

Bis[μ -2-[(2,3-dichlorophenyl)amino]-benzoato- κ O]di- μ -2-ethoxy-octamethyl-di- μ -3-oxo-tetratin(IV)

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Received 12 July 2005

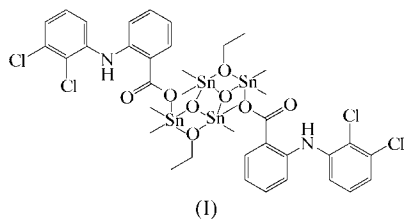
Accepted 15 August 2005

Online 31 August 2005

The title compound, $[\text{Sn}_4(\text{CH}_3)_8(\text{C}_{13}\text{H}_8\text{Cl}_2\text{NO}_2)_2(\text{C}_2\text{H}_5\text{O})_2\text{O}_2]$, is a centrosymmetric dimer, with three linearly fused four-membered Sn—O—Sn—O rings. The coordination polyhedron of the Sn atom bonded to the carboxylate can be described as trigonal-bipyramidal distorted toward square-pyramidal. That of the second Sn atom is similar, but the distortion towards square-pyramidal geometry is greater. The Sn—O and Sn—C distances are 2.020 (2)—2.226 (2) and 2.096 (4)—2.114 (4) Å, respectively. The benzene rings of the 2-[(2,3-dichlorophenyl)amino]benzoate ligand subtend an angle of 50.49 (17)°, the conformation of the ligand is stabilized by intramolecular N—H...Cl and N—H...O hydrogen bonds. The structure is assembled *via* π — π stacking interactions to form chains parallel to $[1\bar{2}0]$.

Comment

2-[(2,3-Dichlorophenyl)amino]benzoic acid is a member of the class of non-steroidal anti-inflammatory drugs (NSAIDs). All NSAIDs are derivatives of *N*-phenylanthranilic acid and many of them are frequently used in medicine (Dokorou *et al.*, 2001;), *e.g.* as analgesics, anti-inflammatories and antipyretics, because they have fewer side effects of sedation, respiratory



depression or addiction than other pharmaceuticals with similar properties, such as steroids (Berner *et al.*, 1970; Vedres *et al.*, 1973; Bauman *et al.*, 2005). NSAIDs inhibit cyclooxygenase (COX) activity and in consequence depress the synthesis of prostaglandins (Insel, 1996; Lands & Hanel, 1983; Reynolds *et al.*, 1993). They have also been used in combination with cytotoxic drugs (Thicher *et al.*, 1994, Gomez-Gavero

et al., 2002). At non-toxic levels, they significantly increase the cytotoxicity of the anthracyclines doxorubicin, daunorubicin, epirubicin, teniposide, VP-16 and vincristine (Duffy *et al.*, 1998). 2-[(2,3-Dichlorophenyl)amino]benzoic acid can be considered as an analogue of tolfenamic and flufenamic acids and other clinically used fenamates (Kovala-Demertzi *et al.*, 2001).

Organotin(IV) carboxylates are an important class of compounds that have very varied applications, from catalysis to biocides (antifouling agents) and as wood preservatives (Davies, 2004; Smith, 1998). However, applications of tin compounds are often limited because of their high toxicity, *e.g.* antifouling paints (WS Atkins International Ltd, 1998). Tin-organic compounds have also shown antitumour activity (Gielen, 1989). Thus, combining in one compound the pharmacologically important 2-[(2,3-dichlorophenyl)amino]benzoate ligand and potentially biologically active organotin moieties could lead to compounds with interesting properties and applications. We have therefore synthesized the title compound, (I), and present its crystal structure here.

A perspective view of the title compound (I) is shown in Fig. 1. All interatomic distances between non-metal atoms can be considered normal. The structure is composed of a centrosymmetric dimer, with three four-membered Sn—O—Sn—O rings in a linearly fused arrangement.

In the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002), 108 compounds can be found containing the $(\text{Sn}_2\text{O}_2)_3$ ring system. In 81 of them there are additional geometrical constraints imposed by chelating or bridging substituents; thus, a comparison of geometries was performed for only 27 compounds (CSD refcodes ASUJED, BEKDAX, CATGOT, CATGUZ, EKAMUY, EKANAF, HUTYIE, HUTYIE, LIRNUV, MASYOU, MOOXOF, NIVXEV, NUZMIE, OLONIM, QASMIG, QAYNOT, QAYNUZ, QIZREW, QOHPUY, QOHQAF, RACFOQ, ROJGIG, TIPSNB, UBIFOA, VOFDAV, XAKSAD, YELRAI and ZABPIB). Except for CATGUZ, in all these compounds the central ring (Sn_2O_2) is ideally planar; in CATGUZ the atoms deviate by only 0.04 Å from the mass-weighted least-squares plane of the ring. The peripheral rings are close to planarity in

