metal-organic papers

Tetrabutylbis(N-phthaloylphenylalaninato)-distannoxane dimer

Karm Hans,[a] Masood Parvez,[a]* Muhammad Ashfaq,[b] Saeed Anwar,[b] Amin Badshah[b] and Abdul Majeed[c]

[a]Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4, [b]Department of Chemistry, Gomal University, Dera Ismail Khan, NWFP, Pakistan, and [c]Department of Chemistry, Islamia University, Bahawalpur, Pakistan

Correspondence e-mail: parvez@ucalgary.ca

The crystal structure of the title compound, $[Sn_4(C_4H_9)_8(C_{17}H_{12}NO_4)_4O_2]$, is composed of centrosymmetric dimers lying about inversion centers. Its central Sn_2O_2 core is fused, with two four-membered (Sn_2O_2) and two six-membered (Sn_2O_3C) rings, incorporating O and C atoms of N-phthaloylphenylalaninate ligands that show different modes of coordination with tin. The endocyclic Sn atoms of the Sn_2O_2 core are six-coordinate in a skew-trapezoidal bipyramidal environment, while the exocyclic Sn atoms are essentially five-coordinate and exhibit distorted trigonal–bipyramidal geometry. The Sn—C distances lie in a narrow range 2.117 (3)–2.137 (5) Å [mean 2.128 (7) Å]. The endocyclic Sn—O distances in the Sn_2O_2 core are 2.057 (3) and 2.157 (3) Å, while the exocyclic Sn—O distances [2.277 (3) and 2.725 (3) Å] indicate a strong and a relatively weak Sn···O interaction. The Sn—O distances involving the exocyclic Sn atom are in the range 2.031 (3)–2.232 (3) Å.

Comment

Organotin compounds are widely used in the biosphere as fungicides, pesticides, antifouling coating materials, PVC stabilizers, catalysts in polymer chemistry, precursors for forming SnO_2 films on glass, wood preservatives and anti-tumourous agents (Molloy *et al.*, 1986; Barbieri *et al.*, 1982; Danish, Alt *et al.*, 1995; Crowe *et al.*, 1980). It has been reported that diorganotin complexes with derivatives of carboxylic acids and amino acids show maximum antitumour activity, low mammalian toxicity and have less nephrotoxicity, unlike *cis*-platin (Sandhu & Verma, 1987; Gielen, El Khloufi, Biesemans, Kayser & Willem, 1993; Gielen, El Khloufi, Biesemans & Willem, 1993; Danish, Ali *et al.*, 1995). In order

(I)
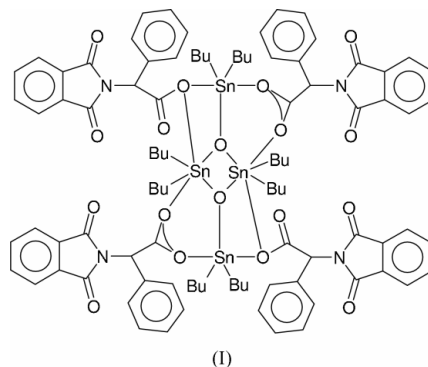
to develop new types of organotin biocides, based on carboxylates and amino acid-containing compounds, we have synthesized a new dimeric organotin(IV)carboxylate, tetrabutylbis(N-phthaloylphenylalaninato)distannoxane dimer, (I), the crystal structure of which is reported in this paper.
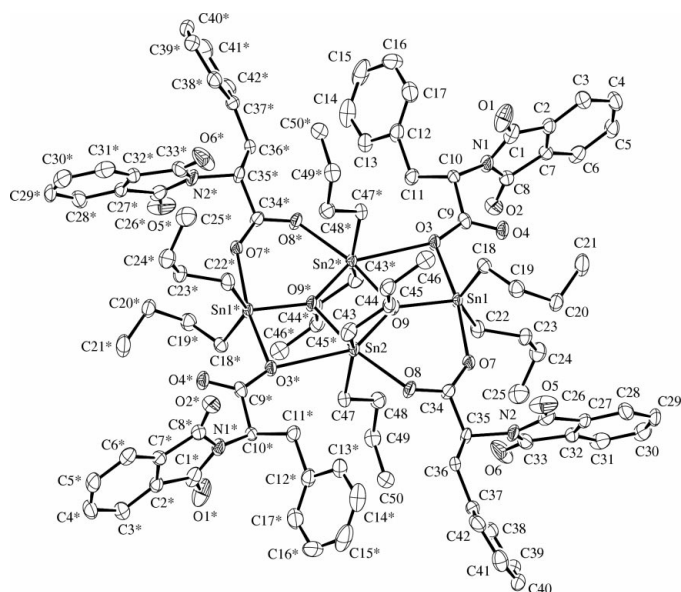
Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I), with displacement ellipsoids plotted at the 40% probability level. H atoms have been omitted for clarity.

