Synthesis and crystal structure of the tetrabutylbis(thiophene gloxylato) distannoxane dimer, {[(C$_4$H$_9$) $_2$SnO$_2$CC(O) C$_4$H$_3$S]$_2$O}$_2$

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Abstract

Reaction of [n]Bu$_2$SnO with thiophene glyoxylic acid yields the title compound which crystallizes as the centrosymmetric distannoxane dimer. Determination of the crystal structure of the compound reveals the presence of two different environments for tin and two distinct carboxylate groups; one of the carboxylate groups bonds to the six-coordinate tin atom via a carboxylate and an α-keto oxygen atom to form a five-membered chelate ring whereas the other carboxylate group forms a unidentate bridge (via one oxygen atom only) across the six-coordinate and five-coordinate tin centres.

Keywords: Crystal structure; Thiopheneglyoxylate; Distannoxane; Dibutyltin oxide

1. Introduction

Recent structural studies of a number of dicarboxyl-ate tetraorganodistannoxanes, {[R$_2$Sn(O$_2$CR′)]$_2$O}$_2$, have shown that the R′ group of the carboxylate ligand causes minor variations in the solid-state structure of these molecules although the planar Sn$_2$O$_2$ skeleton is retained in all cases [1–6]. Furthermore, when the R′ group contains an additional donor atom such as the N atom of pyridine, major structural variations are ob-served [7]. This paper reports the synthesis, crystal structure and spectroscopic characterization of the dis-tannoxane derivative with R = n-butyl and R′CO$_2$ = thiophene glyoxylate anion as it is of interest to deter-mine the structure of the distannoxane derivative in which the carboxylate group contains an α-keto oxygen and sulphur donor atoms derived from thiophene.

2. Experimental details

2.1. General and instrumental

Carbon, hydrogen and nitrogen analyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. Tin was estimated using an Instrumentation Laboratory model aa/ae 357 atomic absorption spectrophotometer. IR spectral data of the compounds were recorded using a beckman IR 20A spectrophotometer in the frequency range 4000–250 cm^{-1}. Samples were prepared as KBr discs. ^{1}H and ^{13}C NMR spectra of the samples dissolved in DMSO-d_6 were recorded on a Bruker 300 MHz AC-P NMR spectrometer.

2.2. Synthesis of di-μ_3-oxobis(μ-thiophene glyoxylato-O)bis(thiophene glyoxylato)tetrakis[dibutyltin(IV)]

Dibutyltin oxide (5.06 g, 20 mmol) and 2-thiophene glyoxylic acid (3.20 g, 20 mmol) and 70 ml of toluene were refluxed until a clear solution was formed. The reflux was continued for 1 h and water was collected using a Dean–Stark apparatus. The reaction mixture was filtered when it was still hot. The solvent was removed by evaporation under vacuum and a light yellow solid was obtained. The solid was recrystalized from toluene/hexane to give crystals of the distannox-ane {[Bu$_2$Sn(O$_2$C(CO)C$_4$H$_3$S]$_2$O}$_2$, m.p. 151–152°C. Analysis: Found: C, 42.55; H, 5.15%. Calculated for C$_{28}$H$_{42}$O$_7$Sn$_2$S$_2$: C 42.42; H 5.30%.

The infrared spectrum (KBr) of the compound dis-plays a strong band at 688 cm^{-1} assigned to the Sn–O–Sn stretch. Carbonyl stretching bands are located at 1613, 1642 and 1667 cm^{-1} (assymetric) and 1316 and

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1332 cm^{-1} (symmetric). ^{1}H NMR (CDCl$_3$) δ: 0.8 (t, 12H, 4C^{1}H$_3$); 1.32 (m, 8H, 4C^{2}H$_2$); 1.61 (s, 8H, 4C^{3}H$_2$); 1.71 (d, 8H, 4C^{4}H$_2$); 7.25 (s, 2H, 2H at aromatic 2C^1); 7.85 (s, 2H, 2H at aromatic 2C^2); 8.35 (s, 2H, 2H at aromatic 2C^3) ppm.

