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Structural chemistry of organotin carboxylates

IX *. Synthesis and characterization of n-butyltinoxo carboxylates: $[^{n}BuSn(O)(O_2CR')]_6$, $R' = {}^{i}Pr$ or ${}^{t}Bu$, and the crystal structure of the latter

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Abstract

Reactions of n-butylstannoic acid with R'COOH ($R' = {}^{i}Pr$ and ${}^{t}Bu$) give butyltinoxo carboxylates, $[^{n}BuSn(O)(O_2CR')]_6$, which contain six-coordinate tin atoms. The compounds have been characterized by elemental analyses, IR spectroscopy and ^{13}C and ^{119}Sn NMR spectroscopy, and shown to adopt the hexameric 'drum' structure. This was confirmed by an X-ray diffraction study for the compound with $R' = {}^{t}Bu$.

Introduction

Recently we have investigated the structural chemistry of a number of dicarboxylato tetraorganodistannoxanes, $\{[R_2Sn(O_2CR')]_2O\}_2$ [1–5]. These studies have shown that the R' group of the carboxylate ligand influences the solid state structure adopted by these molecules although the planar Sn_2O_2 skeleton is retained in all cases. In particular, major structural variations are observed when the R' group contains an additional donor atom, such as a pyridine N atom, available for coordination to the Sn atom [2]. We have now turned our attention to the monoorganotin carboxylates.

Two major prototypes have been structurally characterized for the monoorganotinoxo carboxylates [6,7]. The first of these, of general formula $[RSn(O)(O_2CR')]_6$, adopts a 'drum' structure whereas the other, of formula $\{[RSn(O)(O_2CR')]_2[RSn(O_2CR')_3]\}_2$, is based on a 'ladder' arrangement. This study reports the

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* For part VIII, see Ref. 1.

characterization of two monoorganotinoxo carboxylates with a sterically demanding R′ group, namely $R' = {}^{i}Pr$ and ${}^{t}Bu$. These compounds were chosen in the hope of obtaining a new cluster form, but, in both cases a 'drum' structure was found.

Results and discussion

Reaction of n-butylstannoic acid with trimethylacetic acid or isobutyric acid in 1 : 1 stoichiometry gave hexameric butyltinoxo carboxylates:

$$6\,{}^{n}BuSnOOH + 6\,R'COOH \rightarrow [{}^{n}BuSn(O)(O_2CR')]_6 + 6H_2O$$

($R' = {}^{t}Bu$ and ${}^{i}Pr$)

The ^{119}Sn NMR spectra in $CDCl_3$ solution for these complexes show a single resonance at −485 ppm, which indicates a 'drum' structure, and are consistent with the data reported for similar compounds [8,9]. The interesting feature of these spectra is the presence of tin–tin couplings. As is evident from Fig. 1, three different values of $^{2}J(^{119}Sn\text{–}O\text{–}^{117/119}Sn)$ at approximately 32, 75 and 250 Hz are observed; the individual couplings $^{2}J(^{119}Sn\text{–}^{119}Sn)$ and $^{2}J(^{119}Sn\text{–}^{117}Sn)$ could not be resolved. From a recent survey of such coupling it appears that the observed values depend on the Sn–O–Sn bond angles and Sn–O bond distances [10]. Thus the magnitude of $^{2}J(^{119}Sn\text{–}^{119}Sn)$ has been reported to vary from a few tens of Hz ($[Me_2C(SnMe_3)_2]$, ±19 Hz) to thousands of Hz (*trans*-$[Pt(SnCl_3)_2(PEt_3)_2]$, 36286 Hz) depending on the type of compound [10]. In the more closely related compounds $\{[{}^{n}Bu_2Sn(O_2CC_4H_3N_2)]_2O\}_2$ and $[({}^{n}Bu_2SnCl)_2O]_2$, the $^{2}J(Sn\text{–}O\text{–}Sn)$ are 125 and 75 Hz, respectively [11].

