Tetrakis(μ2-4-aminobenzoato)di-μ3-oxido-tetrakis[dibutyltin(IV)]

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Tetrakis(μ₂-4-aminobenzoato)di-μ₃-oxido-tetrakis[dibutyl-tin(IV)]

Anthony Linden, Tushar S. Basu Baul and Pradip Das

The molecule of the title compound, \([\text{Sn}_4(\text{C}_6\text{H}_5\text{H}_2\text{O}_2\text{Bu}_4)]_2\), lies about an inversion centre and is a tetranuclear bis(tetraorganodistannoxane) complex containing a planar \(\text{Sn}_4\text{O}_2\) core in which two \(\mu_2\)-oxide \(\text{O}\) atoms connect an \(\text{Sn}_4\text{O}_2\) ring to two exocyclic \(\text{Sn}\) atoms. Each \(\text{Sn}\) atom has a highly distorted octahedral coordination. In the molecule, the carboxylate groups of two aminobenzoate ligands bridge the central and exocyclic \(\text{Sn}\) atoms, while two further aminobenzoate ligands have highly asymmetric bidentate chelation to the exocyclic \(\text{Sn}\) atoms plus long \(\text{O}\cdot\cdot\cdot\text{Sn}\) interactions with the central \(\text{Sn}\) atoms. Each \(\text{Sn}\) atom is also coordinated by two pendant \(\text{Bu}\) ligands, which extend roughly perpendicular to the plane of the \(\text{Sn}_4\text{O}_2\) core. Only one of the four unique hydrogen-bond donor sites is involved in a classic \(\text{N}\cdot\cdot\cdot\text{H}\) 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 \(\text{N}\cdot\cdot\cdot\pi\) interactions with neighbouring aminobenzene rings.

Comment

Bis(dicarboxylatotetraorganodistannoxanes), \([\text{R}_2\text{Sn}(\text{O}_2\text{CR'})_2\text{O}]_2\)
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, \(\text{viz.}\ \beta-[\{(E)-(2\text{-}3\text{hydroxy-3\text{-}methylphenyl})\text{ethylidene}\}]\text{aminolpropionate, \(\beta-[\{(Z)-(3\text{-}3\text{-}hydroxy-1\text{-}methyl-2\text{-}butenylidene)}\text{aminolpropionate (Basu Baul, Masharing et al., 2006), and 5-[\{(E)-2\text{-}3\text{-}diazenyl}\}-2\text{-}hydroxybenzoates, where aryl is 2\text{-}methoxy, 3\text{-}methyl (Basu Baul et al., 2007) and 4\text{-}unsaturated, 4\text{-}methyl, 4\text{-}chloro and 4\text{-}bromo (Basu Baul, Rynjah et al., 2006). During an extension of these studies into the coordination chemistry of substituted carboxylates with organotin species, 4\text{-}aminobenzoic acid was reacted with dibutyltin(IV) oxide to form the tetranuclear title compound, \([\text{Bu}_2\text{Sn}(\text{O}_2\text{CC}_6\text{H}_4\text{p-NH}_2)_2\text{O}]_2\) (\(\text{Bu} = \text{n-butyl}\), (I), and its crystal structure is reported here.

The molecular structure of (I) is shown in Fig. 1. The molecule lies about an inversion centre and is a tetranuclear bis(tetraorganodistannoxane) complex containing a planar \(\text{Sn}_4\text{O}_2\) core, in which two \(\mu_2\)-oxide \(\text{O}\) atoms connect an \(\text{Sn}_4\text{O}_2\) ring (endocyclic \(\text{Sn}\) atoms) to two exocyclic \(\text{Sn}\) atoms to give an \(\text{R}_2\text{Sn}_2\text{O}_2\) central unit. The central \(\text{Sn}_2\cdot\cdot\cdot\text{Sn}_2\) contact is 3.3140 (2) \(\AA\), while the two unique exo-\(\text{Sn}\cdot\cdot\cdot\text{endo}\)-\(\text{Sn}\) distances are 3.6334 (2) and 3.7660 (2) \(\AA\). Two symmetry-related aminobenzoate ligands each bridge one endocyclic to one exocyclic \(\text{Sn}\) centre via the two carboxylate \(\text{O}\) atoms, with the \(\text{Sn}\)–\(\text{O}\) distances being quite similar (Table 1). Two additional aminobenzoate ligands each have highly asymmetric bidentate chelation via the two carboxylate \(\text{O}\) atoms to an exocyclic \(\text{Sn}\) atom, with the longer \(\text{Sn}_1\cdot\cdot\cdot\text{O}_5\) interactions being quite long [2.9053 (18) \(\AA\)]. Additionally, the other carboxylate \(\text{O}\) atom in each of these ligands coordinates via a second long \(\text{Sn}_2\cdot\cdot\cdot\text{O}_4(1-x,-y,1-z)\) bond [2.7841 (17) \(\AA\)] to an endocyclic \(\text{Sn}\) atom. Each \(\text{Sn}\) atom is also coordinated by two pendant \(\text{Bu}\) ligands, which subtend angles of about 140° at their parent \(\text{Sn}\) atoms. If the longer \(\text{Sn}_2\cdot\cdot\cdot\text{O}\) 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. \(\text{H}\) atoms bonded to C atoms have been omitted for clarity. [Symmetry code: (i) \(-x+1,-y,-z+1\).]
Benzene rings are slightly tilted out of the plane of the Sn\(_4\)O\(_{10}\) 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.