2.3. X-Ray crystallography

A 0.36 × 0.29 × 0.18 mm specimen was used for measurements on an Enraf-Nonius CAD4 (graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å) diffractometer. The cell constants were refined from the setting angles of the 25 strongest reflections in the $14° \le \Theta \le 15°$ range. The 12 763 reflections were collected by ω–2Θ scans up to $2\Theta_{max} = 50°$ (collection range: $0 \le h \le 15$, $-17 \le k \le 17$, $-23 \le l \le 22$), and the data were corrected for a decay of 42.3% during 57.0 h of X-ray exposure. The 7651 reflections out of the 12 144 independent reflections ($R_{int} = 0.011$) satisfying the $I \ge 3\sigma(I)$ cutoff were used for the solution and refinement. The four Sn atoms were located by direct methods, and the other non-H atoms were obtained from difference Fourier synthesis. The two thienyl rings in both independent asymmetric units are disordered with respect to the sulphur and the 4-carbon atoms. Hydrogen atoms were not refined. Full-matrix least-squares refinement on F for 711 variables converged with a shift-to-error ratio of 0.05 to $R = 0.044$, $R_w = 0.052$ for $S = 0.869$ and $w = [\sigma^2(F) + (0.02F)^2 + 1]^{-1}$ [8]. The final difference map had peaks between $-0.11(5)$ and $0.81(5)$ e Å^{-3} only. All computations

Table 1
Atomic coordinates (×10^4) and B_{eq} (Å^2) values for non-hydrogen atoms with esd values in parentheses