The structure of (I) (Fig. 1) is composed of centrosymmetric dimers lying about inversion centers. The structure contains *N*-phthaloylphenylalaninate anions, one of which, acting as a monodentate ligand, bridges the two Sn atoms *via* O3 and forms a four-membered ring Sn1/O3/Sn2^i/O9 [symmetry code: (i) −*x* 2, −*y* + 1, −*z* + 1], and a second anion that acts as a bidentate ligand and bridges the two Sn atoms resulting in a six-membered ring Sn1/O7/C34/O8/Sn2/O9. There is a central four-membered ring Sn2/O9/Sn2^i/O9^i with Sn1/O3/Sn2^i/O9 and Sn1^i/O3^i/O9^i/Sn2 rings flanking it on opposite sides. The endocyclic Sn atoms of the Sn_2O_2 core are six-coordinate in a C_2SnO_4 skew-trapezoidal bipyramidal environment, wherein Sn2 is coordinated to two α-C atoms of the *n*-butyl groups at axial positions and two bridging O atoms and two O atoms of the anions forming the basal plane. This basal plane (Sn2/O8/O9/O3^i/O9^i) is essentially planar, with a maximum deviation of any atom from the plane of 0.024 (3) Å, and C43 and C47 lie 2.043 (6) and 1.999 (5) Å, respectively, above and below this plane, with the angle C—Sn—C = 144.66 (19)°. The endocyclic Sn—O distances in the Sn_2O_2 core, 2.057 (3) and 2.157 (3) Å, although significantly different from each other, are similar to the corresponding distances reported in similar structures, *e.g.* the tetrabutylbis(*N*-phthaloylglycinato)distannoxane dimer (Parvez *et al.*, 2000), bis[1,1,3,3-tetrabutyl-1,3-bis(picolinato *N*-oxide)] distannoxane hydrate (Ng, 1998) and the tetrabutylbis(*N,N*-diethylthiocarbamoylthio)distannoxane dimer (Ng & Kumar Das, 1995). The exocyclic distances Sn2—O8 [2.277 (3) Å] and Sn2—O3^i [2.725 (3) Å] indicate strong and relatively weak Sn···O interactions similar to those observed in the above-mentioned complexes. The exocyclic Sn1 atom is essentially five-coordinate in a distorted trigonal bipyramidal geometry, with a C—Sn—C angle of 138.35 (17)°; the Sn1—O distances are in the range 2.031 (3)–2.232(3 Å. The Sn—C distances in (I) lie in the narrow range 2.117 (3)−2.137 (5) Å

[mean 2.128 (7) Å] and agree with the values reported for related structures. It is interesting to note that the central portion of the dimer, comprising $Sn_4O_8C_2$, is somewhat flattened wherein three four-membered and two six-membered rings are fused; the maximum deviation of any atom from the plane of these atoms is 0.134 (3) Å. A search of the Cambridge Structural Database (updated April 2002; Allen & Kennard, 1993), resulted in 78 hits containing similar fused-ring systems.

As a result of different modes of coordination of the two ligands, the C9—O3 distance [1.304 (5) Å] in the carboxyl group of the monodentate ligand is significantly longer than C9—O4 [1.237 (5) Å], which is clearly a double bond. The corresponding distances C34—O7 and C34—O8 in the bidentate ligand [1.258 (5) and 1.263 (5) Å, respectively] represent a delocalized system, with bond distances lying between those observed for the monodentate ligand. The mean planes of the phthalimido and the phenyl groups in the monodentate and bidentate ligands are inclined at 82.90 (14) and 62.18 (13)°, respectively.

