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Structural chemistry of organotin carboxylates

XVIII *. Synthesis, characterization and X-ray crystal structure of bis(μ-hydroxo)-bis[di-t-butyltin(IV)acetate]: $[{}^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$

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Abstract

Base hydrolysis of $[{}^tBu_2Sn(O_2CCH_3)_2]$ yields $[{}^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$, which can also be prepared by the reaction of $[{}^tBu_2SnO]_3$ with acetic acid in 1:1 stoichiometry in benzene. The crystal structure of $[{}^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ shows the presence of asymmetrically bridging hydroxy groups leading to a planar Sn_2O_2 unit, Sn–O(1) 2.046(2) and Sn–O(1′) 2.204(2) Å. Each Sn atom is also coordinated by an O atom of a monodentate carboxylate ligand (Sn–O(2) 2.156 (2) Å) and two C atoms of the ${}^tBu$ groups so that the Sn environment is based on a trigonal bipyramid.

Introduction

Recently a number of dicarboxylato tetraorganodistannoxanes, *i.e.* $\{[R_2Sn(O_2CR')]_2O\}_2$, have been investigated. These contain a variety of diorganotin moieties as well as different organic substituents and are known to adopt at least five distinct structural forms as shown by X-ray crystallographic studies [2,3]. These structures feature a planar Sn_2O_2 core with the exocyclic Sn atoms being connected to the core via the O atoms (which has the result that these O atoms are triply bridging) and contain carboxylate ligands which may be monodentate, bidentate or tridentate [2,3]. The $\{[R_2Sn(O_2CR')]_2O\}_2$ compounds are hydrolysis products of monomeric compounds of the formula $[R_2Sn(O_2CR')_2]$ and are

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* For Part XVII, see ref. 1.

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believed to form *via* a hydroxo-tin intermediate, $[R_2Sn(O_2CR')(OH)]$ [4]. The alkaline hydrolysis of $[^tBu_2Sn(O_2CCH_3)_2]$, a complex with bulky R groups bound to the Sn atom, has enabled the isolation and characterization of a hydroxy complex, $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$; the results of this study are reported herein.

Results and discussion

Reaction of $[^tBu_2Sn(O_2CCH_3)_2]$ with one mole of sodium hydroxide gave a hydroxo-bridged dinuclear complex, $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$, as a white crystalline solid. This compound can also be prepared by the reaction of $[^tBu_2SnO]_3$ with acetic acid in 1:1 stoichiometry in benzene solution at room temperature. It is noteworthy that similar reactions with $[^nBu_2SnO]_3$ lead to the formation of $\{[^nBu_2Sn(O_2CCH_3)]_2O\}_2$.

The IR spectrum of $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ displayed a strong band at 1595 cm^{-1} attributable to $\nu(CO)$ suggesting that the carboxylate ligand is chelating the Sn centre as observed in $[^tBu_2Sn(O_2CCH_3)_2]$ [5] and in other $[R_2Sn(O_2CR')_2]$ complexes [4]. However, an X-ray analysis of the compound (see below) revealed that the carboxylate ligand coordinates in the monodentate mode. Unlike the analogous hydroxy halides, the carbonyl O atom in $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ forms an intramolecular hydrogen bond to the bridging hydroxy group which would explain the lowering of the $\nu(CO)$ frequency. The absorption due to $\nu(OH)$ appears to overlap with CH stretching vibrations in the region 2860–3000 cm^{-1}; for $[^tBu_2Sn(\mu\text{-}OH)F]_2$, which has strong intermolecular hydrogen bonding [6], the $\nu(OH)$ absorption appears at 3060 cm^{-1}. Stretching vibrations associated with Sn–O and Sn–C are tentatively assigned at 480 and 540 cm^{-1}, respectively.