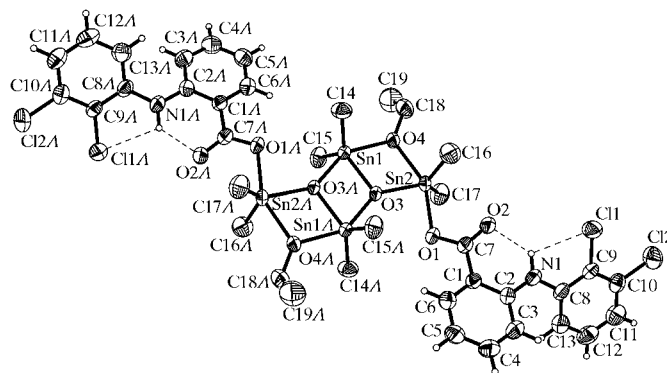


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms of the methyl and ethyl groups have been omitted for clarity. Intramolecular hydrogen bonds are indicated by dashed lines. [Symmetry code: (A) $1 - x, -y, -z$.]

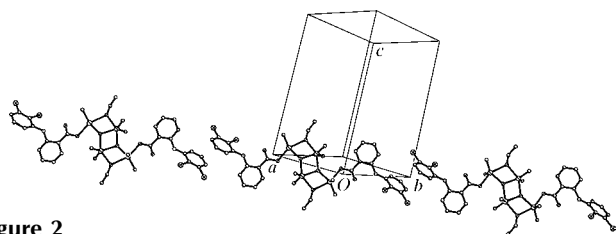


Figure 2
A part of the molecular packing of the title compound, showing intermolecular π - π interactions. H atoms have been omitted for clarity.

all the compounds; the maximum deviation is 0.085 Å for compound TIPSNB. The interplanar angle between the central ring and the peripheral rings varies from 0.58 (in QAYNOT) to 5.61° (in MOQXOF).

In (I), the mass-weighted least-squares plane of the Sn1/O3/Sn2/O4 ring is slightly distorted from planarity [the largest deviation is 0.0665 (10) Å for atom O3] and subtends an angle of 7.62 (17)° with the central Sn1/O3/Sn1ⁱ/O3ⁱ ring, which is planar by symmetry [symmetry code: (i) 1 - x, -y, -z]. The overall arrangement of the central unit is closely similar to those previously reported for bis[3-(4-methylcoumarinyl-7-oxy)- μ -methoxy-1,1,3,3-tetramethyldistannoxane] (Zhang *et al.*, 2003; CSD refcode OOLONIM), bis[[$(\mu_3$ -oxo)[μ_2 -(1,4-oxazin-4-yl)carbonylthioacetato][$(\mu_2$ -(1,4-oxazin-4-yl)carbonylthioacetato)]tetra-*n*-butylditin] ethanol solvate (Ng *et al.*, 2000; CSD refcode QASMIG), and bis[bis(di-*n*-butyl)-(μ_3 -oxo)(μ_2 -2-methoxyphenoxo- κ^2 O,O)(2-methoxyphenoxo- κ O)ditin] (Vatsa *et al.*, 1991; CSD refcode: VOFDVA).

The coordination polyhedron of Sn2 can be described as trigonal-bipyramidal [atoms O1 and O4 are axial, and atoms O3, C16 and C17 are equatorial; the sum of the squares of the deviations from ideal angles, $\Sigma\sigma(\Phi)$, is 1514°² (Favas & Kepert, 1980)] distorted toward a tetragonal pyramid [atom O3 is apical, and atoms O1, O4, C16 and C17 are basal; $\Sigma\sigma(\Phi) = 5326$ °²]. The coordination polyhedron around atom Sn1 is more distorted towards square-pyramidal but can be described in the same general way [trigonal-bipyramidal, with atoms O4 and O3ⁱ axial, and atoms O3, C14 and C15 equatorial, $\Sigma\sigma(\Phi) = 1917$ °², or square-pyramidal with atom O3 apical, and atoms O3ⁱ, O4, C14 and C15 basal, $\Sigma\sigma(\Phi) = 4860$ °²]. The major deformations originate from constraints imposed by the rigid four-membered Sn₂O₂ rings.

