μ-Oxalatobis(tricyclohexyltin), a dinuclear tin compound with isomeric pentacoordinate tin sites

Seik Weng Ng [a] and V.G. Kumar Das [b]

[a] *Institute of Advanced Studies and* [b] *Department of Chemistry, University of Malaya, 5910 Kuala Lumpur (Malaysia)*

Song-Lin Li and Thomas C.W. Mak

Department of Chemistry, Chinese University of Hong Kong, Shatin, New Territories (Hong Kong)

(Received June 2, 1993; in revised form July 8, 1993)

Abstract

An X-ray diffraction study of μ-oxalatobis(tricyclohexyltin) has revealed the presence of two symmetry-independent molecules, each of which contains a pair of tin atoms in an isomeric *cis*-, *trans*-C_3SnO_2 trigonal bipyramidal configuration arising from the quadridentate (chelating and bridging) behavior of the oxalato ligand.

Key words: Tin; Oxalate

1. Introduction

Triorganotin carboxylates generally form linear carboxylate-bridged chains with the five-coordinate tin atoms occupying *trans*-C_3SnO_2 trigonal bipyramidal sites [1]. This geometry is also found in bis(triorganotin) dicarboxylates, but these adopt three-dimensional network structures arising from the linking of the triorganostannyl groups to all four carboxyl oxygen atoms of the dicarboxylato unit; examples are bis(trimethyltin) malonate [2] and bis(triphenyltin) succinate (which crystallizes as a 1/1 complex with *N,N*-dimethylformamide) [3]. The crystal structure of μ-oxalatobis(tricyclohexyltin) is described below.

2. Experimental details

μ-Oxalatobis(tricyclohexyltin), μ-$(O_2CCO_2)[(c\text{-}C_6H_{11})_3Sn]_2$, was obtained in the attempt to prepare $[(CH_3)_4N]^+[(c\text{-}C_6H_{11})_3SnO_2CCO_2]^-$ by the reaction of $[(CH_3)_4N]Cl$, $(c\text{-}C_6H_{11})_3SnCl$ and $Ag_2O_2CCO_2$ in methanol. The mixture was stirred for several hours and then filtered while hot. Slow cooling of the methanol solution gave large transparent crystals, m.p. 178°C (decomp.). Analysis. Found: C, 54.90; H, 8.13%. Calc. for $C_{38}H_{66}O_4Sn_2$: C, 55.37; H, 8.07%. Carbon-13 NMR in $CDCl_3$ [$\delta(^nJ|^{119}Sn–^{13}C|$ in Hz)]: $C_\alpha = 34.4$ ($^1J = 328.0$), $C_\beta = 30.0$ ($^2J = 13.5$), $C_\gamma = 28.8$ ($^3J = 65.4$), $C_\delta = 26.7$, $-CO_2 = 165.6$ ppm. The tin-119m Mössbauer Isomer Shift (IS) and Quadrupole Splitting (QS) (linewidth at half-height) values at 80 K for the two doublets are IS = 1.44, QS = 2.96 (Γ_1 0.90, Γ_2 0.93) and IS = 1.54, QS = 3.87 (Γ_1 0.83, Γ_2 0.89) mm s^{-1}.

In the crystallography study 10924 reflections were measured at room temperature on an Enraf-Nonius CAD4 diffractometer (graphite-monochromatized Mo $K\alpha$, 0.71073 Å) by ω–2θ scans ($2\theta_{max}$ 45°; $0 \leq h \leq 15$, $-15 \leq k \leq 15$, $-22 \leq l \leq 22$) in shells of about 2000 reflections per shell since the crystal underwent considerable decay in the X-ray beam. Peak profiles were calculated [4] and a non-linear intensity correction was applied. The structure was solved by a combination of direct and heavy-atom methods and the data were then corrected for absorption [5] following isotropic refinement. Further calculations were performed with the SHELXTL-PC package on a 486DX personal computer [6]. Blocked-matrix least-squares refinements on F for

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Correspondence to: Professor S.W. Ng.