The ^1H NMR spectrum of $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ exhibited two singlets at δ 1.35 $[^3J(^{119}Sn-^1H)$ 116 Hz] and 1.95 ppm with a relative integration 6:1 as expected. Except for the integration of individual resonances, the spectrum was similar to that of $[^tBu_2Sn(O_2CCH_3)_2]$ [5]. It is possible that the $SnOH$ proton resonance is obscured by the resonance due to the ^tBu protons; in triorganotin hydroxides the OH resonance is observed at *ca.* 1.0 ppm [7]. The ^{13}C NMR shifts for $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ were significantly different from those for the $[^tBu_2Sn(O_2CCH_3)_2]$ compound [5]. The magnitude of $^1J(^{119}Sn-^{13}C)$ (604 Hz) is increased compared to that in $[^tBu_2Sn(O_2CCH_3)_2]$ (507 Hz) [5]. The ^{119}Sn NMR spectrum of the complex displayed only one resonance, as expected, at δ -267 ppm which is considerably shielded from that of $[^tBu_2Sn(O_2CCH_3)_2]$ [5] (δ -211 ppm) and indicates that the Sn atom has a coordination number greater than four. It is noted that two ^{119}Sn NMR signals at δ -204 and -219 ppm are observed for $\{[^tBu_2Sn(O_2CCH_3)]_2O\}_2$. Unambiguous structure assignment of $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ was obtained from a single-crystal X-ray diffraction study.

The molecular structure of $[^tBu_2Sn(O_2CCH_3)(\mu\text{-}OH)]_2$ is shown in Fig. 1 and selected interatomic parameters are listed in Table 1. The structure is dimeric with the two Sn atoms being bridged by two hydroxy groups disposed about a crystallographic centre of inversion at (0, 0, 0). The hydroxy bridges are not symmetrical with the Sn–O(1) and Sn–O(1') (symmetry operation: $-x$, $-y$, $-z$) bond distances being 2.046(2) and 2.204(2) Å, respectively. Each Sn atom is also coordinated by an O atom derived from a monodentate carboxylate ligand, Sn–O(2) 2.156(2) Å and two C atoms of the ^tBu groups. The pendant O atom, O(3), is

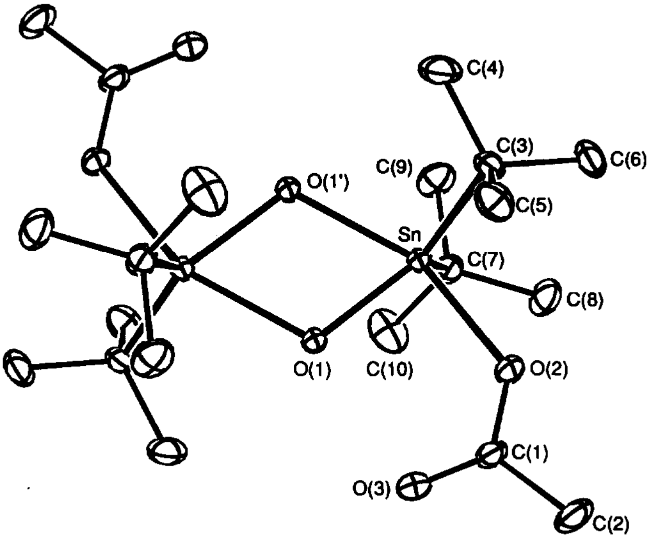

Fig. 1. Molecular structure and crystallographic numbering scheme employed for [^{t}Bu$_2$Sn(O$_2$CCH$_3$)(μ-OH)]$_2$.

3.402(3) Å from the Sn atom, a distance too long to be considered as a bonding interaction. Support for this proposition is found in the disparity of the C–O bond distances with the C(1)–O(2) bond of 1.267(5) Å, *i.e.* involving the O atom coordinated to the Sn atom, being significantly longer than the C(1)–O(3) bond distance of 1.213(5) Å. Each Sn atom is thus five coordinate.