Atom	x	y	z	B_{eq} [a]	Atom	x	y	z	B_{eq} [a]
Sn(1a)	0.23085(4)	−0.56209(5)	−0.51098(3)	5.56(1)	C(13a)	0.4922(8)	−0.6777(8)	−0.7621(6)	7.6(3)
Sn(2a)	0.04390(4)	−0.49792(5)	−0.41383(3)	4.98(1)	C(4a)	0.4153(8)	−0.6554(8)	−0.8149(5)	7.2(3)
S(1a)	0.3155(4)	−0.6235(3)	−0.7925(2)	7.8(1)	C(15a)	−0.0402(8)	−0.6154(8)	−0.3703(6)	7.8(3)
S(2a)	0.4148(3)	−0.5783(3)	−0.1775(2)	8.2(1)	C(16a)	−0.014(1)	−0.704(1)	−0.3807(8)	11.9(4)
O(1a)	0.1551(4)	−0.5593(5)	−0.6200(3)	6.5(2)	C(17a)	−0.095(2)	−0.782(1)	−0.351(1)	14.9(6)
O(2a)	0.1513(6)	−0.5675(7)	−0.7337(4)	10.5(2)	C(18a)	−0.059(2)	−0.864(2)	−0.350(1)	20.0(10)
O(3a)	0.3481(5)	−0.6060(5)	−0.5919(3)	7.0(2)	C(19a)	0.1104(9)	−0.3617(8)	−0.3658(7)	8.5(3)
O(1a)	0.2125(4)	−0.5387(5)	−0.3884(3)	6.3(2)	C(20a)	0.176(2)	−0.300(1)	−0.395(1)	19.7(7)
O(5a)	0.2404(5)	−0.5281(5)	−0.2717(3)	7.4(2)	C(21a)	0.221(2)	−0.203(1)	−0.353(1)	21.0(10)
O(6a)	0.4046(5)	−0.5849(5)	−0.3795(3)	7.5(2)	C(22a)	0.271(3)	−0.152(2)	−0.387(2)	33.0(10)
O(7a)	0.0859(4)	−0.5750(4)	−0.5060(3)	5.0(1)	C(23a)	0.2693(7)	−0.5440(7)	−0.3251(5)	5.7(2)
C(1a)	0.2039(9)	−0.7056(7)	−0.4945(6)	7.5(3)	C(24a)	0.3780(7)	−0.5733(6)	−0.3230(5)	5.7(2)
C(2a)	0.154(2)	−0.769(1)	−0.5572(9)	13.6(6)	C(25a)	0.4464(7)	−0.5881(6)	−0.2554(5)	6.1(2)
C(3a)	0.115(2)	−0.875(1)	−0.545(1)	18.5(8)	C(26a)	0.5593(4)	−0.6209(4)	−0.2562(4)	8.6(2)
C(1a)	0.198(3)	−0.902(2)	−0.516(2)	27.0(10)	C(27a)	0.5966(9)	−0.6230(8)	−0.1745(6)	9.0(3)
C(5a)	0.3554(7)	−0.4366(7)	−0.4908(5)	6.6(3)	C(28a)	0.527(1)	−0.6053(8)	−0.1354(6)	9.0(3)
C(6a)	0.365(1)	−0.3737(8)	−0.5508(6)	8.9(3)	Sn(1b)	−0.25873(4)	−0.00054(4)	−0.03817(3)	4.55(1)
C(7a)	0.449(1)	−0.2820(9)	−0.5246(7)	10.2(4)	Sn(2b)	−0.50814(4)	−0.11082(3)	0.01324(3)	4.34(1)
C(8a)	0.459(2)	−0.215(1)	−0.580(1)	17.0(7)	S(1b)	−0.2591(3)	−0.4281(2)	−0.0097(2)	7.2(1)
C(9a)	0.1946(8)	−0.5745(7)	−0.6736(5)	6.9(3)	S(2b)	−0.0293(3)	0.3475(2)	−0.1420(2)	7.33(9)