0022-328X/94/$7.00
SSDI 0022-328X(93)24004-O

TABLE 1. Atomic coordinates and equivalent [a] isotropic temperature factors

Atom	x	y	z	U_{eq}
Sn1a	0.59736(8)	0.78478(8)	0.34936(6)	0.0782(5)
Sn2a	0.78980(6)	0.45172(7)	0.26687(5)	0.0577(4)
O1a	0.6836(7)	0.6513(8)	0.3212(6)	0.096(6)
O2a	0.6640(6)	0.4902(7)	0.3055(4)	0.068(4)
O3a	0.5066(6)	0.6487(7)	0.3419(5)	0.066(4)
O4a	0.4719(7)	0.4881(7)	0.3176(5)	0.070(4)
C1a	0.480(1)	0.850(1)	0.3813(9)	0.101(5)
C2a	0.385(2)	0.829(2)	0.330(1)	0.150(8)
C3a	0.302(2)	0.876(2)	0.354(1)	0.164(9)
C4a	0.294(2)	0.851(2)	0.417(1)	0.168(9)
C5a	0.386(2)	0.874(2)	0.468(1)	0.18(1)
C6a	0.465(2)	0.824(2)	0.441(1)	0.130(7)
C7a	0.608(2)	0.816(2)	0.2573(8)	0.137(7)
C8a (50%)	0.611(3)	0.734(1)	0.203(1)	0.15(2)
C8aa (50%)	0.543(3)	0.755(2)	0.192(2)	0.15(2)
C9a	0.579(2)	0.769(2)	0.136(1)	0.25(2)
C10a	0.648(2)	0.862(2)	0.136(1)	0.24(2)
C11a	0.653(2)	0.941(2)	0.192(2)	0.27(2)
C12a (50%)	0.692(2)	0.899(2)	0.256(1)	0.24(3)
C12aa (50%)	0.618(3)	0.922(1)	0.246(1)	0.11(1)
C13a	0.732(1)	0.824(1)	0.4256(8)	0.090(5)
C14a	0.757(1)	0.931(1)	0.443(1)	0.121(6)
C15a	0.860(2)	0.959(2)	0.492(1)	0.139(8)
C16a	0.860(1)	0.920(1)	0.554(1)	0.123(7)
C17a	0.834(2)	0.816(2)	0.537(1)	0.160(9)
C18a	0.736(2)	0.781(2)	0.483(1)	0.127(7)
C19a	0.636(1)	0.565(1)	0.3162(7)	0.061(6)
C20a	0.5282(9)	0.567(1)	0.3262(6)	0.060(6)
C21a	0.798(1)	0.343(1)	0.3284(7)	0.080(4)
C22a	0.778(2)	0.242(2)	0.290(1)	0.157(9)
C23a	0.777(2)	0.163(2)	0.342(1)	0.20(1)
C24a	0.881(2)	0.188(2)	0.387(1)	0.19(1)
C25a	0.901(2)	0.285(2)	0.422(1)	0.161(9)
C26a	0.894(1)	0.356(1)	0.3770(9)	0.113(6)
C27a	0.895(1)	0.581(1)	0.2987(1)	0.100(5)
C28a	0.922(1)	0.628(1)	0.3693(7)	0.112(6)
C29a	1.006(1)	0.716(1)	0.3874(7)	0.140(8)
C30a	0.997(2)	0.784(1)	0.3364(9)	0.27(2)
C31a	0.995(1)	0.727(1)	0.2703(8)	0.144(8)
C32a	0.902(2)	0.648(1)	0.249(7)	0.170(9)
C33a	0.701(1)	0.415(1)	0.1655(7)	0.097(5)
C34a	0.652(2)	0.501(1)	0.144(1)	0.29(2)
C35a	0.602(2)	0.471(2)	0.069(1)	0.37(3)
C36a	0.515(1)	0.387(2)	0.0617(9)	0.155(9)