The coordination geometry about each Sn atom is based on a trigonal bipyramid with the axial positions being occupied by the O(1') and O(2) atoms such that O(1')–Sn–O(2) is 155.8(1)°. The Sn atom lies 0.0434(2) Å out of the basal plane in the direction of the O(2) atom. Notable in the structure is the presence of an intramolecular hydrogen bonding contact between the non-coordinating O(3) atom

Table 1

Selected interatomic parameters (Å, deg) for [^{t}Bu$_2$Sn(O$_2$CCH$_3$)(μ-OH)]$_2$

Sn–O(1)	2.046(2)	Sn–O(1')[a]	2.204(2)
Sn–O(2)	2.156(2)	Sn–C(3)	2.177(4)
Sn–C(7)	2.171(4)	C(1)–O(2)	1.267(5)
C(1)–O(3)	1.213(5)	C(1)–C(2)	1.491(6)
O(1)–Sn–O(1')	70.6(1)	O(1)–Sn–O(2)	85.3(1)
O(1)–Sn–C(3)	120.4(1)	O(1)–Sn–C(7)	116.6(1)
O(1')–Sn–O(2)	155.8(1)	O(1')–Sn–C(3)	100.0(1)
O(1')–Sn–C(7)	94.9(1)	O(2)–Sn–C(3)	91.7(1)
O(2)–Sn–C(7)	96.4(1)	C(3)–Sn–C(7)	122.8(2)
Sn–O(1)–Sn'	109.4(2)	Sn–O(2)–C(1)	130.2(2)
O(2)–C(1)–O(3)	124.2(4)	O(2)–C(1)–C(2)	116.2(4)
O(3)–C(1)–C(2)	119.6(4)		

[a] Primed atoms are related by a crystallographic centre of inversion.

and the hydroxy proton, which was not located in the X-ray study, such that the O(1) · · · O(3) separation is 2.579(8) Å.

There are two other organotin carboxylate structures in the literature of the general formula [$R_2Sn(O_2CR')X$], namely [$Me_2Sn(O_2CCH_3)Cl$] [8] and [$Me_2Sn(O_2CC_5H_4N$-*o*)Cl] [9]; both structures are polymeric. In [$Me_2Sn(O_2CCH_3)Cl$] [8] the Sn atom is five coordinate, trigonal bipyramidal with the basal plane defined by the two Me groups and the Cl atom. The polymeric structure arises as a result of bridging acetate groups which link neighbouring Sn centres. Distorted octahedral Sn atom geometries are found in the structure of [$Me_2Sn(O_2CC_5H_4N$-*o*)Cl] [9] in which both the carboxylate O atoms as well as the N atom of the R′ heterocycle bridge adjacent Sn atoms. The formation of the isolated dimeric structure of [$^tBu_2Sn(O_2CCH_3)(\mu$-OH)$]_2$ may reflect the inherent stability of the central Sn_2O_2 unit.

Experimental

[$^tBu_2SnO]_3$ and [$^tBu_2Sn(O_2CCH_3)_2$] were prepared by published methods [5]; [$^tBu_2Sn(O_2CCH_3)_2$] was sublimed *in vacuo* (1.5 mmHg) before use. IR spectra were recorded as a Nujol mull or in benzene solution on a Perkin–Elmer 577 spectrometer. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded in $CDCl_3$ solutions on a Varian FT-80A spectrometer, operating at 79.54, 20.00 and 29.63 MHz, respectively. Chemical shifts are reported in ppm from internal chloroform (7.26 ppm for ^1H and 77.0 ppm for ^{13}C) and from external 33% Me_4Sn in C_6D_6 for ^{119}Sn.

