 Å and N1*B*—H13···*Cg*1^{i} = 168°; symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$]. The interaction appears to involve only the minor conformation of the disordered aminobenzene ring; although the major conformation of

the aminobenzene ring has an H atom at a similar distance from the plane of the $Cg1^{i}$ ring, it is significantly offset from the centre of the ring.

Experimental

A suspension of Bu_2SnO (1.036 g, 3.64 mmol) and 4-aminobenzoic acid (0.5 g, 3.64 mmol) in anhydrous toluene (50 ml) were refluxed for 3 h in a flask equipped with a Dean–Stark water separator and a water-cooled condenser. After the reaction, a clear solution was obtained and this was filtered while hot. The solvent was evaporated *in vacuo*, and the white residue was washed thoroughly with hexane and dried *in vacuo*. The residue was dissolved in chloroform and the solution was filtered to remove any undissolved particles. The filtrate was left to crystallize at room temperature. The crude product was obtained after evaporation and this was then recrystallized from a chloroform–hexane solution (1:1 *v*/*v*) to give colourless prismatic crystals of (I) in 65% yield (m.p. 379–381 K). Analysis calculated for $C_{60}H_{96}N_4O_{10}Sn_4$: C 47.78, H 6.42, N 3.71%; found: C 47.80, H 6.23, N 3.66%. IR (KBr, cm^{-1}): 1621 $\nu(OCO)_{asym}$, 643 $\nu(Sn-O-Sn)$; ^1H NMR ($CDCl_3$, δ, p.p.m.): 7.91 (*br d*, 2H, H2), 6.68 (*d*, 2H, H3), 4.0 (*br s*, 2H, NH_2); Sn–^{n}Bu skeleton: 0.80 (*br m*, 6H, H4*), 1.35 (*br m*, 4H, H3*), 1.70 (*br m*, 8H, H1* and H2*); ^{13}C NMR ($CDCl_3$, δ, p.p.m.), ligand skeleton: 113.7 (C3), 123.2 (C1), 131.9 (C2), 150.0 (C4), 172.8 (CO_2); Sn–^{n}Bu skeleton: 28.1, 27.7, 27.4, 26.8 and 26.1 (C1*, C2* and C3*), 13.6 (C4*). For the ^1H and ^{13}C NMR assignments, atoms marked with an asterisk (*) refer to the *n*-butyl ligand numbered outwards from the Sn atom; the other C atoms belong to the aminobenzene ring, starting from the ring C atom closest to the carboxylate group.

Crystal data

$[Sn_4(C_4H_9)_8(C_7H_6NO_2)_4O_2]$
M_r = 1507.84
Monoclinic, $P2_1/c$
a = 12.3017 (1) Å
b = 17.1436 (1) Å
c = 15.8633 (1) Å
β = 103.3015 (5)°
V = 3255.75 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.57 mm^{-1}
T = 160 K
0.22 × 0.20 × 0.17 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.646, T_{max} = 0.764
94040 measured reflections
9527 independent reflections
7900 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.078
S = 1.13
9520 reflections
428 parameters
231 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.89 e Å^{-3}

The entire aminobenzene moiety of one of the two symmetry-independent carboxylate ligands is disordered over two conformations. Two sets of overlapping positions were defined for the atoms of this group and the site-occupation factors of each conformation were refined while restraining their sum to unity. The site-occupation factor of the major conformation refined to 0.585 (5). Similarity restraints with tolerance s.u. values of 0.005 Å were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, while neighbouring atoms within and between each conformation were restrained to have similar atomic displacement parameters within a tolerance s.u. of 0.01 Å^2. Each conformation of the disordered aminobenzene group was further restrained to be planar, also with a tolerance s.u. of 0.01 Å. The H atoms of the ordered amine group were placed in the positions indicated by a difference electron-density map and their positions were allowed to refine, together with individual isotropic displacement parameters. The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å), with $U_{iso}(H) = 1.5U_{eq}(C)$, but were allowed to rotate freely about the adjacent C—C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 (aromatic) or 0.99 Å (methylene) and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. Seven low-angle reflections were omitted from the final cycles of refinement because their observed intensities were much lower than the calculated values as a result of being partially obscured by the beam stop.

Table 1
Selected geometric parameters (Å, °).

Sn1—O1	2.2717 (18)	Sn2—O7	2.0534 (16)
Sn1—O4	2.1886 (16)	Sn2—O7^{i}	2.1501 (16)
Sn1—O5	2.9053 (18)	Sn2—C23	2.123 (2)
Sn1—O7	2.0249 (16)	Sn2—C27	2.125 (2)
Sn1—C19	2.123 (2)	O1—C1	1.259 (3)
Sn1—C15	2.135 (3)	O2—C1	1.268 (3)
Sn2—O2	2.2359 (17)	O4—C8	1.302 (3)
Sn2—O4^{i}	2.7841 (17)	O5—C8	1.239 (3)
O7—Sn1—C19	108.76 (9)	C27—Sn2—O7^{i}	97.58 (8)
O7—Sn1—C15	112.17 (9)	O7—Sn2—O2	88.46 (7)
C19—Sn1—C15	138.45 (10)	C23—Sn2—O2	88.68 (8)
O7—Sn1—O4	79.92 (6)	C27—Sn2—O2	82.42 (8)
C19—Sn1—O4	100.72 (8)	O7^{i}—Sn2—O2	163.35 (7)
C15—Sn1—O4	93.19 (9)	O7—Sn2—O4^{i}	140.86 (6)
O7—Sn1—O1	91.49 (7)	C23—Sn2—O4^{i}	80.82 (8)
C19—Sn1—O1	88.19 (8)	C27—Sn2—O4^{i}	79.19 (8)
C15—Sn1—O1	83.94 (9)	O7^{i}—Sn2—O4^{i}	65.13 (5)
O4—Sn1—O1	169.20 (7)	O2—Sn2—O4^{i}	130.68 (6)
O7—Sn1—O5	128.92 (6)	C1—O1—Sn1	131.46 (16)
C19—Sn1—O5	81.85 (8)	C1—O2—Sn2	131.68 (16)
C15—Sn1—O5	78.25 (8)	C8—O4—Sn1	110.17 (14)
O4—Sn1—O5	49.10 (5)	C8—O4—Sn2^{i}	154.62 (15)
O1—Sn1—O5	139.47 (6)	Sn1—O4—Sn2^{i}	93.11 (6)
O7—Sn2—C23	103.05 (9)	C8—O5—Sn1	77.77 (14)
O7—Sn2—C27	111.14 (8)	Sn1—O7—Sn2	134.87 (8)
C23—Sn2—C27	144.31 (10)	Sn1—O7—Sn2^{i}	120.95 (8)
O7—Sn2—O7^{i}	75.95 (7)	Sn2—O7—Sn2^{i}	104.05 (7)
C23—Sn2—O7^{i}	100.39 (8)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···O5^{ii}	0.82 (4)	2.26 (4)	3.051 (4)	164 (3)

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3152). Services for accessing these data are described at the back of the journal.

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