Novel hydroxo bidentate carboxylate bridging in diorganotin(IV) carboxylate complex

Synthesis and crystal structure of μ-hydroxo-μ-trichloroacetato-O,O'-bis(trichloroacetato-O)-bis[dibutyltin(IV)], $Sn_2(C_4H_9)_4(O_2CCCl_3)_3(OH)$

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Abstract

The crystal structure determination of the title compound reveals that it appears to be entirely novel. It does not contain a stannoxane ring, but both Sn atoms are held together by hydroxide and acetate bridges, forming a six-membered ring. Both Sn atoms occupy distorted trigonal bipyramidal environments with one bidentate bridging trichloroacetate group and one monodentate trichloroacetate group in axial positions, whilst the butyl groups and the bridging OH group lie in the equatorial plane.

Keywords: Carboxylate; Crystal structure; Bidentate bridging; Trichloroacetate; Dibutyltin(IV); Diorganotin (IV)

1. Introduction

The structural chemistry of organotin carboxylate compounds has attracted considerable attention owing to their industrial and agricultural applications [1–4], and, more recently, to their anti-tumour activity [5]. These compounds may adopt a variety of structural modes depending on the nature of organic substituent on the Sn atom and/or the carboxylate ligand [6,7]. Attempts to predict structures of these systems have proved difficult, since small changes in chemical composition may result in major changes in the structure actually adopted, at least in the solid state. Therefore, although the complexes prepared were characterised analytically and spectroscopically, their structural variety has meant that full identification was only possible by X-ray crystallographic studies.

There have been numerous crystallographic studies of the dicarboxylato tetraorganostannoxanes, of formula $\{[R_2Sn(O_2CR')]_2O\}_2$ [6,7]. Preliminary X-ray crystallo-graphic data have been reported for trichloroacetato derivatives ($R' = CCl_3$ and $R = C_6H_5$, n-C_4H_9, CH_3) [8–12]. The initial aim of this investigation was to synthesize and characterize the usual monomeric diorganotin dicarboxylate structure, $R_2Sn(O_2CR')_2$ derived from the reaction of dibutyltin oxide with tri-chloroacetic acid in 1:2 stoichiometry. However, the unexpected title product was obtained where the complex formed adopts a tin:ligand ratio of 2:3 with the structural formula $Bu_4Sn_2(O_2CCl_3)_3OH$; its structure is described in this paper.

2. Experimental details

2.1. General and instrumental

Dibutyltin oxide and trichloroacetic acid were purchased from Fluka Chemie AG.

Microanalyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. The IR spectra were recorded for KBr disc on

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a Perkin–Elmer FTIR 1650 spectrophotometer in the frequency range $4000-450\,cm^{-1}$. The ^1H NMR spectra were recorded on a Bruker AC-P 300 MHz NMR spectrometer with the sample dissolved in $CDCl_3$.

2.2. Synthesis of μ-hydroxy-μ-trichloroacetato-O,O'-bis(trichloroacetato-O)-bis[dibutyltin(IV)], $Sn_2(C_4H_9)_4(O_2CCl_3)_3(OH)$

Dibutyltin oxide (3.0 g, 12 mmol) and trichloroacetic acid (3.94 g, 24 mmol) in 70 ml of toluene were refluxed for 1 h until a clear colourless solution was obtained. The reaction mixture was filtered while it was still hot. The solvent was removed by evaporation under vacuum until solid product was obtained. The solid was recrystallized from toluene–hexane and left at 0 °C for 24 h. Clear colourless crystals formed and were filtered off; m.p. 119–121 °C. Anal. Found: C, 27.35; H, 3.68. $C_{22}H_{37}Cl_9O_7Sn_2$. Calc.: C, 27.24; H, 3.84%. IR(KBr): $\nu(COO_{asym})$ 1694, 1650; $\nu(COO_{sym})$ 1365, 1330; ν(Sn–O–Sn) 684; ν(Sn–C) 575; ν(Sn–O) 510, $485\,cm^{-1}$. ^1H NMR($CDCl_3$): δ(t, 12H, $4CH_3$) 0.94; δ(m, 8H, $4CH_2$) 1.42; δ(m, 16H, $4CH_2CH_2$) 1.80 ppm.