The structures of many dimeric dicarboxylatotetraorgano-distannoxanes are known and have been reviewed (Tiekink, 1991, 1994). Five predominant patterns of carboxylate ligand coordination about the Sn\(_4\)O\(_{10}\) core seem to recur, but by far 59\% of the molecules.

The Sn\(_4\)O\(_{10}\) core of the molecule forms an essentially planar system, although the six-membered ring formed by Sn1, Sn2, the \(\mu_3\)-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) \(\AA\), respectively. The aminobenzene rings are slightly tilted out of the plane of the Sn\(_4\)O\(_{10}\) core, with dihedral angles between the benzene ring planes and core plane in the range 12.8 (3)–24.6 (2)\(^\circ\) (the presented range includes both disordered conformations of one aminobenzoate ligand). Nonetheless, the Sn\(_4\)O\(_{10}\) 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 conformational positions.

The disposition of the pendant \(n\)-butyl ligands perpendicular to the plane of the Sn\(_4\)O\(_{10}\) 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 2

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.

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 crosslinks 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 \(R_2^2(22)\).

There are no significant \(\pi\n\pi\) interactions in the structure of (I), but one unique N—H···\(\pi\) 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 Cg1) in a neighbouring molecule [N1B···Cg1\(^1\) = 3.706 (10) \(\AA\), H13···Cg1\(^1\) = 2.84 \(\AA\), H13···ring plane = 2.67 \(\AA\) and N1B—H13···Cg1\(^1\) = 168\(^\circ\)]. 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...
metal-organic compounds

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

Experimental
A suspension of Bu2SnO (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 re-crystallized 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 C47H48N2O8Sn2: C 47.80, H 6.23, N 3.71%; found: C 47.80, H 6.23, N 3.66%. IR (KBr, cm⁻¹): 1621 v(OCO)asym, 643 v(Sn–O–Sn); 1H NMR (CDCl3, δ, p.p.m.): 7.91 (br d, 2H, H2), 6.68 (d, 2H, H3), 4.0 (br s, 2H, NH2); Sn–Bu skeleton: 28.1, 27.7, 27.4, 26.8 and 26.1 (C1*, C2* and C3*), 13.6 (C4*). For the 1H and 13C NMR assignments, atoms marked with an asterisk (*) refer to the n-butyl ligand numbered from the ring C atom closest to the carboxylate group.

Crystal data

\[
\begin{align*}
\text{[Sn}_4\text{C}_4\text{H}_{12}\text{(C}_7\text{H}_6\text{NO}_2)\text{Sn}_2\text{O}_2]\quad V = 3255.75 (4) \text{ Å}^3 \\
M_r = 1597.84 \\
\text{Mo Kα radiation} \\
a = 12.3017 (1) \text{ Å} \\
b = 17.1436 (1) \text{ Å} \\
c = 15.8633 (1) \text{ Å} \\
\beta = 103.3015 (5)^\circ
\end{align*}
\]

Data collection
Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan
Blessing, 1995
Tmin = 0.646, Tmax = 0.764

Refinement

\[
\begin{align*}
R(F^2 > 2\sigma(F^2)) = 0.032 \\
\text{wR}(F^2) = 0.078 \\
S = 1.13 \\
9520 \text{ reflections with } I > 2\sigma(I) \quad R_{int} = 0.060 \\
\text{231 restraints}
\end{align*}
\]

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 Å². Each conformation of the disordered aminobenzene group was further restrained to be planar, also with a tolerance s.u. of 0.01 Å². The methyl H atoms were constrained to an ideal geometry (C–H = 0.98 Å), with Uiso(H) = 1.5Ueq(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 Uiso(H) = 1.2Ueq(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.

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: SIR20 (Altomare et al., 1994); program(s) used to refine structure: SHEXL97 (Sheldrick, 2008); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHEXL97 (Sheldrick, 2008) and PLATON (Spek, 2009).

Table 1
Selected geometric parameters (Å, °).

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

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<th>3.051 (4)</th>
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| N–H = 0.88 Å, and with Uiso(H) = 1.5Ueq(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 Uiso(H) = 1.2Ueq(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.

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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.

References
