

Abderrahmane Yahyi,^a
Abdelkader Et-touhami,^a
Abdelkrim Ramdani,^a
Nour-eddine Benchat,^a Brahim
El-Bali^b and Michael Bolte^{c*}

^aLaboratoire de Chimie Organique Physique, Faculté des Sciences, Oujda, Morocco, ^bLaboratoire de Matériaux et Protection de l'Environnement, Département de Chimie, Faculté des Sciences DM, BP1796, Fès, Morocco, and ^cInstitut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany

Correspondence e-mail:
bolte@chemie.uni-frankfurt.de

Key indicators

Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{C}-\text{C}) = 0.010 \text{ \AA}$
Disorder in main residue
R factor = 0.022
wR factor = 0.049
Data-to-parameter ratio = 13.2

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

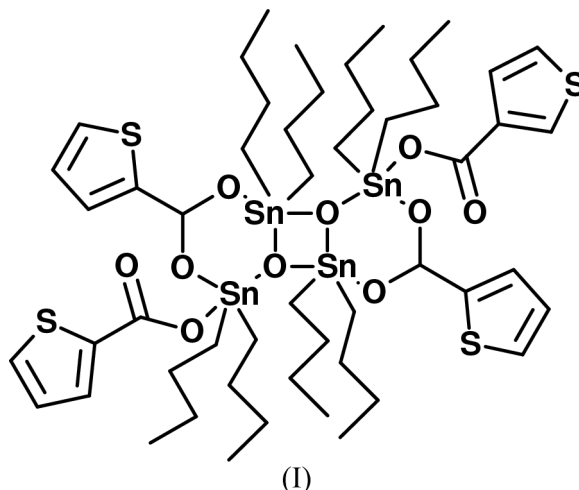
Redetermination of bis[di-*n*-butylbis(thiophene-2-carboxylato-*O,O'*)tin(VI) oxide] at low temperature

The title compound, octa-*n*-butyl- $1\kappa^2\text{C}, 2\kappa^2\text{C}, 3\kappa^2\text{C}, 4\kappa^2\text{C}$ -di- μ_3 -oxo-1:2:3 $\kappa^3\text{O}; 2:3:4:\kappa^3\text{O}$ -tetrakis(thiophene-2-carboxylate)- $1\kappa\text{O}; 1:2\kappa^2\text{O}; \text{O}'; 3:4\kappa^2\text{O}; \text{O}'; 4\kappa\text{O}$ -tetratin(VI), $[\text{Sn}_4\text{O}_2(\text{C}_4\text{H}_9)_8(\text{C}_5\text{H}_3\text{O}_2\text{S})_4]$, contains a planar Sn_2O_2 ring. The crystal structure is a racemic twin and shows pseudo-centrosymmetry. A previous structure determination of the title compound [Vatsa *et al.* (1990). *J. Organomet. Chem.* **396**, 9–18] showed the same cell parameters but a centrosymmetric molecule in space group $P2_1/c$.

Comment

The success of cisplatin as an antitumour agent has led to the investigation of antitumour activity in a variety of organotin complexes (Huber *et al.*, 1989; Tiekink, 1991). Some di-*n*-butyltin complexes have been synthesized and tested; and some of them have been found to be more active *in vitro* than cisplatin (Et-touhami *et al.*, 1991; Gielen, 1994). To continue this investigation, we have recently reported the crystal structure of di-*n*-butylbis(thiophene-2-carboxylato-*O,O'*)-tin(IV) (Yahyi *et al.*, 2001).

The crystal structure determination of the title complex, (I), was carried out in order to determine the constitution of the reaction product. Compound (I) contains a planar Sn_2O_2 ring. The other two Sn atoms and the carboxyl groups lie in the plane of this ring. A previous structure determination of (I) (Vatsa *et al.*, 1990) showed the same cell parameters but a centrosymmetric molecule in space group $P2_1/c$. At low temperature, however, we discovered (I) to be a racemic twin showing pseudo-centrosymmetry.