2.3. Crystal structure determination of $Sn_2(C_4H_9)_4(O_2CCl_3)_3(OH)$

Intensity data for a single crystal with dimensions $0.2 \times 0.3 \times 0.4\,mm^3$ were measured at room temperature on a Siemens P4 diffractometer fitted with graphite

Table 1
Crystal data and details of structure refinement for $Sn_2(C_4H_9)_4(O_2CCl_3)_3(OH)$

Formula	$C_{22}H_{37}Cl_9O_7Sn_2$
Formula weight	969.9
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	13.8200(10)
b (Å)	18.218(2)
c (Å)	15.087(2)
β (deg)	91.340(10)
V (Å³)	3797.5(7)
Z	4
D_c (Mgm⁻³)	1.697
μ (mm⁻¹)	1.983
$F(000)$	1912
Reflections collected	10273
Independent reflections	8626 (R_{int} = 0.0346)
Observed reflections	4686 ($F > 4.0\sigma(F)$)
No. of parameters refined	361
R	0.0590
R_w	0.0660 $w = [\sigma^2(F)+0.0004F^2]^{-1}$
Largest diff. peak and hole (e Å⁻³)	0.82 and −0.71

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Sn(1)	6820.0(4)	1664.7(3)	2424.5(4)	65.3(2)
Sn(2)	6894.8(5)	3823.0(3)	2352.2(5)	80.0(3)
Cl(1)	3278(3)	2184.8(18)	2302(3)	124.4(15)
Cl(2)	3438(2)	3632.6(17)	1612(3)	144(2)
Cl(3)	3919(3)	2396(2)	544(2)	129(2)
Cl(4)	10243(4)	747(4)	2545(4)	268(4)
Cl(5)	9692(3)	808(3)	4302(3)	194(2)
Cl(6)	10819(3)	1905(2)	3622(4)	196(3)
Cl(7)	10504(3)	4094(2)	2418(3)	161(2)
Cl(8)	10249(2)	5508.2(15)	3206(3)	128.7(14)
Cl(9)	9877(3)	4198(2)	4170(3)	153(2)
O(1)	7294(4)	2763(3)	2557(4)	74(2)
O(2)	5406(5)	3356(3)	1998(6)	122(4)
O(3)	5368(6)	2185(4)	2125(7)	138(4)
O(4)	8298(4)	1345(3)	2794(5)	96(3)
O(5)	8933(7)	2352(4)	3241(9)	185(6)
O(6)	8396(4)	3962(3)	2734(5)	88(3)
O(7)	8304(4)	5160(3)	2653(4)	84(2)
C(1)	5033(7)	2767(5)	1930(7)	81(4)
C(2)	3953(7)	2766(5)	1611(8)	91(4)
C(3)	8936(7)	1698(5)	3106(7)	85(4)
C(4)	9883(7)	1288(6)	3345(8)	98(4)
C(5)	8739(6)	4602(4)	2817(5)	63(3)
C(6)	9798(6)	4604(4)	3125(6)	73(3)
C(7)	6285(9)	1413(5)	3678(7)	104(5)
C(8)	6224(9)	1987(6)	4351(8)	102(5)
C(9)	5878(10)	1781(7)	5211(8)	122(6)
C(10)	5756(13)	2404(8)	5867(10)	158(8)
C(11)	6291(8)	4232(7)	3516(9)	121(6)
C(12)	6918(10)	4219(7)	4349(10)	134(7)
C(13)	6479(11)	4525(8)	5191(12)	159(9)
C(14)	7180(12)	4536(10)	5938(11)	186(10)
C(15)	6998(13)	1496(7)	1086(7)	138(7)
C(16)	7479(19)	1832(14)	568(12)	313(19)
C(17)	7645(14)	1768(16)	−382(15)	245(17)
C(18)	8563(17)	1669(10)	−584(12)	226(14)
C(19)	7005(10)	4114(8)	1023(9)	139(7)
C(20)	7920(14)	4156(10)	634(9)	185(11)
C(21)	8383(16)	4302(14)	−445(15)	294(19)
C(22)	7586(14)	4718(10)	−790(12)	304(21)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. The $\theta-2\theta$ scan method was used to measure a total of 10273 reflections in the $3.0 \le 2\theta \le 55.0°$ shell. Corrections were applied for Lorentz and polarization effects but not for absorption. There were 8626 independent reflections, of which 4686 satisfied the $F > 4.0\sigma(F)$ criterion of observability and were used in the subsequent analysis. The structure was solved by using direct methods and refined by a full-matrix least squares procedures based on F using Siemens' SHELXTL (PC Version) system [13]. Hydrogen atoms were placed in their calculated positions (C–H = 0.96 Å) and refined isotropically. A weighting scheme of the form $w =$