C(10a)	0.3058(7)	−0.6041(7)	−0.6544(5)	6.0(2)	C(1b)	−0.3472(4)	−0.1517(3)	−0.0045(3)	5.2(1)
C(11a)	0.3586(7)	−0.6294(6)	−0.7091(5)	5.6(2)	C(2b)	−0.3784(5)	−0.2993(4)	0.0182(4)	7.6(2)
C(12a)	0.4724(3)	−0.6662(3)	−0.6856(2)	5.5(1)	C(3b)	−0.1603(4)	−0.1661(4)	−0.0389(3)	6.0(1)
O(1b)	−0.2678(4)	0.1426(3)	−0.0497(3)	5.2(1)	C(13b)	−0.0923(8)	−0.4391(6)	−0.0588(6)	7.1(3)
O(6b)	−0.2082(5)	0.2872(4)	−0.0773(4)	6.9(2)	C(14b)	−0.1769(8)	−0.4864(6)	−0.0341(6)	7.3(3)
O(6b)	−0.0957(4)	0.0948(4)	−0.0840(3)	5.7(1)	C(15b)	−0.4717(8)	−0.1323(8)	0.1227(5)	7.3(3)
O(7b)	−0.4060(3)	0.0044(3)	−0.0117(3)	4.4(1)	C(16b)	−0.370(1)	−0.095(2)	0.1642(7)	16.0(7)
C(1b)	−0.1380(7)	0.0105(6)	0.0573(5)	5.9(2)	C(17b)	−0.360(1)	−0.115(2)	0.2451(8)	16.9(7)
C(2b)	−0.1069(9)	0.0974(8)	0.1029(6)	8.4(3)	C(18b)	−0.272(2)	−0.116(2)	0.279(1)	23(1)
C(3b)	−0.019(1)	0.0899(9)	0.1706(7)	10.2(4)	C(19b)	−0.6050(7)	−0.1958(6)	−0.0785(5)	6.2(2)
C(4b)	0.013(2)	0.169(1)	0.219(1)	18.0(8)	C(20b)	−0.650(1)	−0.2970(9)	−0.0642(7)	9.8(4)
C(5b)	−0.3103(8)	−0.0603(7)	−0.1433(5)	6.6(3)	C(21b)	−0.724(1)	−0.356(1)	−0.1308(8)	14.1(5)
C(6b)	−0.319(1)	0.0038(9)	−0.2018(6)	10.6(4)	C(22b)	−0.833(1)	−0.356(1)	−0.1434(9)	13.4(6)
C(7b)	−0.361(2)	−0.059(1)	−0.2745(7)	16.6(7)	C(23b)	−0.2016(6)	0.2068(5)	−0.0724(4)	4.7(2)
C(8b)	−0.380(2)	−0.002(2)	−0.326(1)	24(1)	C(24b)	−0.1042(6)	0.1754(5)	−0.0949(4)	4.6(2)
C(9b)	−0.3236(6)	−0.2312(5)	−0.0003(4)	4.7(2)	C(25b)	−0.0280(6)	0.2386(6)	−0.1264(4)	4.9(2)
C(10b)	−0.2169(6)	−0.2367(5)	−0.0243(4)	4.6(2)	C(26b)	0.0707(4)	0.2070(4)	−0.1485(3)	6.3(1)
C(11b)	−0.1872(6)	−0.3280(5)	−0.0294(4)	4.7(2)	C(27b)	0.1252(9)	0.2913(9)	−0.1767(5)	8.3(3)
C(12b)	−0.0776(4)	−0.3289(3)	−0.0614(3)	6.1(1)	C(28b)	0.080(1)	0.3672(8)	−0.1749(5)	8.4(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = \frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$.