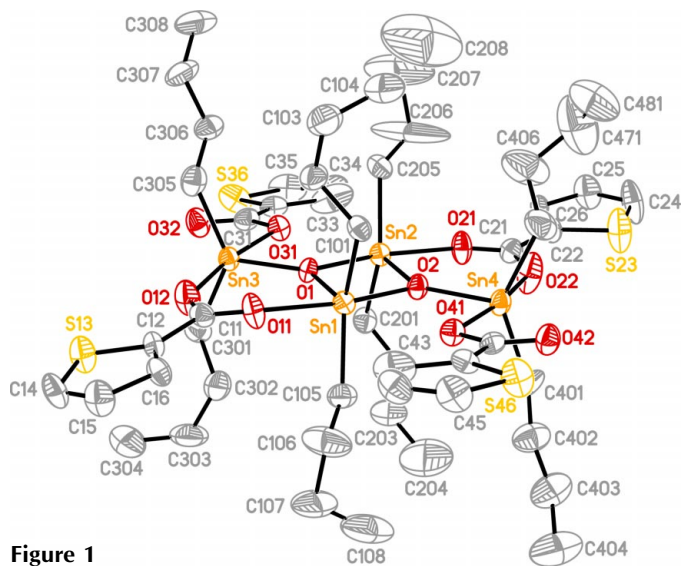


Figure 1

A perspective view of the title compound with the atom-numbering scheme. Displacement ellipsoids are at the 30% probability level. H atoms and the minor component of the disordered atoms have been omitted for clarity.

Experimental

The title compound was obtained by refluxing for 6 h equimolar (10 mmol) quantities of thiophene-2-carboxylic acid and dibutyltin oxide in a solution of 200 ml chloroform and 50 ml ethanol. The generated azeotrope was distilled off and evaporated under vacuum. Crystals were obtained by recrystallization from an ethanol solution.

Crystal data

$[\text{Sn}_4\text{O}_2(\text{C}_5\text{H}_3\text{O}_2\text{S})_4(\text{C}_4\text{H}_9)_8]$
 $M_r = 1472.19$
 Monoclinic, $P2_1$
 $a = 13.495$ (2) Å
 $b = 17.324$ (3) Å
 $c = 13.471$ (2) Å
 $\beta = 93.01$ (1)°
 $V = 3145.0$ (9) Å³
 $Z = 2$

$D_x = 1.555$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 492 reflections
 $\theta = 1\text{--}25^\circ$
 $\mu = 1.75$ mm⁻¹
 $T = 173$ (2) K
 Block, colourless
 $0.46 \times 0.42 \times 0.34$ mm

Data collection

Siemens CCD three-circle diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.470$, $T_{\max} = 0.550$
 12 639 measured reflections
 8637 independent reflections
 7626 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$
 $\theta_{\text{max}} = 27.2^\circ$
 $h = -16 \rightarrow 16$
 $k = -21 \rightarrow 10$
 $l = 0 \rightarrow 16$
 83 standard reflections
 frequency: 1200 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.049$
 $S = 0.96$
 8637 reflections
 653 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0240P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.57$ e Å⁻³
 Absolute structure: Flack (1983)
 Flack parameter = 0.50 (2)

Table 1

Selected geometric parameters (Å, °).

