

A novel trinuclear *n*-butyltin cluster incorporating three ferrocene carboxylate substituents

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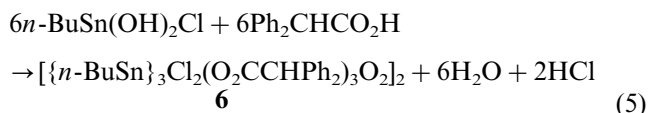
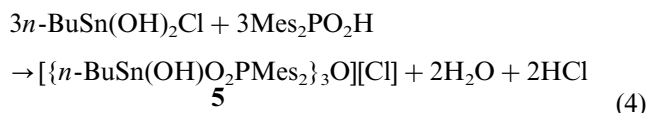
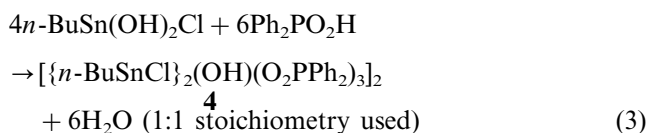
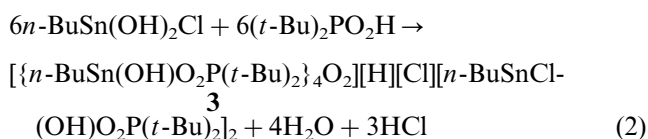
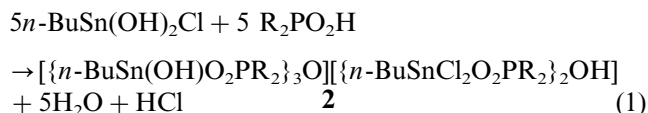
Abstract

The trinuclear compound $\{n\text{-BuSnCl}(\text{O}_2\text{CC}_5\text{H}_4\text{-Fe-C}_5\text{H}_5)\}_3(\text{O})(\text{OH})$ (**7**) has been synthesized by the 1:1 stoichiometric reaction of $n\text{-BuSn}(\text{OH})_2\text{Cl}$ (**1**) with ferrocene carboxylic acid. The structure in the solid state, as revealed by X-ray crystallography, shows three tin atoms connected by three bridging ferrocene carboxylates. Whereas two of these tins are hexacoordinated, the third one is essentially pentacoordinated with an additional weak interaction to a chlorine bonded to one of the other tin atoms of the same molecule. The relationship of this compound, as an intermediate, to the 'ladder' compound with the formula $\{n\text{-BuSn}(\text{O}_2\text{CCHPh}_2)\}_6\text{Cl}_4\text{O}_4$ which is formed in the analogous reaction of **1** with diphenyl acetic acid is highlighted. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carboxylates; Ferrocene; Tin

1. Introduction

Despite the fact that a rich variety of monoorganotin oxocarboxylate/phosphinate cages and clusters have been characterized unequivocally by X-ray crystallography [1–7], the pathways leading to the formation of this class of compound remain unclear because a large number of labile Sn–O and Sn–Cl bonds need to be broken and reformed/reorganized to get to one structure from another [8]¹. Such a feature is clearly manifested even in the simple 1:1 stoichiometric reaction of $n\text{-BuSn}(\text{OH})_2\text{Cl}$ (**1**) with different phosphinic/carboxylic acids (Eqs. (1)–(5)) [6,7]. Products such as **2–6** may be good catalysts for transesterification and selective ring opening of oxiranes [9–13]; thus a knowledge of the reactivity of these compounds can be useful in understanding their catalytic behaviour.