Table 2
Bond distances ($\AA$) and angles (°) with esds in parentheses

Bond distances			
Sn(1a)–O(1a)	2.141(6)	C(5a)–C(6a)	1.51(1)
Sn(1a)–O(3a)	2.553(6)	C(6a)–C(7a)	1.53(2)
Sn(1a)–O(1a)	2.479(6)	C(7a)–C(8a)	1.48(2)
Sn(1a)–O(1a)	2.047(5)	C(9a)–C(10a)	1.54(1)
Sn(1a)–C(1a)	2.11(1)	C(10a)–C(11a)	1.46(1)
Sn(1a)–C(5a)	2.12(1)	C(1a)–(12a)	1.63(1)
Sn(2a)–Sn(2a)	3.300(1)	C(12a)–C(13a)	1.58(1)
Sn(2a)–O(1a)	2.297(5)	C(13a)–C(14a)	1.35(1)
Sn(2a)–O(7a)	2.040(5)	C(5a)–C(16a)	1.44(2)
Sn(2a)–O(7a)	2.099(5)	C(16a)–C(17a)	1.57(2)
Sn(2a)–C(15a)	2.12(1)	C(17a)–C(18a)	1.37(3)
Sn(2a)–C(19a)	2.11(1)	C(19a)–C(20a)	1.32(2)
S(1a)–C(1a)	1.61(1)	C(20a)–C(21a)	1.57(4)
S(1a)–C(14a)	1.58(1)	C(21a)–C(22a)	1.17(6)
S(2a)–C(25a)	1.67(1)	C(23a)–C(24a)	1.52(1)
S(2a)–C(28a)	1.62(1)	C(24a)–C(25a)	1.46(1)
C(1a)–C(9a)	1.29(1)	C(25a)–C(26a)	1.61(1)
C(2a)–C(9a)	1.20(1)	C(26a)–C(27a)	1.56(1)
C(3a)–C(10a)	1.22(1)	C(27a)–C(28a)	1.34(2)
C(4a)–C(23a)	1.30(1)	Sn(1b)–O(1b)	2.434(5)
C(5a)–C(23a)	1.21(1)	Sn(1b)–O(4b)	2.146(5)
O(6a)–C(24a)	1.24(1)	Sn(1b)–C(7b)	2.057(4)
C(1a)–C(2a)	1.46(2)	Sn(1b)–C(1b)	2.118(9)
C(2a)–C(3a)	1.57(3)	Sn(1b)–C(5b)	2.13(1)
C(3a)–C(4a)	1.22(4)	Sn(2b)–Sn(2b)	3.278(1)
Sn(2b)–O(1b)	2.339(5)	C(6b)–C(7b)	1.60(2)
Sn(2b)–C(7b)	2.034(5)	C(7b)–C(8b)	1.33(3)
Sn(2b)–C(7b)	2.088(5)	C(9b)–C(10b)	1.54(1)
Sn(2b)–C(5b)	2.13(1)	C(10b)–C(11b)	1.48(1)
Sn(2b)–C(9b)	2.14(1)	C(1b)–C(2b)	1.645(9)
S(b)–C(11b)	1.654(9)	C(12b)–C(13b)	1.59(1)
S(1b)–C(14b)	1.62(1)	C(13b)–C(14b)	1.33(1)
S(2b)–C(25b)	1.638(9)	C(15b)–C(16b)	1.36(2)
S(2b)–C(28b)	1.63(1)	C(16b)–C(17b)	1.59(3)
O(1b)–C(9b)	1.268(9)	C(17b)–C(18b)	1.17(3)
O(2b)–C(9b)	1.199(9)	C(19b)–C(20b)	1.53(1)
O(3b)–C(10b)	1.206(9)	C(20b)–C(21b)	1.55(2)
O(4b)–C(23b)	1.274(9)	C(21b)–C(22b)	1.35(2)
O(5b)–C(23b)	1.208(9)	C(23b)–C(24b)	1.55(1)
O(6b)–C(24b)	1.231(9)	C(24b)–C(25b)	1.44(1)
C(1b)–C(2b)	1.47(1)	C(25b)–C(26b)	1.56(1)
C(2b)–C(3b)	1.55(2)	C(26b)–C(27b)	1.46(1)
C(3b)–C(4b)	1.41(2)	C(27b)–(28b)	1.36(2)
C(6b)–C(6b)	1.49(1)		