Table 3
Bond lengths (Å) and angles (deg) with e.s.d.s in parentheses for non-hydrogen atoms

Sn(1)-O(1)	2.113(5)	Sn(1)-O(3)	2.255(8)
Sn(1)-O(4)	2.184(6)	Sn(1)-C(7)	2.097(11)
Sn(1)-C(15)	2.063(11)	Sn(2)-O(1)	2.031(5)
Sn(2)-O(2)	2.278(7)	Sn(2)-O(6)	2.155(6)
Sn(2)-C(11)	2.098(13)	Sn(2)-C(19)	2.083(14)
Cl(1)-C(2)	1.768(11)	Cl(2)-C(2)	1.731(9)
Cl(3)-C(2)	1.745(12)	Cl(4)-C(4)	1.644(13)
Cl(5)-C(4)	1.714(12)	Cl(6)-C(4)	1.757(11)
Cl(7)-C(6)	1.734(10)	Cl(8)-C(6)	1.764(8)
Cl(9)-C(6)	1.743(10)	O(2)-C(1)	1.194(11)
O(3)-C(1)	1.192(12)	O(4)-C(3)	1.180(12)
O(5)-C(3)	1.209(13)	O(6)-C(5)	1.263(9)
O(7)-C(5)	1.205(10)	C(1)-C(2)	1.558(14)
C(3)-C(4)	1.542(14)	C(5)-C(6)	1.524(12)
C(7)-C(8)	1.462(15)	C(8)-C(9)	1.443(17)
C(9)-C(10)	1.519(19)	C(11)-C(12)	1.512(19)
C(12)-C(13)	1.525(22)	C(13)-C(14)	1.469(23)
C(15)-C(16)	1.204(27)	C(16)-C(17)	1.461(30)
C(17)-C(18)	1.323(30)	C(19)-C(20)	1.407(23)
C(20)-C(21)	1.784(28)	C(21)-C(22)	1.426(30)
O(1)-Sn(1)-O(3)	83.9(2)	O(1)-Sn(1)-O(4)	86.7(2)
O(3)-Sn(1)-O(4)	170.3(3)	O(1)-Sn(1)-C(7)	103.7(3)
O(3)-Sn(1)-C(7)	86.7(4)	O(4)-Sn(1)-C(7)	93.4(4)
O(1)-Sn(1)-C(15)	100.9(4)	O(3)-Sn(1)-C(15)	89.6(5)
O(4)-Sn(1)-C(15)	94.5(5)	C(7)-Sn(1)-C(15)	154.5(5)
O(1)-Sn(2)-O(2)	85.5(2)	O(1)-Sn(2)-O(6)	79.3(2)
O(2)-Sn(2)-O(6)	164.8(2)	O(1)-Sn(2)-C(11)	108.9(4)
O(2)-Sn(2)-C(11)	87.4(4)	O(6)-Sn(2)-C(11)	97.7(4)
O(1)-Sn(2)-C(19)	111.2(4)	O(2)-Sn(2)-C(19)	87.4(4)
O(6)-Sn(2)-C(19)	97.8(4)	C(11)-Sn(2)-C(19)	139.0(5)
Sn(1)-O(1)-Sn(2)	143.5(3)	Sn(2)-O(2)-C(1)	137.9(7)
Sn(1)-O(3)-C(1)	139.7(7)	Sn(1)-O(4)-C(3)	129.9(6)
Sn(2)-O(6)-C(5)	119.5(5)	O(2)-C(1)-O(3)	127.9(10)
O(2)-C(1)-C(2)	115.9(8)	O(3)-C(1)-C(2)	116.1(8)
Cl(1)-C(2)-Cl(2)	108.9(6)	Cl(1)-C(2)-Cl(3)	108.1(5)
Cl(2)-C(2)-Cl(3)	110.5(6)	Cl(1)-C(2)-C(1)	109.5(7)
Cl(2)-C(2)-C(1)	112.9(6)	Cl(3)-C(2)-C(1)	106.8(7)
O(4)-C(3)-O(5)	126.7(10)	O(4)-C(3)-C(4)	116.8(9)
O(5)-C(3)-C(4)	116.4(9)	Cl(4)-C(4)-Cl(5)	111.6(7)
Cl(4)-C(4)-Cl(6)	108.9(6)	Cl(5)-C(4)-Cl(6)	104.6(6)
Cl(4)-C(4)-C(3)	112.8(8)	Cl(5)-C(4)-C(3)	107.3(7)
Cl(6)-C(4)-C(3)	111.2(7)	O(6)-C(5)-O(7)	125.0(8)
O(6)-C(5)-C(6)	112.9(7)	O(7)-C(5)-C(6)	122.0(7)
Cl(7)-C(6)-Cl(8)	109.9(5)	Cl(7)-C(6)-Cl(9)	107.7(5)
Cl(8)-C(6)-Cl(9)	108.6(5)	Cl(7)-C(6)-C(5)	111.1(6)
Cl(8)-C(6)-C(5)	111.1(5)	Cl(9)-C(6)-C(5)	108.3(6)
Sn(1)-C(7)-C(8)	119.8(7)	C(7)-C(8)-C(9)	117.7(10)
C(8)-C(9)-C(10)	115.8(11)	Sn(2)-C(11)-C(12)	117.3(8)
C(11)-C(12)-C(13)	117.1(12)	C(12)-C(13)-C(14)	112.0(13)
Sn(1)-C(15)-C(16)	129.7(14)	C(15)-C(16)-C(17)	134.2(23)
C(16)-C(17)-C(18)	114.3(19)	Sn(2)-C(19)-C(20)	120.1(10)
C(19)-C(20)-C(21)	137.2(15)	C(20)-C(21)-C(22)	97.0(16)