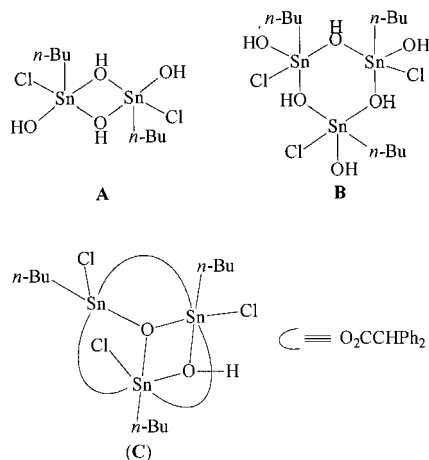
The results for the phosphinates were rationalized by assuming feasible dimer (**A**) and trimer (**B**) forms for **1**; however no intermediates were isolated [6]. Obviously,

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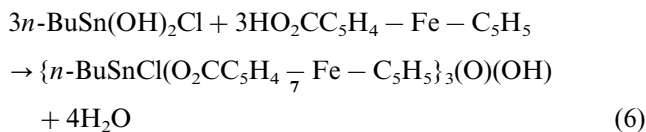
¹ Even the structures of the two key precursors, $n\text{-BuSn}(\text{O})(\text{OH})$ and $n\text{-BuSn}(\text{OH})_2\text{Cl}$, remain unknown to date. Based on ¹¹⁹Sn NMR, $n\text{-BuSn}(\text{O})(\text{OH})$ [$\delta(\text{Sn})$: –282.0, –465.0; Aldrich sample (see Ref. [8a]) is likely to have a structure similar to $\{n\text{-BuSn}\}_{12}\text{O}_{14}(\text{OH})_2\cdot 4i\text{-PrOH}$ [$\delta(\text{Sn})$: –280.1, –447.1] reported by Banse et al. [8b].

in solution, condensation products with different stages of phosphinate/carboxylate substitution must be present and one such intermediate species (C) was proposed for the formation of the carboxylate **6** [7]. We now report the isolation and structural characterization of the novel trinuclear cluster $\{n\text{-BuSnCl}(\text{O}_2\text{CC}_5\text{H}_4\text{-Fe-C}_5\text{H}_5)_3(\text{O})(\text{OH})\}$ (**7**) that has the structure of the intermediate C and incorporates three ferrocenyl residues in it.



2. Results and discussion

Compound **7** is prepared readily according to Eq. (6) and is isolated in 60% yield. It is not very soluble in common organic solvents. It decomposes in CDCl_3 solution over a period of 1–2 days and turns black. The integrated intensities in the $^1\text{H-NMR}$ and elemental analysis are consistent with the formula; in the IR spectrum a $\nu(\text{OH})$ band at 3316 cm^{-1} and two strong $\nu(\text{C}=\text{O})$ bands at 1525 and 1479 cm^{-1} are observed.



In the molecule of **7** (Fig. 1; bond lengths and angles in Table 1), the three ferrocene carboxylate residues bridge the three tin atoms. While the two tin atoms Sn(1) and Sn(3) are clearly hexacoordinated, Sn(2) is essentially pentacoordinated considering the long Sn(2)–Cl(3) distance ($2.842(5) \text{ \AA}$). The Sn–O and Sn–C bond lengths are in the normal range [3,6,7]; no significant difference between Sn–O (tricoordinated) and Sn–O (carboxylate) bond lengths is observed. The oxygen atom O(1) is away from the mean plane of the three tin atoms by 0.44 \AA . The Sn(1)–Cl(1) ($2.441(4) \text{ \AA}$) and Sn(2)–Cl(2) ($2.341(5) \text{ \AA}$) bonds are also in the normal range [6,7] but Sn(3)–Cl(3) ($2.519(5) \text{ \AA}$) is slightly out-

side the range observed so far, probably because of the proximity of Cl(3) to Sn(2). The molecules of **7** form hydrogen bonded dimers using Cl(1) and O(2) (Cl(1)–O(2) 3.12 \AA); no other significant interactions were found in the crystal.