Bond angles			
O(1a)–Sn(1a)–O(3a)	67.5(2)	O(7a)–Sn(2a)–C(5a)	115.5(4)
O(1a)–Sn(1a)–O(1a)	145.6(2)	O(7a)–Sn(2a)–C(9a)	116.2(4)
O(1a)–Sn(1a)–O(7a)	78.1(2)	O(2a)–Sn(2a)–C(15a)	100.4(3)
O(1a)–Sn(1a)–C(1a)	103.4(4)	O(7a)–Sn(2a)–C(19a)	101.1(4)
O(1a)–Sn(1a)–C(5a)	103.1(3)	C(15a)–Sn(2a)–C(19a)	127.5(5)
O(3a)–Sn(1a)–O(4a)	147.0(2)	C(1a)–S(1a)–C(14a)	96.3(6)
O(3a)–Sn(1a)–O(7a)	145.6(2)	C(25a)–S(2a)–C(28a)	93.2(7)
O(3a)–Sn(1a)–C(1a)	82.4(3)	Sn(1a)–O(1a)–C(9a)	127.8(6)
O(3a)–Sn(1a)–C(5a)	83.4(3)	Sn(1a)–O(3a)–C(10a)	113.1(6)
O(1a)–Sn(1a)–O(7a)	67.4(2)	Sn(1a)–O(4a)–Sn(2a)	97.7(2)
O(4a)–Sn(a)–C(1a)	86.5(3)	Sn(1a)–O(4a)–C(23a)	137.8(6)
O(4a)–Sn(1a)–C(5a)	86.6(3)	Sn(2a)–O(4a)–C(23a)	124.5(6)
O(7a)–Sn(1a)–C(1a)	105.5(3)	Sn(1a)–C(7a)–Sn(2a)	123.5(2)
O(7a)–Sn(1a)–C(5a)	105.9(3)	Sn(1a)–O(7a)–Sn(2a)	130.8(3)
C(1a)–Sn(1a)–C(5a)	142.2(4)	Sn(2a)–O(7a)–Sn(2a)	105.7(2)
Sn(2a)–Sn(2a)–O(4a)	109.1(2)	Sn(a)–C(1a)–C(2a)	116(1)
Sn(2a)–Sn(2a)–O(7a)	37.8(1)	C(1a)–C(2a)–C(3a)	117.(2)