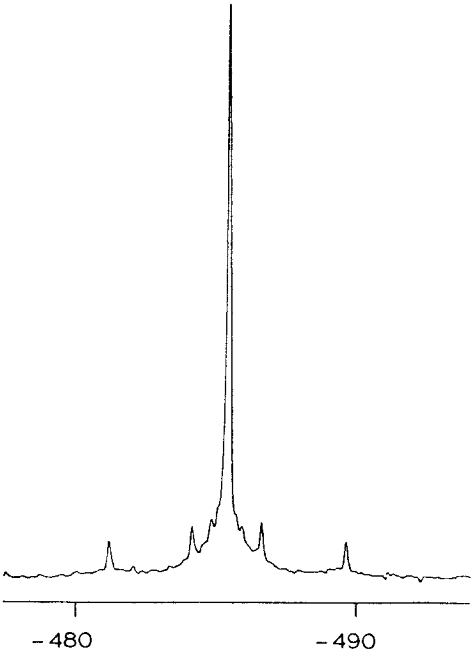

Fig. 1. $^{119}Sn\{^{1}H\}$ NMR spectrum of $[{}^{n}BuSn(O)(O_2C{}^{t}Bu)]_6$.

The ^{13}C NMR spectra exhibited singlets for the butyltin carbon atoms. The $^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ of approximately 1200 Hz is fairly large for six-coordinate organotin(IV) compounds, which may suggest increased *s* character in the Sn–C

Table 1

Selected interatomic parameters for $[^n\mathrm{BuSn(O)(O_2C^tBu)}]_6$

Sn(1)–O(1)	2.090(5)	Sn(1)–O(2)	2.087(5)
Sn(1)–O(3)	2.075(5)	Sn(1)–O(4)	2.165(6)
Sn(1)–O(6)	2.164(6)	Sn(1)–C(11)	2.124(9)
Sn(2)–O(1)	2.074(5)	Sn(2)–O(2)	2.086(5)
Sn(2)–O(7)	2.170(6)	Sn(2)–O(3′) [a]	2.090(5)
Sn(2)–O(8′)	2.151(6)	Sn(2)–C(21)	2.20(1)
Sn(3)–O(1)	2.092(5)	Sn(3)–O(3)	2.089(5)
Sn(3)–O(5)	2.156(6)	Sn(3)–O(9)	2.155(6)
Sn(3)–O(2′)	2.085(5)	Sn(3)–C(31)	2.140(9)
C(1)–O(6)	1.26(1)	C(1)–O(7)	1.25(1)
C(1)–C(2)	1.54(1)	C(4)–O(4)	1.27(1)
C(4)–O(5)	1.25(1)	C(4)–C(5)	1.51(1)
C(7)–O(8)	1.24(1)	C(7)–O(9)	1.26(1)
C(7)–C(8)	1.54(1)		
O(1)–Sn(1)–O(2)	77.7(2)	O(1)–Sn(1)–O(3)	78.1(2)
O(1)–Sn(1)–O(4)	88.6(2)	O(1)–Sn(1)–O(6)	88.0(2)
O(1)–Sn(1)–C(11)	177.9(3)	O(2)–Sn(1)–O(3)	104.1(2)
O(2)–Sn(1)–O(4)	160.4(2)	O(2)–Sn(1)–O(6)	86.9(2)
O(2)–Sn(1)–C(11)	101.9(3)	O(3)–Sn(1)–O(4)	86.5(2)
O(3)–Sn(1)–O(6)	159.9(2)	O(3)–Sn(1)–C(11)	100.0(3)
O(4)–Sn(1)–O(6)	78.6(2)	O(4)–Sn(1)–C(11)	92.2(3)
O(6)–Sn(1)–C(11)	94.1(3)	O(1)–Sn(2)–O(2)	78.1(2)
O(1)–Sn(2)–O(7)	86.7(2)	O(1)–Sn(2)–O(8)	160.0(2)
O(1)–Sn(2)–O(3′)	103.8(2)	O(1)–Sn(2)–C(21)	98.6(3)
O(2)–Sn(2)–O(7)	87.8(2)	O(2)–Sn(2)–O(3′)	78.0(2)
O(2)–Sn(2)–O(8′)	87.8(2)	O(2)–Sn(2)–C(21)	176.7(3)
O(3′)–Sn(2)–O(7)	160.1(2)	O(3′)–Sn(2)–O(8′)	86.9(2)
O(3′)–Sn(2)–C(21)	102.7(3)	O(7)–Sn(2)–O(8′)	78.5(2)
O(7)–Sn(2)–C(21)	92.2(3)	O(8′)–Sn(2)–C(21)	95.4(3)
O(1)–Sn(3)–O(3)	77.8(2)	O(1)–Sn(3)–O(5)	86.3(2)
O(1)–Sn(3)–O(2′)	104.1(2)	O(1)–Sn(3)–O(9)	159.5(2)
O(1)–Sn(3)–C(31)	99.6(3)	O(3)–Sn(3)–O(5)	88.6(2)
O(3)–Sn(3)–O(2′)	78.1(2)	O(3)–Sn(3)–O(9)	87.8(2)
O(3)–Sn(3)–C(31)	177.1(3)	O(5)–Sn(3)–O(2′)	160.7(2)
O(5)–Sn(3)–O(9)	78.8(2)	O(5)–Sn(3)–C(31)	92.6(3)
O(2′)–Sn(3)–O(9)	86.8(2)	O(2′)–Sn(3)–C(31)	101.4(3)
O(9)–Sn(3)–C(31)	95.1(3)	Sn(1)–O(1)–Sn(2)	100.4(2)
Sn(1)–O(1)–Sn(3)	99.8(2)	Sn(2)–O(1)–Sn(3)	133.0(3)
Sn(1)–O(2)–Sn(2)	100.0(2)	Sn(1)–O(2)–Sn(3′)	132.6(2)
Sn(2)–O(2)–Sn(3′)	100.1(2)	Sn(1)–O(3)–Sn(2′)	133.3(2)
Sn(1)–O(3)–Sn(3)	100.4(2)	Sn(2′)–O(3)–Sn(3)	99.9(2)
Sn(1)–O(4)–C(4)	129.3(6)	Sn(3)–O(5)–C(4)	130.3(6)
Sn(1)–O(6)–C(1)	129.3(6)	Sn(2)–O(7)–C(1)	129.7(6)
Sn(2′)–O(8)–C(7)	130.0(6)	Sn(3′)–O(9)–C(7)	130.2(6)
O(4)–C(4)–O(5)	125.7(8)	O(6)–C(1)–O(7)	126.5(8)
O(8)–C(7)–O(9)	126.4(8)		