C37a	0.559(2)	0.300(1)	0.087(1)	0.26(2)
C38a	0.614(2)	0.330(1)	0.160(1)	0.20(1)
Sn1b	−0.04110(7)	0.19198(8)	0.08647(5)	0.0696(5)
Sn2b	0.29257(6)	0.44197(7)	0.29271(5)	0.0593(4)
O1b	0.0999(7)	0.2939(8)	0.1703(5)	0.084(5)
O2b	0.1255(6)	0.3992(7)	0.2624(5)	0.076(4)
O3b	−0.0927(6)	0.2966(7)	0.1434(5)	0.068(4)
O4b	−0.0710(7)	0.4040(7)	0.2314(5)	0.083(5)
C1b	−0.192(1)	0.152(1)	0.0264(8)	0.096(5)
C2b	−0.196(2)	0.101(2)	−0.038(1)	0.160(9)
C3b	−0.302(2)	0.067(2)	−0.084(1)	0.140(8)
C4b	−0.367(2)	0.009(2)	−0.049(1)	0.153(8)
C5b	−0.370(2)	0.064(2)	0.015(1)	0.164(9)
C6b	−0.261(2)	0.097(2)	0.060(1)	0.130(7)
C7b	0.047(1)	0.238(2)	0.024(1)	0.118(6)
C8b	0.032(2)	0.332(2)	0.002(1)	0.19(1)
C9b	0.098(2)	0.361(2)	−0.050(1)	0.19(1)
C10b	0.188(2)	0.326(2)	−0.040(2)	0.23(1)
C11b	0.192(2)	0.234(2)	−0.027(2)	0.20(1)
C12b	0.133(2)	0.203(2)	0.021(1)	0.21(1)
C13b	−0.008(1)	0.081(1)	0.1435(7)	0.081(4)
C14b	−0.040(1)	0.091(1)	0.2086(8)	0.102(5)
C15b	−0.017(2)	0.014(2)	0.0249(1)	0.131(7)
C16b	0.088(1)	0.002(2)	0.260(1)	0.124(7)
C17b	0.113(1)	−0.020(1)	0.1952(9)	0.110(6)
C18b	0.094(1)	0.060(1)	0.1553(9)	0.111(6)
C19b	0.074(1)	0.348(1)	0.2105(9)	0.066(7)
C20b	−0.0399(9)	0.351(1)	0.1949(8)	0.062(6)
C21b	0.282(1)	0.510(1)	0.3856(8)	0.087(5)
C22b	0.374(2)	0.529(2)	0.440(1)	0.131(7)
C23b	0.355(2)	0.578(2)	0.505(1)	0.167(9)
C24b	0.278(2)	0.514(2)	0.519(1)	0.165(9)
C25b	0.185(2)	0.503(2)	0.470(1)	0.20(1)
C26b	0.194(2)	0.460(2)	0.405(1)	0.18(1)
C27b	0.290(1)	0.534(1)	0.2186(8)	0.091(5)
C28b	0.202(1)	0.590(1)	0.2113(3)	0.110(6)
C29b	0.208(2)	0.658(2)	0.159(1)	0.160(9)
C30b	0.225(2)	0.622(2)	0.101(1)	0.162(9)
C31b	0.314(2)	0.573(2)	0.110(1)	0.156(9)
C32b	0.317(2)	0.504(2)	0.161(1)	0.137(7)
C33b	0.324(1)	0.300(1)	0.2834(7)	0.076(4)
C34b	0.391(1)	0.280(1)	0.3461(9)	0.115(6)
C35b	0.416(2)	0.179(2)	0.337(1)	0.164(9)
C36b	0.454(2)	0.157(2)	0.284(1)	0.143(8)
C37b	0.393(2)	0.173(2)	0.223(1)	0.144(8)
C38b	0.372(1)	0.276(1)	0.2267(9)	0.111(6)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U tensor.