Table 2 (continued)

Bond angles

Angle	Value	Angle	Value
Sn(2a)–Sn(2a)–O(7a)	36.5(1)	C(2a)–C(3a)–C(1a)	107.(4)
Sn(2a)–Sn(2a)–C(15a)	112.4(3)	Sn(1a)–C(5a)–C(6a)	117.7(7)
Sn(2a)–Sn(2a)–C(19a)	113.3(4)	C(5a)–C(6a)–C(7a)	110.(1)
O(4a)–Sn(2a)–O(7a)	71.4(2)	C(6a)–C(7a)–C(8a)	114.(1)
O(4a)–Sn(2a)–O(7a)	145.6(2)	O(1a)–C(9a)–O(2a)	125(1)
O(4a)–Sn(2a)–C(15a)	94.9(3)	O(1a)–C(9a)–C(10a)	113.8(9)
O(4a)–Sn(2a)–C(19a)	93.3(4)	C(2a)–C(9a)–C(10a)	121.(1)
O(7a)–Sn(2a)–O(7a)	74.3(2)	O(3a)–C(10a)–C(9a)	117.8(9)
O(3a)–C(10a)–C(11a)	121.5(9)	S(2a)–C(28a)–C(27a)	116.(1)
C(9a)–C(10a)–C(1a)	120.8(9)	O(1b)–Sn(1b)–O(4b)	145.7(2)
S(1a)–C(11a)–C(10a)	126.1(8)	O(1b)–Sn(1b)–O(7b)	68.9(2)
S(1a)–C(11a)–C(12a)	115.5(6)	O(1b)–Sn(b)–C(1b)	87.5(3)
C(10a)–C(11a)–C(12a)	118.4(7)	O(1b)–Sn(1b)–C(5b)	86.2(3)
C(11a)–C(12a)–C(13a)	96.3(6)	O(4b)–Sn(1b)–C(7b)	76.9(2)
C(12a)–C(13a)–C(14a)	115.7(9)	O(4b)–Sn(1b)–C(7b)	101.3(3)
S(1a)–C(14a)–C(13a)	116.1(9)	C(4b)–Sn(1b)–C(5b)	103.3(3)
Sn(2a)–C(15a)–C(16a)	118.7(9)	O(7b)–Sn(1b)–C(1b)	106.8(3)
C(15a)–C(16a)–C(17a)	109.(1)	O(7b)–Sn(1b)–C(5b)	103.2(3)
C(16a)–C(17a)–C(18a)	109.(2)	C(1b)–Sn(1b)–C(5b)	144.7(4)
Sn(2a)–C(19a)–C(20a)	120.(1)	Sn(2b)–Sn(2b)–O(1b)	109.1(1)
C(19a)–C(20a)–C(21a)	114.(2)	Sn(2b)–Sn(2b)–O(7b)	37.9(1)
C(20a)–C(21a)–C(22a)	108.(5)	Sn(2b)–Sn(2b)–O(7b)	36.7(1)
O(4a)–C(23a)–O(5a)	124.5(8)	Sn(2b)–Sn(2b)–C(15b)	111.1(3)
O(4a)–C(23a)–C(24a)	113.8(8)	Sn(2b)–Sn(2b)–C(19b)	110.5(3)
O(5a)–C(23a)–C(24a)	121.7(9)	O(1b)–Sn(2b)–C(7b)	71.2(2)
O(6a)–C(24a)–C(23a)	118.3(8)	O(1b)–Sn(2b)–O(7b)	145.8(2)
O(6a)–C(24a)–C(25a)	122.2(9)	O(1b)–Sn(2b)–C(15b)	93.4(3)
C(23a)–C(24a)–C(25a)	119.5(9)	O(1b)–Sn(2b)–C(19b)	90.7(3)
S(2a)–C(25a)–C(24a)	125.5(8)	O(7b)–Sn(2b)–O(7b)	74.6(2)
S(2a)–C(25a)–C(26a)	116.9(6)	O(7b)–Sn(2b)–C(15b)	112.7(4)
C(24a)–C(25a)–C(26a)	117.6(9)	O(7b)–Sn(2b)–C(19b)	111.9(3)
C(25a)–C(26a)–C(27a)	95.6(8)	O(7b)–Sn(2b)–C(15b)	100.9(3)
C(26a)–C(27a)–C(28a)	118.(1)	O(7b)–Sn(2b)–C(19b)	100.7(3)
C(15b)–Sn(2b)–C(19b)	134.1(4)	S(1b)–C(11b)–C(12b)	118.5(5)
C(11b)–S(1b)–C(14b)	92.3(6)	C(10b)–C(11b)–C(12b)	116.3(7)
C(25b)–S(2b)–C(28b)	95.7(6)	C(1b)–C(12b)–C(3b)	93.5(6)
Sn(1b)–O(1b)–Sn(2b)	97.3(2)	C(12b)–C(13b)–C(14b)	117.8(9)
Sn(1b)–O(1b)–C(9b)	134.7(5)	S(1b)–C(14b)–C(13b)	117.8(9)
Sn(2b)–O(1b)–C(9b)	127.8(5)	Sn(2b)–C(15b)–C(16b)	121.1(9)
Sn(1b)–O(1b)–C(23b)	127.9(5)	C(15b)–C(16b)–C(17b)	114.(1)
Sn(1b)–O(7b)–Sn(2b)	122.4(2)	C(16b)–C(17b)–C(18b)	118.(3)
Sn(1b)–O(7b)–Sn(2b)	132.0(2)	S(2b)–C(19b)–C(20b)	113.9(7)
Sn(2b)–O(7b)–Sn(2b)	105.4(2)	C(19b)–C(20b)–C(21b)	113.(1)
Sn(1b)–C(1b)–C(2b)	119.5(7)	C(20b)–C(21b)–C(22b)	116.(1)
C(1b)–C(2b)–C(3b)	111(1)	O(4b)–C(23b)–O(5b)	126.3(7)
C(2b)–C(3b)–C(1b)	115.(1)	O(4b)–C(23b)–C(24b)	114.8(7)
Sn(1b)–C(5b)–C(6b)	118.3(8)	O(5b)–C(23b)–C(24b)	118.9(8)
C(5b)–C(6b)–C(7b)	108.(1)	O(6b)–C(24b)–C(23b)	116.7(7)
C(6b)–C(7b)–C(8b)	108.(2)	O(6b)–C(24b)–C(25b)	122.5(8)
O(1b)–C(9b)–O(2b)	125.4(8)	C(23b)–C(24b)–C(25b)	120.8(7)
O(1b)–C(9b)–C(10b)	114.3(7)	S(2b)–C(25b)–C(24b)	126.8(7)
O(2b)–C(9b)–C(10b)	120.2(7)	S(2b)–C(25b)–C(26b)	112.5(5)
O(3b)–C(10b)–C(9b)	118.8(7)	C(24b)–C(25b)–C(26b)	120.7(7)
O(3b)–C(10b)–C(1b)	121.7(7)	C(25b)–C(26b)–C(27b)	102.1(8)
C(9b)–C(10b)–C(11b)	119.5(8)	C(26b)–C(27b)–C(28b)	117.(1)
S(1b)–C(11b)–C(10b)	125.1(6)	S(2b)–C(28b)–C(27b)	113.1(9)

were performed with the MOLEN package running on a MicroVAX minicomputer [9]. Tables of hydrogen atom coordinates and anisotropic temperature factors have been deposited at the Cambridge Crystallographic Data Centre.