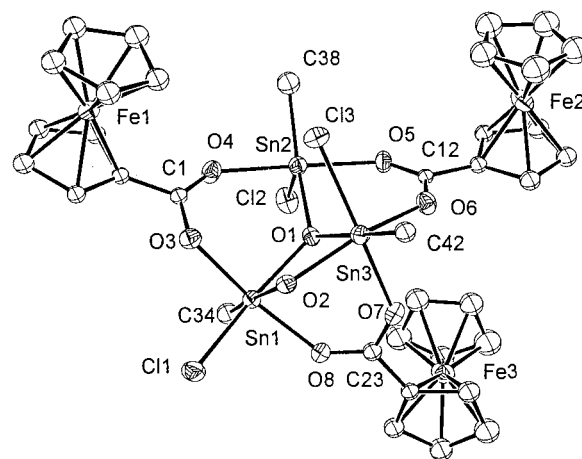


Fig. 1. ORTEP drawing showing the molecular structure of **7**. Only the α -carbons of the *n*-butyl groups are shown for clarity. Labelling is shown only on selected atoms.

Table 1
Selected interatomic distances (Å) and angles (°) for **7** with S.D. in parentheses

Bond lengths (Å)			
Sn(1)–O(1)	2.129(9)	Sn(2)–C(38)	2.128(19)
Sn(1)–O(2)	2.089(10)	Sn(2)–Cl(2)	2.341(5)
Sn(1)–O(3)	2.131(10)	Sn(2)–Cl(3)	2.842(5)
Sn(1)–O(8)	2.119(10)	Sn(3)–O(1)	2.072(9)
Sn(1)–C(34)	2.104(19)	Sn(3)–O(2)	2.110(10)
Sn(1)–Cl(1)	2.441(4)	Sn(3)–O(6)	2.096(11)
Sn(2)–O(1)	2.006(10)	Sn(3)–O(7)	2.124(11)
Sn(2)–O(4)	2.158(10)	Sn(3)–C(42)	2.090(16)
Sn(2)–O(5)	2.139(10)	Sn(3)–Cl(3)	
Bond angles (°)			
O(1)–Sn(1)–O(2)	75.1(4)	O(5)–Sn(2)–Cl(2)	92.3(3)
O(1)–Sn(1)–O(3)	89.9(4)	O(5)–Sn(2)–Cl(3)	86.6(3)
O(1)–Sn(1)–O(8)	85.5(4)	C(38)–Sn(2)–Cl(2)	107.6(6)
O(1)–Sn(1)–C(34)	101.4(6)	C(38)–Sn(2)–Cl(3)	81.9(5)
O(1)–Sn(1)–Cl(1)	161.3(3)	Cl(2)–Sn(2)–Cl(3)	170.5(2)
O(2)–Sn(1)–O(3)	83.0(4)	O(1)–Sn(3)–O(2)	75.8(4)
O(2)–Sn(1)–O(8)	84.5(4)	O(1)–Sn(3)–O(6)	89.0(4)
O(2)–Sn(1)–C(34)	174.3(6)	O(1)–Sn(3)–O(7)	88.7(4)
O(2)–Sn(1)–Cl(1)	86.3(3)	O(1)–Sn(3)–C(42)	173.6(5)
O(3)–Sn(1)–O(8)	167.4(4)	O(1)–Sn(3)–Cl(3)	81.1(3)
O(3)–Sn(1)–C(34)	101.6(6)	O(2)–Sn(3)–O(6)	160.5(4)
O(3)–Sn(1)–Cl(1)	89.0(3)	O(2)–Sn(3)–O(7)	83.3(4)
O(8)–Sn(1)–C(34)	90.8(6)	O(2)–Sn(3)–C(42)	99.4(5)
O(8)–Sn(1)–Cl(1)	91.6(3)	O(2)–Sn(3)–Cl(3)	99.6(3)
C(34)–Sn(1)–Cl(1)	97.1(6)	O(6)–Sn(3)–O(7)	84.1(4)
O(1)–Sn(2)–O(4)	89.9(4)	O(6)–Sn(3)–C(42)	96.5(5)
O(1)–Sn(2)–O(5)	86.2(4)	O(6)–Sn(3)–Cl(3)	90.0(3)
O(1)–Sn(2)–C(38)	156.3(6)	O(7)–Sn(3)–C(42)	95.0(5)
O(1)–Sn(2)–Cl(2)	96.1(3)	O(7)–Sn(3)–Cl(3)	168.4(3)
O(1)–Sn(2)–Cl(3)	74.4(3)	C(42)–Sn(3)–Cl(3)	95.7(5)
O(4)–Sn(2)–O(5)	174.1(4)	Sn(1)–O(1)–Sn(2)	127.5(5)
O(4)–Sn(2)–C(38)	89.4(6)	Sn(1)–O(1)–Sn(3)	103.0(4)
O(4)–Sn(2)–Cl(2)	92.5(3)	Sn(2)–O(1)–Sn(3)	115.9(4)
O(4)–Sn(2)–Cl(3)	88.2(3)	Sn(1)–O(2)–Sn(3)	103.1(4)
O(5)–Sn(2)–C(38)	92.4(6)		