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

bonds [12]. Interestingly, the carbonyl carbon atoms show tin couplings of 33 Hz. Such couplings are not usually observed for organotin carboxylates in solution [13]. The solid state structure of the $R' = {}^{t}Bu$ compound was determined by X-ray crystallography and shown to be consistent with the observations made on solutions.

The $[{}^{n}BuSn(O)(O_2C{}^{t}Bu)]_6$ compound is hexameric and adopts the 'drum' structure [14]. The molecular structure is shown in Fig. 2 and selected interatomic parameters are listed in Table 1. The molecular is situated about a crystallographic centre of inversion so that half the molecule comprises the asymmetric unit and the unit cell contains one hexamer.

Each of the lids of the 'drum' comprises a hexagonal Sn_3O_3 ring of alternating Sn and O atoms. The top lid is twisted by approximately 60° relative to the lower thereby enabling the formation of six Sn–O bonds which connect the lids; the rectangular sides of the drum thus formed may be considered as Sn_2O_2 stannoxane groups. The hexagonal lids are not planar, however, and a better description of their conformations is one based on a somewhat flattened chair conformation. The Sn atoms of each rectangular face are bridged by a carboxylate ligand which forms equivalent Sn–O bonds. As has been observed for similar structures, the framework Sn–O bond distances are significantly shorter than the Sn–O bonds involving the carboxylate ligands [8,9,14–16]. The coordination geometry about each Sn atom is completed by a C atom of the ${}^{n}Bu$ group which occupies a position *trans* to a framework O atom. Thus each Sn atom is coordinated by three 'framework' O atoms, two carboxylate O atoms and a C atom such that the O_5C donor set defines a distorted octahedron.

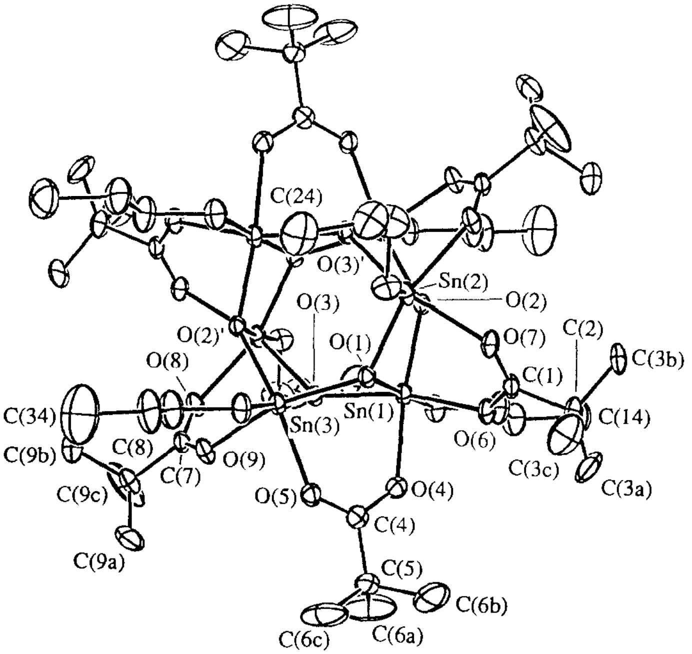

Fig. 2. Molecular structure and crystallographic numbering scheme employed for $[{}^{n}BuSn(O)(O_2C{}^{t}Bu)]_6$.