Crystal data: $C_{36}H_{84}O_{14}S_4Sn_4$, FW = 1584.3, triclinic, $P\bar{1}$; $a = 12.6725(6)$, $b = 14.710(2)$, $c = 19.519(2)$ Å; $\alpha = 90.919(9)$, $\beta = 102.532(7)$, $\gamma = 102.465(9)°$; $D_{calc} = 1.518$; $F(000) = 1592$; $\mu = 15.99$ cm^{-1} for $Z = 2$.
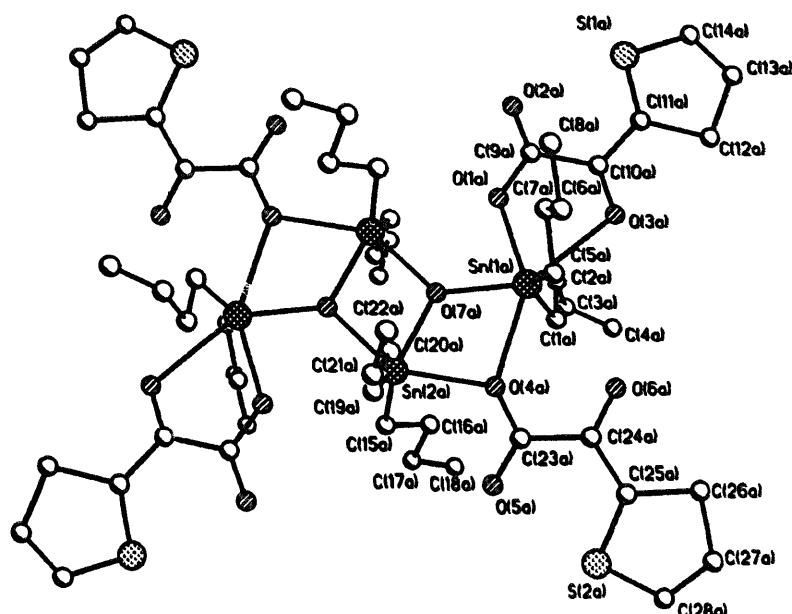
Fig. 1. Molecular structure and crystallographic numbering scheme for {[(C$_4$H$_9$)$_2$SnO$_2$CC(O)C$_4$H$_3$S]$_2$O}$_2$.

3. Results and discussion

The crystal structure of {[(C$_4$H$_9$)$_2$SnO$_2$CC(O)C$_4$H$_3$-S]$_2$O}$_2$ reveals the presence of two crystallographically independent molecules (designated a and b) in the triclinic unit cell each of which is positioned about a centrosymmetric centre such that two half formula units comprise the asymmetric unit. Atomic coordinates are listed in Table 1 while bond distances and angles are given in Table 2. The molecular structure of one of the independent units (molecule a) and the numbering scheme employed is shown in Fig. 1.

Each molecule consists of a central planar Sn$_2$O$_2$ four-membered ring with two Bu$_2$Sn[O$_2$CC(O)C$_4$H$_3$S]$_2$ units attached to each of the two bridging O atoms via the Sn atom. One of the two thiophene glyoxylic anions [O$_2$CC(O)C$_4$H$_3$S] is chelated to the peripheral Sn atom via a carboxylate and an α-keto oxygen atom forming a five-membered ring while the other forms an unidentate bridge between the central and peripheral Sn atoms. Thus the central and outer Sn atoms exhibit five- and six-coordination geometry, respectively. The sulphur atoms in the thiophene rings associated with the two distinct thiophene glyoxlic anionic ligands, which are disordered with respect to rotation about the C(10)–C(11) and C(24)–C(25) bonds, are not involved in coordination to any of the Sn atoms.

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