$[\sigma^2(F) + 0.0004F^2]^{-1}$ was used, and the refinement continued to final $R = 0.059$ and $R_w = 0.066$. The crystal data and refinement details are given in Table 1. Fractional atomic coordinates and their equivalent isotropic displacement parameters are listed in Table 2 and bond lengths and angles in Table 3. Additional data, including anisotropic displacement coefficients and hydrogen atom coordinates, and a list of observed and calculated structure factors are available from the authors.

3. Results and discussion

The molecular structure of the title compound, depicted in Fig. 1, shows that both of the Sn atoms exist in distorted trigonal bipyramidal geometries with two carboxylate O atoms at an axial position and the bridging OH atom and two butyl groups in the equatorial plane. The principal distortion arises from decreases in O(3)–Sn(1)–O(4) and O(2)–Sn(2)–O(6) axial angles to 170.3(3)° and 164.8(2)° respectively, which is coupled with severe angular distortion in the equatorial planes. Angular distortions in the equatorial planes seem to be only an effect on the adjustment of bond angles according to the electronegativity of the attached groups [10]. The mutual repulsions between the two butyl groups which are less electronegative than the O-hydroxy result in expanding of the C–Sn–C angle from 120° to 154.5(5)° in C(7)–Sn(1)–C(15) and to 139.0(5)° in C(11)–Sn(2)–C(19), whereas for the C–Sn–O(1), the mean value is only 106.2°.