An alternative structure may be found for monoorganotin carboxylates based on the closely related formulation $\{[RSn(O)(O_2CR')]_2[RSn(O_2CR')_3]\}_2$ [8,9,16]. Crystal structures for several of these have shown that the structure is based on a Sn_4O_4 'ladder' with bridging and chelating carboxylate ligands. This study provides two further examples of the 'drum' hexameric form. We note that this structural type has now been observed for a range of carboxylate bound R′ groups such as CH_3 [15], CCl_3 [16] and c-C_6H_{11} [14] suggesting that the R′ group does not play a significant role in determining the structure. This observation may be rationalized in terms of the solid state structure which show that the R′ groups are peripheral to the framework of the cluster.

Experimental

Preparation of compounds

^{n}BuSnCl$_3$, ^{t}BuCOOH, ^{i}PrCOOH were obtained from Fluka A.G. Butylstannoic acid was prepared from ^{n}BuSnCl$_3$ by hydrolysis. Experimental techniques were similar to those reported earlier [3].

To a benzene suspension of butylstannoic acid (1.51 g, 7.3 mmol) was added a benzene solution (20 cm^3) of trimethylacetic acid (0.74 g, 7.3 mmol). The mixture was heated under reflux with stirring for 5 h. The water formed during the reaction was removed azeotropically with a Dean and Stark apparatus. The clear solution thus obtained was evaporated under vacuum to leave a white solid, which was

Table 2

Crystal data and refinement details for $[^{n}BuSn(O)(O_2C^{t}Bu)]_6$

Formula	$C_{54}H_{108}O_{18}Sn_6$
Mol. wt.	1757.5
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	12.655(2)
b, Å	14.305(3)
c, Å	12.025(2)
α, deg	104.43(2)
β, deg	106.32(1)
γ, deg	106.16(2)
V, Å^3	1875.8
Z	1 (hexamer)
D_c, g cm^{-3}	1.556
$F(000)$	876
μ, cm^{-1}	18.62
No. of data collected	3995
No. of unique data	3502
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	2454
R	0.029
k	0.5
g	0.002
R_w	0.032
Residual ρ_{max}, e Å^{-3}	0.57

recrystallized from hexane containing 5% benzene in 50% (1.06 g) yield; m.p. 299–300 °C. (Found: C, 36.65; H, 6.09; Sn, 40.58. $C_9H_{18}O_3Sn$ calcd.: C, 36.90; H, 6.19; Sn, 40.52%). $^{13}C\{^1H\}$ NMR in $CDCl_3$—Bu–Sn: $\delta(CH_2\ \alpha)$ 26.2 $^1J(^{119}Sn-^{13}C)$ 1192 Hz, $^1J(^{117}Sn-^{13}C)$ 1135 Hz; $\delta(CH_2\ \beta)$ 26.5; $\delta(CH_2\ \gamma)$ 27.5; $\delta(CH_3)$ 13.7; $\delta(CO_2)$ 185.6, $^2J(^{117/119}Sn-^{13}C)$ 34 Hz, $\delta(Me_3C)$ 40.6, $\delta(CH_3)$ 27.5 ppm. $^{119}Sn\{^1H\}$ NMR in $CDCl_3$: $\delta - 485$ ppm, $^2J(^{119}Sn\text{-}O\text{-}^{117/119}Sn)$ 31, 74, 250 Hz. IR (Nujol): $\nu(C{=}O)$ 1580 cm^{-1}.