In addition to the fact that three ferrocenyl residues can be readily incorporated in one molecule [14]², the isolation of **7** is significant in that it throws light on the pathways of stannoxane cluster formation, particularly that of the open [or ladder] type as shown in Scheme 1.

In this scheme, **F'** has the same structure as **7** and **H** has the reported ladder structure **6**; the dimeric form (cf **E**) with bridging phosphinates has been found in compound **3**. Elimination of a molecule of HCl from **F'** followed by dimerization leads to the ladder **H**. It is also important to note that the relative dispositions of carboxylates, *n*-butyl carbons and the unique oxygen (O(1) in **7**) are maintained the same way in **6** and **7**.

In summary, a new structural type for monoorganotin carboxylates which incorporates three ferrocenyl residues is structurally characterized; the isolation of

this species has been useful in understanding the pathways in the reaction of monorganotin substrates with carboxylic acids.

3. Experimental

Solvents were dried and distilled prior to use. Chemicals were purchased from Aldrich or local sources. NMR spectra were recorded in CDCl₃ solutions on a Bruker 200 MHz NMR spectrometer. IR spectra were recorded on a Jasco FT/IR 5300 spectrophotometer. Elemental analyses were carried out on a Perkin–Elmer 240C CHN analyzer.

3.1. Synthesis of the trinuclear cluster

{*n*-BuSnCl(O₂CC₅H₄–Fe–C₅H₅)₃(O)(OH)} (7)

A mixture of *n*-BuSn(OH)₂Cl (**1**) (0.32 g, 1.3 mmol) and ferrocene carboxylic acid (0.3 g, 1.3 mmol) in toluene (20 ml) was heated under reflux for 1 h and water was removed by azeotropic distillation. The solvent was removed completely and from the residue and compound **7** (red coloured) was crystallized using a 2:3 dichloromethane–hexane mixture. Yield: 0.175 g (60%). M.p. 152–160°C. IR (major bands): 3316 (ν(OH)), 1525, 1479, 1391, 1360, 505 cm⁻¹. ¹H-NMR: δ 0.80–2.30 (m, 27H, *n*-Bu-*H*), 4.00–5.00 (m, 27H, Cp-*H*), 7.10–7.30 (br, 1H, OH). Over a period of 1–2 days the solution turned black and the spectrum showed broad resonances. ¹³C-NMR: δ 13.8 (CH₃), 25.7, 27.2 and 27.8 (SnCH₂CH₂CH₂), 70.2, 71.2 and 72.3 (Cp-C). The signal due to CO₂ was not observed probably because of its low intensity. Although several attempts were made, ¹¹⁹Sn-NMR signals could not be obtained, probably because of structural interconversions in solution; such behaviour in this class of compound has been reported previously [7]. Anal. Calc. for C₄₅H₅₅Cl₃Fe₃O₈Sn₃: C, 39.95, H, 4.02. Found: C, 39.88; H, 4.18.

A suitable crystal was mounted on a glass fibre and X-ray data were collected at 293 K on an Enraf–Nonius MACH3 diffractometer using graphite monochromated Mo–K_α radiation (λ = 0.71073 Å). Three control reflections collected every 90 min showed no significant changes in the intensities. The structure was solved and refined by conventional methods [15]. A statistical absorption correction was applied [16]. Only tin, oxygen and iron were refined anisotropically; remaining nonhydrogen atoms were refined isotropically. All the hydrogen atoms except the one on O(2) were fixed by geometry. No attempt was made to fix/locate this hydrogen atom on O(2).