The benzene rings of the 2-[(2,3-dichlorophenyl)amino]benzoate ligand subtend an angle of 50.49 (17)°. The carboxylate group makes an angle of 12.3 (5)° with its parent aromatic ring. The C1-C7-O1-Sn2 torsion angle is 177.5 (2)°. The conformation of the ligand is stabilized by intramolecular N-H...Cl and N-H...O hydrogen bonds involving the same H atom (Table 2 and Fig. 1). The packing further involves π - π stacking interactions (Hunter & Sanders, 1990) between pairs of adjacent chlorine-bearing aromatic rings [symmetry code: 2 - x, -y - 1, -z; distance between ring centroids 3.929 (6) Å, perpendicular distance between symmetry-parallel rings -3.504 (6) Å, angle between the vector linking ring centroids and the normal to one plane = 26.9 (3)°, offset = 1.777 (6) Å]. A π -bonded chain is created parallel to [1 $\bar{2}$ 0] (Fig. 2) *via* these interactions.

Experimental

The title compound was prepared according to the method of Dokorou (2005). The crystals used for data collection were grown from an ethanol solution by slow evaporation.

Crystal data

[Sn ₄ (CH ₃) ₈ (C ₁₃ H ₈ Cl ₂ NO ₂) ₂ ·(C ₂ H ₅ O) ₂ O ₂]	$D_x = 1.785 \text{ Mg m}^{-3}$
$M_r = 1279.36$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6140 reflections
$a = 14.0875 \text{ (6) \AA}$	$\theta = 2\text{--}20^\circ$
$b = 9.7613 \text{ (4) \AA}$	$\mu = 2.35 \text{ mm}^{-1}$
$c = 17.5858 \text{ (8) \AA}$	$T = 291.0 \text{ (3) K}$
$\beta = 100.106 \text{ (3)^\circ}$	Needle, orange
$V = 2380.74 \text{ (18) \AA}^3$	$0.53 \times 0.07 \times 0.07 \text{ mm}$
$Z = 2$	

Data collection

Kuma KM-4 CCD area-detector diffractometer	4230 independent reflections
ω scans	3656 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1999)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.518, T_{\text{max}} = 0.894$	$\theta_{\text{max}} = 25.1^\circ$
27541 measured reflections	$h = -16 \rightarrow 16$
	$k = 10 \rightarrow 11$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 0.8584P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.063$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.15$	$\Delta\rho_{\text{max}} = 1.10 \text{ e \AA}^{-3}$
4230 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
259 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Sn1—O3	2.036 (2)	Sn2—O3	2.020 (2)
Sn1—C14	2.109 (4)	Sn2—O4	2.226 (2)
Sn1—C15	2.114 (4)	Sn2—C16	2.096 (4)
Sn1—O3 ⁱ	2.122 (2)	Sn2—C17	2.103 (4)
Sn1—O4	2.137 (2)	Sn2—O1	2.169 (3)
O3—Sn1—C14	118.17 (15)	O3—Sn2—C16	109.31 (16)
O3—Sn1—C15	113.89 (15)	O3—Sn2—C17	119.36 (15)
C14—Sn1—C15	127.94 (18)	C16—Sn2—C17	129.99 (19)
O3—Sn1—O3 ⁱ	73.92 (10)	O3—Sn2—O1	81.33 (9)
C14—Sn1—O3 ⁱ	94.68 (13)	C16—Sn2—O1	100.01 (15)
C15—Sn1—O3 ⁱ	99.06 (15)	C17—Sn2—O1	97.92 (16)
O3—Sn1—O4	73.61 (9)	O3—Sn2—O4	72.00 (9)
C14—Sn1—O4	96.61 (14)	C16—Sn2—O4	92.61 (15)
C15—Sn1—O4	97.98 (14)	C17—Sn2—O4	91.84 (15)
O3 ⁱ —Sn1—O4	147.22 (9)	O1—Sn2—O4	153.04 (9)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...Cl1	0.92	2.51	2.908 (4)	107
N1—H1N...O2	0.92	1.97	2.639 (4)	128

All C-bound H atoms were placed in calculated positions and were refined as riding on their adjacent C atom, with C—H distances in the range 0.93–0.97 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

The methyl groups were allowed to rotate about their local threefold axis (AFIX 137). The N-bound H atom was found in the difference Fourier synthesis and was refined as riding on its parent N atom at an N–H distance of 0.92 Å, with the isotropic displacement parameter free to refine.

Data collection: *CrysAlis CCD* (UNIL IC and Kuma, 2000); cell refinement: *CrysAlis RED* (UNIL IC and Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990b) and *ORTEP-3 for Windows* (Version 1.062; Farrugia 1997); software used to prepare material for publication: *SHELXL97*.

This work was financed by funds allocated by the Ministry of Scientific Research and Information Technology to the Institute of General and Ecological Chemistry, Technical University of Łódź. The authors thank Professor Kovala-Demertzi for providing the compound.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1743). Services for accessing these data are described at the back of the journal.

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