Although the Sn atom environments are similar, there are two distinct carboxylate groups in the structure. There is a total of three trichloroacetate ions in the title compound. One of these is bidentate bridging and bridges both the Sn atoms via O(2) and O(3) atoms. These Sn=O distances, 2.255(3) Å and 2.278(7) Å are dissimilar, so that the trichloroacetato ligand bridges the tin atoms in an asymmetric fashion. As a result of this one might expect that the C(1)=O bonds within the trichloroacetato ligand would also be of different lengths [14,15]. However, the values of C(1)=O(2) and C(1)=O(3) are 1.194(11) Å and 1.192(12) Å respectively, and these are identical. The other two trichloroacetato ligands coordinate to each Sn atom in the monodentate mode via the O(4) and O(6) atoms respectively. The
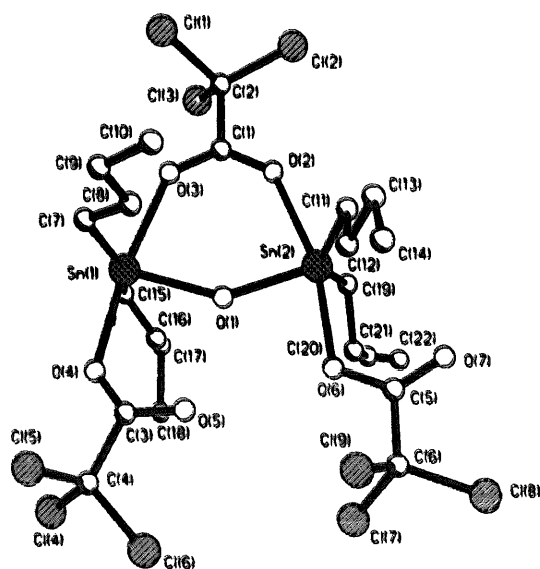
non-coordinating atoms of these second carboxylate ligands, O(5) and O(7), are orientated so that they are directed away from the rest of the molecule. The hydroxy bridge is almost symmetrical, the difference between Sn(1)–O(1) and Sn(2)–O(1) bond distances being only 0.082 Å.

The Sn–O and C–O bond distances are non-equivalent between the bidentate and the monodentate ligands. The Sn–O bond lengths for the bidentate trichloroacetate ligand (2.255(8) Å and 2.278(7) Å) are both longer than those for Sn–O in the monodentate trichloroacetate ligands (2.184(6) Å and 2.155(6) Å respectively). The difference in the C–O bond length in the bidentate trichloroacetate is small, only 0.002 Å, indicating delocalization of the double bond, whereas for the monodentate trichloroacetate the significant difference of C–O bond lengths is attributed to an increase in double bond character of one C–O at the expense of the other C–O bond of the carboxylate. The tin–carbon distances (mean value 2.085 Å) appear to be normal [10].

Infrared spectra of the complex, the free acid and its sodium salt have been recorded in KBr discs (4000–450 cm^{-1}). The free acid shows a broad band due to O–H absorption of COOH group in the 3600–3050 cm^{-1} region which is absent in the spectrum of the complex, indicating the deprotonation and coordination of the carboxylate group. There are two ν(COO)$_{asym}$ and ν(COO)$_{sym}$ absorptions present in the IR spectrum of the complex. For the COO asymmetric stretching, one near 1694 cm^{-1} is attributed to the monodentate trichloroacetate group and the other near 1650 cm^{-1} is ascribed to the bidentate trichloroacetate group [10]. Simultaneously, the band near 1330 cm^{-1} is assigned to COO symmetric stretching of monodentate trichloroacetate group and the band near 1365 cm^{-1} corresponds to the chelate carboxylate group. These observation are supported by the $\Delta \nu$ value ($\Delta \nu = \nu$(COO)$_{asym}$ – ν(COO)$_{sym}$). The $\Delta \nu$ of the monodentate trichloroacetate group is 364 cm^{-1} and this lies between $\Delta \nu$ value of the free acid (480 cm^{-1}) and $\Delta \nu$ value of the sodium salt of the ligand (289 cm^{-1}). For the chelated carboxylate group, the $\Delta \nu$ value (285 cm^{-1}) is lower than that observed in the spectrum of the free acid and is comparable with that of the sodium salt of the acid. A strong band at 684 cm^{-1} is assigned to ν(Sn–O–Sn), which indicates an Sn–O–Sn bridged structure for the complex [16]. The absorption bands at 575 cm^{-1} and two bands at 485 and 510 cm^{-1} are attributed to ν(Sn–C) and ν(Sn–O) respectively [16,17].

The ^{1}H NMR spectra of the ligand and the complex have been recorded in CDCl$_3$ solution. The absence of the signal (δ 9.8 ppm) in the spectrum of the complex indicates the replacement of the carboxyl proton by organotin(IV) on complexation. The ^{1}H NMR spectra show the expected integration and peak multiplicities.

Fig. 1. Molecular structure with atom labelling for Sn$_2$(C$_4$H$_9$)$_4$(O$_2$CCCl$_3$)$_3$(OH).

For the ^{1}H NMR spectrum of the complex the signals observable at 0.94, 1.42 and 1.80 ppm are ascribable to the proton of the butyl groups with the integration ratio 3:2:4.

Acknowledgements

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