The complex $[^nBuSn(O)(O_2C^iPr)]_6$ was prepared similarly; m.p. 255–256 °C (Found: C, 35.20; H, 6.04; Sn, 43.13. $C_8H_{16}O_3Sn$ calcd.: C, 34.45; H, 5.78; Sn, 42.55%). $^{13}C\{^1H\}$ NMR in $CDCl_3$—Bu–Sn: $\delta(CH_2\ \alpha)$ 26.5 $^1J(^{119}Sn-^{13}C)$ 1202 Hz,

Table 3

Fractional atomic coordinates ($\times 10^5$ for Sn and $\times 10^4$ for remaining atoms) for $[^nBuSn(O)(O_2C^tBu)]_6$

Atom	*x*	*y*	*z*
Sn(1)	−17925(5)	44062(4)	30784(5)
Sn(2)	7468(5)	42583(4)	34151(5)
Sn(3)	1490(5)	66938(4)	47253(5)
O(1)	−65(5)	5332(4)	3381(5)
O(2)	−830(4)	3512(4)	3600(4)
O(3)	−1345(5)	5603(4)	4724(5)
O(4)	−2438(5)	5365(5)	2145(5)
O(5)	−1010(6)	6950(5)	3235(6)
O(6)	−2003(6)	3624(4)	1195(5)
O(7)	−207(6)	3568(5)	1422(6)
O(8)	975(6)	2792(5)	3007(5)
O(9)	−300(5)	7893(4)	5740(6)
C(1)	−1254(11)	3401(7)	791(8)
C(2)	−1706(11)	2855(9)	−623(9)
C(3a)	−2841(12)	2858(13)	−1290(10)
C(3b)	−1533(21)	1867(13)	−871(13)
C(3c)	−816(16)	3590(15)	−1025(13)
C(4)	−1965(9)	6335(9)	2369(9)
C(5)	−2651(9)	6743(7)	1495(10)
C(6a)	−3790(15)	6594(19)	1529(24)
C(6b)	−2892(21)	6131(19)	167(17)
C(6c)	−1966(14)	7802(13)	1670(20)
C(7)	711(8)	2088(8)	3420(9)
C(8)	869(10)	1075(7)	2836(10)
C(9a)	948(16)	457(11)	3678(13)
C(9b)	−274(15)	411(11	1667(13)
C(9c)	1829(17)	1285(11)	2391(23)
C(11)	−3532(8)	3486(7)	2843(10)
C(12)	−4181(10)	2495(9)	1731(11)
C(13)	−5400(10)	1900(10)	1622(13)
C(14)	−6008(12)	908(12)	519(17)
C(21)	2320(9)	5092(8)	3231(10)
C(22)	3316(11)	4787(11)	3573(15)
C(23)	4458(11)	5496(14)	3486(15)
C(24)	5026(15)	6539(14)	4384(17)
C(31)	1708(8)	7748(7)	4696(9)
C(32)	2353(10)	8745(9)	5758(12)
C(33)	3482(12)	9402(10)	5649(15)
C(34)	4110(19)	10373(19)	6612(25)

${}^{1}J({}^{117}Sn-{}^{13}C)$ 1145 Hz; $\delta(CH_2\ \beta)$ 26.2; $\delta(CH_2\ \gamma)$ 27.3; $\delta(CH_3)$ 13.6; $\delta(CO_2)$ 184.4, ${}^{2}J({}^{117/119}Sn-{}^{13}C)$ 32 Hz, $\delta(CH)$ 36.6, $\delta(CH_3)$ 19.3, 19.2 ppm. ${}^{119}Sn\{{}^{1}H\}$ NMR in $CDCl_3$: δ −485 ppm, ${}^{2}J({}^{119}Sn-O-{}^{117/119}Sn)$ 32, 75, 248 Hz. IR (Nujol): $\nu(C{=}O)$ 1595 cm^{-1}.

Crystallography

Intensity data were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The $\omega:2/3\theta$ scan technique was employed to measure data up to a maximum Bragg angle of 20.0°. The data were corrected for Lorentz and polarization effects but not for absorption owing to the spherical shape of the crystal; relevant crystal data are collected in Table 2.

The structure was solved by direct methods [17] and refined by a full-matrix least-squares procedure based on F [18]. All non-H atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions. After the inclusion of a weighting scheme of the form, $w = k/[\sigma^2(F) + g|F|^2]$, the refinement was continued until convergence. Final refinement details are listed in Table 2. Fractional atomic coordinates are listed in Table 3 and the numbering scheme employed are shown in Fig. 2 which was drawn with ORTEP [19] at 15% probability ellipsoids. Scattering factors were as incorporated in the SHELX76 program [18] and refinement was performed on a SUN4/280 computer. Other crystallographic details, comprising thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors are available from E.R.T.T.

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