Even at temperature as low as 120 (2) K, the C atoms C10, C11, C35 and C36 of the ligands and C44 and C45 of a butyl group were found to be disordered. Therefore, the distances N—C and C—C involving these atoms were restrained during the refinements. The rest of the molecular dimensions in the ligands were normal.

Experimental

The ligand was prepared by heating equimolar quantities of phthalic anhydride and D-phenylalanine, contained in a Pyrex test tube, in a paraffin oil bath at 353–358 K. The title compound was prepared by the method reported in the literature (Gielen, El Khloufi, Biesemans, Kayser & Willem, 1993; Gielen, El Khloufi, Biesemans & Willem, 1993). Equimolar amounts of dibutyltin(IV) oxide and phenylalanine were dissolved in a mixture of toluene (150 ml) and ethanol (50 ml). The solution was refluxed for 6 h and the ternary azeotrope water/toluene/ethanol was distilled off with a Dean–Stark funnel. The excess solvent was removed by rotary evaporator. On slow evaporation of the remaining solution at room temperature, crystals were formed which were washed with ethanol. Crystals suitable for X-ray crystallographic study were grown from chloroform.

Crystal data

[Sn4(C4H9)8(C17H12NO4)4O2]	$Z = 1$
$M_r = 2140.76$	$D_x = 1.498$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.0412$ (3) Å	Cell parameters from 19979
$b = 13.6473$ (3) Å	reflections
$c = 15.6097$ (5) Å	$\theta = 1.0$–27.4°
$\alpha = 103.5885$ (11)°	$\mu = 1.11$ mm^{-1}
$\beta = 94.9563$ (13)°	$T = 120$ (2) K
$\gamma = 115.8557$ (17)°	Prismatic, colourless
$V = 2372.76$ (11) Å^3	$0.13 \times 0.13 \times 0.13$ mm

Data collection

Nonius KappaCCD diffractometer	8196 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.032$
Absorption correction: multi-scan	$\theta_{max} = 27.4°$
(*SORTAV*; Blessing, 1997)	$h = -16 \rightarrow 15$
$T_{min} = 0.874$, $T_{max} = 0.874$	$k = -17 \rightarrow 17$
19979 measured reflections	$l = -20 \rightarrow 20$
10658 independent reflections	

Refinement

Refinement on F^2		$w = 1/[\sigma^2(F_o^2) + (0.042P)^2$	
$R[F^2 > 2\sigma(F^2)] = 0.048$		$+ 6.64P]$	
$wR(F^2) = 0.117$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.08$		$(\Delta/\sigma)_{max} = 0.001$	
10658 reflections		$\Delta\rho_{max} = 1.43$ e Å^{-3}	
589 parameters		$\Delta\rho_{min} = -1.37$ e Å^{-3}	
H-atom parameters constrained			

Table 1
Selected geometric parameters (Å, °).