the 441 variables with 6801 unique $F \geq 4\sigma|F|$ data converged to $R = 0.076$; $R_w = 0.010$ ($w = [\sigma|F|^2 + 0.0012|F_o|^2]^{-1}$). The Sn, O and oxalato-C atoms were refined anisotropically. The C-atoms of the cyclohexyl rings were refined isotropically; three cyclohexyl rings that did not refine well (C7a to C12a, C27a to C32a, C33a to C38a) were subjected to distance constraints of 1.55 ± 0.01 and 2.50 ± 0.01 Å for pairs of 1,2- and 1,3-related C-atoms, respectively. Two C-atoms in one cyclohexyl ring were two-fold disordered and were represented by C8a, C8aa and C12a, C12aa of half site occupancy. H-atoms in the well-behaved cyclohexyl rings were placed at calculated positions (C–H = 0.95 Å, $U = 0.14$ Å^2 for the H-atom bonded to the C_α atom and $U = 0.20$ Å^2 for the methylene C-atoms) and allowed to ride on the parent C-atoms. Fractional atomic coordinates are listed in Table 1 and the molecular structure is depicted in Fig. 1. A full list of bond lengths and angles, hydrogen atom coordinates and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre.

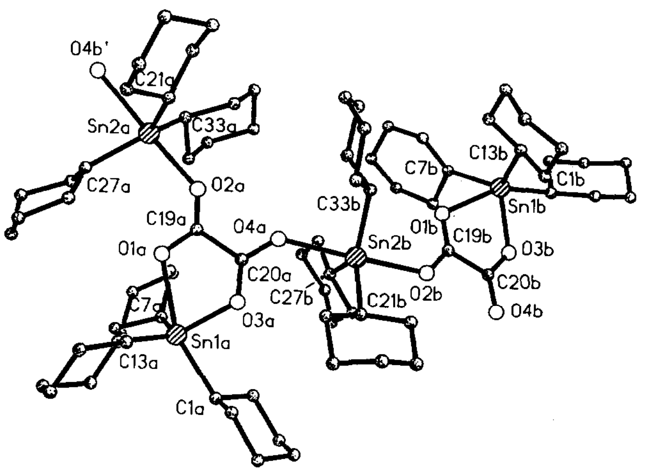

Fig. 1. Molecular structure of μ-oxalatobis(tricyclohexyltin). Selected bond distances and angles: Sn1a–C1a = 2.20(2), Sn1a–C7a = 2.09(2), Sn1a–C13a = 2.13(1), Sn1a–O1a = 2.48(1), Sn1a–O3a = 2.119(9), Sn2a–C21a = 2.14(2), Sn2a–C27a = 2.11(1), Sn2a–C33a = 2.18(1), Sn2a–O2a = 2.22(1), Sn2a–O4b′ = 2.40(1), Sn1b–C1b = 2.15(2), Sn1b–C7b = 2.10(2), Sn1b–C13b = 2.14(2), Sn1b–O1b = 2.471(8), Sn1b–O3b = 2.12(1), Sn2b–C21b = 2.14(2), Sn2b–C27b = 2.15(2), Sn2b–C33b = 2.13(2), Sn2b–O4a = 2.410(9), Sn2b–O2b = 2.242(8) Å; C1a–Sn1a–C7a = 111.4(8), C1a–Sn1a–C13a = 108.6(6), C1a–Sn1a–O1a = 155.7(5), C1a–Sn1a–O3a = 87.7(5), C7a–Sn1a–C13a = 115.9(7), C7a–Sn1a–O1a = 82.7(7), C7a–Sn1a–O3a = 111.1(6), C13a–Sn1a–O1a = 80.6(5), C13a–Sn1a–O3a = 118.6(5), O1a–Sn1a–O3a = 68.5(4), C21a–Sn2a–C27a = 117.7(5), C21a–Sn2a–33a = 119.2(6), C21a–Sn2a–O2a = 87.9(5), C21a–Sn2a–O4b′ = 88.3(5), C27a–Sn2a–C33a = 121.3(6), C27a–Sn2a–O2a = 101.0(5), C27a–Sn2a–O4b′ = 79.9(5), C33a–Sn2a–O2a = 94.3(5), C33a–Sn2a–O4b′ = 88.5(5), O2a–Sn2a–O4b′ = 176.0(4), C1b–Sn1b–C7b = 105.8(7), C1b–Sn1b–13b = 109.2(6), C1b–Sn1b–O1b = 155.9(6), C1b–Sn1b–O3b = 87.4(5), C7b–Sn1b–C13b = 121.6(8), C7b–Sn1b–O1b = 81.9(5), C7b–Sn1b–O3b = 118.9(6), C13b–Sn1b–O1b = 84.4(4), C13b–Sn1b–O3b = 108.0(5), O1b–Sn1b–O3b = 69.2(3), C21b–Sn2b–C27b = 115.3(7), C21b–Sn2b–C33b = 119.5(6), C21b–Sn2b–O4a = 94.2(5), C21b–Sn2b–O2b = 89.2(5), C27b–Sn2b–C33b = 124.7(6), C27b–Sn2b–O4a = 85.5(5), C27b–Sn2b–O2b = 91.4(5), C33b–Sn2b–O4a = 83.6(5), C33b–Sn2b–O2b = 96.4(5), O4a–Sn2b–O2b = 176.2(4)°. Translational code (′): $1 + x, y, z$.