² Of course in [*n*-BuSnO(O₂CC₅H₄–FeC₅H₅)₆], six ferrocenyl residues are incorporated quite readily; see for example Ref. [14a,b].

3.2. Crystal data

Empirical formula: $C_{45}H_{55}Cl_3Fe_3O_8Sn_3$. Colour: red. Shape: irregular. Formula wt. 1353.86. Crystal system: triclinic. Space group: $P\bar{1}$. $a = 11.997(6)$, $b = 14.449(3)$, $c = 16.153(4)$ Å; $\alpha = 75.26(2)$, $\beta = 88.55(3)$, $\gamma = 69.42(3)^\circ$. $V = 2528.7(14)$ Å³. $Z = 2$. $\lambda + 0.71073$ Å. $\mu = 2.503$ mm⁻¹. Crystal size: $0.1 \times 0.3 \times 0.4$ mm. θ range: 1.56–22.68. Reflections collected: 6760. Independent reflections: 6760 [$R_{int} = 0.0000$]. Observed reflections ($I > 2\sigma(I)$): 3091. Number of parameters refined: 337. Refinement on F^2 . H atoms: fixed by geometry. GOF: 1.041. $R[I > 2\sigma(I)]$: 0.0568. wR_2 : 0.1209. Largest difference peak and hole: 0.76 and -0.83 e Å⁻³.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 116031 for compound **7**. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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References

- [1] R.R. Holmes, Acc. Chem. Res. 22 (1989) 190.
- [2] K.C. Kumara Swamy, C.G. Schmid, R.O. Day, R.R. Holmes, J. Am. Chem. Soc. 112 (1990) 223.
- [3] K.C. Kumara Swamy, M.A. Said, S. Nagabrahmanandachari, D.M. Poojary, A. Clearfield, J. Chem. Soc. Dalton Trans. (1998) 1645.
- [4] R.R. Holmes, R.O. Day, K.C. Kumara Swamy, C.G. Schmid, S.D. Burton, J.M. Holmes, Main Group Metal Chem. 13 (1989) 291.
- [5] C.G. Schmid, R.O. Day, R.R. Holmes, Phosph. Sulfur Silicon 41 (1989) 69.
- [6] K.C. Kumara Swamy, R.O. Day, R.R. Holmes, Inorg. Chem. 31 (1992) 4184.
- [7] S. Nagabrahmanandachari, C. Hemavathi, K.C. Kumara Swamy, D.M. Poojary, A. Clearfield, Main Group Metal Chem. 21 (1998) 789.
- [8] (a) S. Nagabrahmanandachari, Ph.D. Thesis, University of Hyderabad, Hyderabad, India, 1996. (b) F. Banse, F. Ribot, P. Toledano, J. Maquet, C. Sanchez, Inorg. Chem. 34 (1995) 6371.
- [9] J. Otera, T. Yano, E. Kunimoto, T. Nakata, Organometallics 3 (1984) 426.
- [10] J. Otera, Y. Niibo, N. Tatsumi, H. Nozaki, J. Org. Chem. 53 (1988) 275.
- [11] J. Otera, Y. Niibo, H. Nozaki, Tetrahedron 36 (1991) 7625.
- [12] J. Otera, N. Dan-Oh, H. Nozaki, J. Org. Chem. 56 (1991) 5307.
- [13] J. Otera, Chem. Rev. 93 (1993) 1449.
- [14] (a) K.C. Kumara Swamy, S. Nagabrahmanandachari, Phosph. Sulf. Silicon 65 (1992) 9. (b) V. Chandrasekhar, S.S. Nagendran, S. Bansal, A. Vij, International Symposium on Metalloorganic Chemistry, Jaipur, India, March 16–18, 1998, Abstract I-3.
- [15] G.M. Sheldrick, SHELXL 97, University of Göttingen, Göttingen, Germany, 1997.
- [16] N. Walker, D. Stuart, Acta Crystallogr. A 39 (1983) 158.