Sn1—O1	2.049 (3)	Sn3—O31	2.192 (3)
Sn1—C101	2.132 (5)	Sn3—O12	2.248 (3)
Sn1—C105	2.142 (6)	Sn4—C401	2.122 (7)
Sn1—O2	2.172 (3)	Sn4—C405	2.130 (6)
Sn1—O11	2.253 (3)	Sn4—O41	2.194 (3)
O1—Sn3	2.034 (3)	Sn4—O22	2.234 (3)
O1—Sn2	2.166 (3)	O11—C11	1.244 (5)
Sn2—O2	2.046 (3)	C11—O12	1.265 (5)
Sn2—C205	2.110 (6)	O21—C21	1.245 (6)
Sn2—C201	2.128 (5)	C21—O22	1.255 (6)
Sn2—O21	2.258 (3)	O31—C31	1.296 (6)
O2—Sn4	2.030 (3)	C31—O32	1.216 (6)
Sn3—C305	2.110 (7)	O41—C41	1.316 (5)
Sn3—C301	2.109 (6)	C41—O42	1.216 (6)
O1—Sn1—C101	107.19 (18)	C305—Sn3—C301	135.7 (2)
O1—Sn1—C105	103.91 (18)	O1—Sn3—O31	80.62 (11)
C101—Sn1—C105	148.4 (2)	C305—Sn3—O31	98.98 (19)
O1—Sn1—O2	76.22 (11)	C301—Sn3—O31	97.88 (17)
C101—Sn1—O2	96.63 (17)	O1—Sn3—O12	90.26 (11)
C105—Sn1—O2	95.8 (2)	C305—Sn3—O12	85.6 (2)
O1—Sn1—O11	92.31 (12)	C301—Sn3—O12	84.14 (18)
C101—Sn1—O11	85.40 (17)	O31—Sn3—O12	170.74 (12)
C105—Sn1—O11	88.1 (2)	O2—Sn4—C401	110.8 (2)
O2—Sn1—O11	168.45 (12)	O2—Sn4—C405	110.9 (2)
Sn3—O1—Sn1	136.05 (14)	C401—Sn4—C405	137.1 (3)
Sn3—O1—Sn2	120.00 (13)	O2—Sn4—O41	80.27 (12)
Sn1—O1—Sn2	103.73 (12)	C401—Sn4—O41	98.3 (2)
O2—Sn2—C205	105.25 (19)	C405—Sn4—O41	98.2 (2)
O2—Sn2—C201	108.50 (19)	O2—Sn4—O22	89.42 (12)
C205—Sn2—C201	146.0 (2)	C401—Sn4—O22	83.9 (2)
O2—Sn2—O1	76.42 (11)	C405—Sn4—O22	86.9 (2)
C205—Sn2—O1	95.26 (19)	O41—Sn4—O22	169.59 (12)
C201—Sn2—O1	96.74 (17)	C11—O11—Sn1	133.2 (3)
O2—Sn2—O21	92.03 (12)	O11—C11—O12	125.7 (4)
C205—Sn2—O21	89.1 (2)	C11—O12—Sn3	138.6 (3)
C201—Sn2—O21	85.46 (17)	C21—O21—Sn2	134.3 (3)
O1—Sn2—O21	168.36 (12)	O21—C21—O22	124.7 (5)
Sn4—O2—Sn2	137.17 (15)	C21—O22—Sn4	140.3 (3)
Sn4—O2—Sn1	119.10 (13)	C31—O31—Sn3	108.2 (3)
Sn2—O2—Sn1	103.63 (12)	C41—O41—Sn4	109.1 (3)
O1—Sn3—C305	109.88 (19)	C102—C101—Sn1	113.8 (3)
O1—Sn3—C301	113.12 (19)		

Two thiophene rings are disordered. The resolution of the data did not allow two distinct positions for the S and C atoms to be distinguished. Only one peak was found for each atom in the difference map. Thus, a C and an S atom were refined sharing the same position and the same displacement parameters and just refining the site occupation factor of the respective C and S atoms in order to determine the ratio of the different orientations, which turned out to be 0.760 (7) for C33 and S36, 0.240 (7) for S33 and C36, 0.808 (6) for C43 and S46, and 0.192 (6) for S43 and C46. All H atoms except those of the disordered atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C}_{\text{methyl}})$] using a riding model with aromatic C—H = 0.95 Å, methyl C—H = 0.98 Å or methylene C—H = 0.99 Å. One butyl group was refined with a disorder model for the three terminal atoms. Distance restraints of 1.52 (1) and 2.52 (1) Å were applied to the 1–2 and 1–3 C—C distances in the disordered group and for the residues C205, C206, C207 and C208. The ratio of the two twin components refined to 0.50 (2). The displacement ellipsoid of C206 is elongated perpendicular to the methylene chain, which might indicate disorder and displays a very short C—C bond.

Data collection: SMART (Siemens, 1995); cell refinement: SMART; data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: XP in *SHELXTL-Plus* (Siemens, 1991).

References

- Et-touhami, A., Biesemans, M., Willem, R., Mahieu, B., de Vos, D., Lelieveld, P. & Gielen, M. (1991). *Bull. Soc. Chem. Belg.* **100**, 367–374.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gielen, M. (1994). *Metal Based Drugs*, **1**, 213–219.
- Huber, F., Preut, H., Hoffmann, E. & Gielen, M. (1989). *Acta Cryst.* **C45**, 51–54.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Tiekink, E. R. T. (1991). *Appl. Organomet. Chem.* **5**, 1–23.
- Vatsa, C., Jain, V. K., Das, T. K. & Tiekink, E. R. T. (1990). *J. Organomet. Chem.* **396**, 9–18.
- Yahyi, A., Et-touhami, A., Zidane, I., Benchat, N., El Bali, B. & Bolte, M. (2001). *Acta Cryst.* **E57**, m65–66.