Crystal data: $C_{38}H_{66}O_4Sn_2$, FW = 824.33, triclinic, $P\bar{1}$ (No. 2), $a = 13.967(1)$, $b = 14.215(2)$, $c = 21.237(2)$ Å, $\alpha = 96.492(9)$, $\beta = 103.364(7)$, $\gamma = 98.460(9)°$, $V = 4009.8(7)$ Å^3, $D = 1.365$ g cm^{-3}, $F(000) = 1074$, $\mu = 12.83$ cm^{-1} for $Z = 4$.

3. Results and discussion

The tin-119m Mössbauer spectrum of μ-oxalatobis(tricyclohexyltin) exhibits two quadrupole-split doublets of almost equal intensities, implicating the presence of two tin sites in the molecule. A *trans*-trigonal bipyramidal site accounts for the quadrupole splitting of 3.87 mm s^{-1}, but either a tetrahedral or a *cis*-trigonal bipyramidal site is in accord with the smaller QS of 2.96 mm s^{-1} as the QS/IS ratio for this latter site is less than 2.1 [7]. The crystal structure determination resolved this ambiguity.

Figure 1 shows the two symmetry-independent (*a* and *b*) molecules of μ-oxalatobis(tricyclohexyltin). In each molecule, anisobidentate chelation of a tricyclohexyltin group by the oxalato unit renders this tin atom five-coordinate in a *cis*-trigonal bipyramidal configuration (molecule *a*: $\mathrm{Sn} < -\mathrm{O_{ax}} = 2.48(1)$, $\mathrm{Sn{-}O_{eq}} = 2.119(9)$ Å, $\mathrm{O_{ax}} > -\mathrm{Sn{-}O_{eq}} = 68.5(4)°$; molecule *b*: $\mathrm{Sn} < -\mathrm{O_{ax}} = 2.471(8)$, $\mathrm{Sn{-}O_{eq}} = 2.12(1)$ Å, $\mathrm{O_{ax}} - > \mathrm{Sn} - \mathrm{O_{eq}} = 69.2(3)°$). Chelation permits the remaining two oxygen atoms of the oxalato ligand to bind axially to two adjacent planar tricyclohexyltin girdles, one of which is half of the molecule under consideration and the other is the corresponding half of the symmetry-independent partner (molecule *a*: Sn–O = 2.22(1), Sn < –O = 2.40(1) Å, O–Sn < –O = 176.0(4)°; molecule *b*: Sn–O = 2.242(8), Sn < –O = 2.410(9) Å, O–Sn < –O = 176.2(4)°). This leads to a linear chain structure parallel to the *a*-axis.

In chloroform solution, μ-oxalatobis(tricyclohexyltin) dissociates into a molecule having two magnetically-equivalent four-coordinate tin centers, as indicated by the observation of only one set of tin-carbon couplings in the ^{13}C NMR spectrum. The spectrum yields a ^1J value of 328.0 Hz, which is fairly close to that (352.7 Hz) reported for tricyclohexyltin hydroxide [8], a compound that has a tetrahedral structure in solution.

Acknowledgments

This research was generously supported by the National Science Council for R&D, Malaysia (Grant No. 2-07-04-06), the University of Malaya (PJP 152/91) and the Hong Kong Research Grants Council (Grant No. CUHK 22/91).

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