Sn1—O9	2.031 (3)	O4—C9	1.237 (5)
Sn1—C22	2.131 (5)	O5—C26	1.202 (6)
Sn1—C18	2.137 (5)	O6—C33	1.204 (7)
Sn1—O3	2.214 (3)	O7—C34	1.258 (5)
Sn1—O7	2.232 (3)	O8—C34	1.263 (5)
Sn2—O9	2.057 (3)	N1—C8	1.394 (7)
Sn2—C43	2.117 (5)	N1—C1	1.404 (7)
Sn2—C47	2.125 (5)	N1—C10′	1.490 (5)
Sn2—O9^i	2.157 (3)	N1—C10	1.497 (6)
Sn2—O8	2.277 (3)	N2—C33	1.390 (7)
Sn2—O3^i	2.725 (3)	N2—C26	1.399 (7)
O1—C1	1.209 (6)	N2—C35′	1.491 (5)
O2—C8	1.213 (7)	N2—C35	1.491 (6)
O3—C9	1.304 (5)		
O9—Sn1—C22	110.61 (15)	C43—Sn2—O3^i	81.00 (15)
O9—Sn1—C18	111.03 (15)	C47—Sn2—O3^i	78.41 (14)
C22—Sn1—C18	138.35 (17)	O9^i—Sn2—O3^i	66.68 (9)
O9—Sn1—O3	79.76 (11)	O8—Sn2—O3^i	125.36 (10)
C22—Sn1—O3	93.41 (16)	C9—O3—Sn1	113.0 (3)
C18—Sn1—O3	93.34 (15)	C34—O7—Sn1	139.1 (3)
O9—Sn1—O7	90.66 (11)	C34—O8—Sn2	134.8 (3)
C22—Sn1—O7	87.22 (16)	Sn1—O9—Sn2	137.14 (14)
C18—Sn1—O7	92.81 (15)	Sn1—O9—Sn2^i	119.72 (13)
O3—Sn1—O7	169.99 (11)	Sn2—O9—Sn2^i	103.14 (11)
O9—Sn2—C43	107.76 (16)	C8—N1—C1	111.6 (4)
O9—Sn2—C47	105.90 (15)	C8—N1—C10′	113.8 (5)
C43—Sn2—C47	144.66 (19)	C1—N1—C10′	133.0 (5)
O9—Sn2—O9^i	76.86 (11)	C8—N1—C10	140.4 (6)
C43—Sn2—O9^i	99.18 (16)	C1—N1—C10	105.2 (6)
C47—Sn2—O9^i	98.61 (16)	C33—N2—C26	111.9 (4)
O9—Sn2—O8	91.08 (11)	C33—N2—C35′	135.9 (5)
C43—Sn2—O8	84.67 (16)	C26—N2—C35′	111.3 (5)
C47—Sn2—O8	84.24 (16)	C33—N2—C35	105.7 (5)
O9^i—Sn2—O8	167.93 (10)	C26—N2—C35	141.1 (6)
O9—Sn2—O3^i	143.48 (10)		

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

The C atoms C10, C11, C35 and C36 of the ligands, and C44 and C45 of a butyl group were disordered over two sites with inequivalent site-occupancy factors. The distances N—C and C—C involving these

atoms were restrained using the command DFIX in *SHELXL*97 during the refinements. H atoms were included in the refinements at geometrically idealized positions, with C—H = 0.95–1.00 Å. The isotropic displacement parameters of the H atoms were set equal to 1.2 and 1.5 times the U_{eq} of the non-methyl and methyl C atoms to which they were bonded, respectively. The final difference map was essentially featureless with some electron density in the vicinity of the Sn atoms.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALE-PACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1994); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Barbieri, R., Pellerite, L., Ruisi, G. & Lo Guidice, M. T. (1982). *Inorg. Chim. Acta*, **66**, L39–L40.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Crowe, A. J., Smith, P. J. & Atassi, G. (1980). *Chem. Biol. Interact.* **32**, 171–178.
Danish, M., Alt, H. G., Badshah, A., Ali, S., Mazhar, M. & Nazar-ul-Islam, (1995). *J. Organomet. Chem.* **486**, 51–56.
Danish, M., Ali, S., Mazhar, M., Badshah, A., Choudhary, M. I., Alt, H. G. & Kehr, G. (1995). *Polyhedron*, **14**, 3115–3123.
Fan, H.-F. (1991). *SAPI*91. Rigaku Corporation, Tokyo, Japan.
Gielen, M., El Khloufi, A., Biesemans, M., Kayser, F. & Willem, R. (1993). *Appl. Organomet. Chem.* **7**, 201–206.
Gielen, M., El Khloufi, A., Biesemans, M. & Willem, R. (1993). *Appl. Organomet. Chem.* **7**, 119–125.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1994). *TEXSAN*. Single Crystal Structure Analysis Software. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molloy, K. C., Purcell, T. G., Hahn, E., Schumann, H. & Zuckerman, J. J. (1986). *Organometallics*, **5**, 85–89.
Ng, S. W. (1998). *Acta Cryst.* **C54**, 752–755.
Ng, S. W. & Kumar Das, V. G. (1995). *Acta Cryst.* **C51**, 1774–1776.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Parvez, M., Anwar, S., Badshah, A., Ahmad, B., Majeed, A. & Ashfaq, M. (2000). *Acta Cryst.* **C56**, 159–160.
Sandhu, G. K. & Verma, S. P. (1987). *Polyhedron*, **6**, 587–592.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.