Preparation of [$^tBu_2Sn(O_2CCH_3)(\mu$-OH)$]_2$

(a) To an acetone solution (20 cm^3) of [$^tBu_2Sn(O_2CCH_3)_2$] (1.76 g, 5.03 mmol) at room temperature a NaOH solution (10.4 cm^3, 0.485 *N*, 5.04 mmol) was added with vigorous stirring. A white solid separated, and was filtered off, washed with water, and dried *in vacuo*. A colourless, crystalline solid was obtained by recrystallization from a chloroform/acetone (1/1) solution of the compound; yield 1.33 g, 86%. [Found: C 38.9; H, 7.3; Sn, 38.9. $C_{20}H_{44}O_6Sn_2$ calc: C, 38.9; H, 7.2; Sn, 38.4%] $^{13}C\{^1H\}$ NMR data in $CDCl_3$: δ 179.9 (CO_2) 40.2 (C_t of ^tBu), 29.8 (Me of ^tBu), 23.4 (O_2CCH_3) ppm.

(b) To a benzene suspension of [$^tBu_2SnO]_3$ (958 mg, 3.85 mmol) was added a benzene solution (10 cm^3) of acetic acid (231 mg, 3.85 mmol). The mixture was stirred at room temperature for 3 h, giving a clear solution. The solvent was evaporated *in vacuo* to give a white solid, which was recrystallized, and found to have properties identical with those set out under (a).

Crystallography

Intensity data for [$^tBu_2Sn(O_2CCH_3)(\mu$-OH)$]_2$ were measured at 293 K on an Enraf-Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The $\omega:2\theta$ scan technique was employed to measure 3027 data up to a maximum Bragg angle of 22.5°. The data set was corrected for Lorentz and polarization effects and for absorption using an analytical procedure [10]; max. and min. transmission factors were 0.767 and 0.635, respectively. Relevant crystal data are given in Table 2.

Table 2

Crystal data and refinement details for $[{}^t\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_3)(\mu\text{-OH})]_2$

Formula	$C_{20}H_{44}O_6Sn_2$
Mol. wt.	617.9
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	8.672(1)
b, Å	12.062(1)
c, Å	13.105(1)
β, deg	96.48(1)
V, Å^3	1362.1
Z	2 (dimers)
D_c, g cm^{-3}	1.507
$F(000)$	624
μ, cm^{-1}	17.11
T, K	293
No. of data collected	3027
No. of unique data	1773
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	1478
R	0.022
g	0.0018
R_w	0.025
Residual $\rho_{\max}$, e Å^{-3}	0.51

The structure was solved by interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure based on F [10]. The crystallographic asymmetric unit is comprised of one half molecule located about a crystallographic centre of inversion at (0, 0, 0). Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model in their calculated positions except for the hydroxy H atom which was not located. After

Table 3

Fractional atomic coordinates ($\times 10^5$ for Sn, $\times 10^4$ for remaining atoms) for $[{}^t\mathrm{Bu}_2\mathrm{Sn}(\mathrm{O}_2\mathrm{CCH}_3)(\mu\text{-OH})]_2$

Atom	x	y	z
Sn	9281(2)	11968(2)	4792(2)
O(1)	−1193(2)	558(2)	−63(2)
O(2)	−313(3)	2723(2)	648(3)
O(3)	−2719(4)	2165(3)	647(4)
C(1)	−1742(5)	2889(3)	709(3)
C(2)	−2207(6)	4060(4)	875(5)
C(3)	2385(4)	1974(3)	−566(3)
C(4)	3465(6)	1123(4)	−956(5)
C(5)	1413(6)	2536(4)	−1436(4)
C(6)	3335(5)	2875(4)	80(4)
C(7)	1679(5)	957(3)	2101(3)
C(8)	1930(6)	2080(4)	2641(4)
C(9)	3188(6)	316(4)	2212(4)
C(10)	457(7)	314(5)	2590(4)

the inclusion of a weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$, the refinement was continued until convergence; final refinement details are listed in Table 2. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied. Fractional atomic coordinates are listed in Table 3 and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP [11] at 15% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [10] and the refinement was performed on a SUN4/280 computer. Other crystallographic details (available from ERTT) comprise thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors.

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