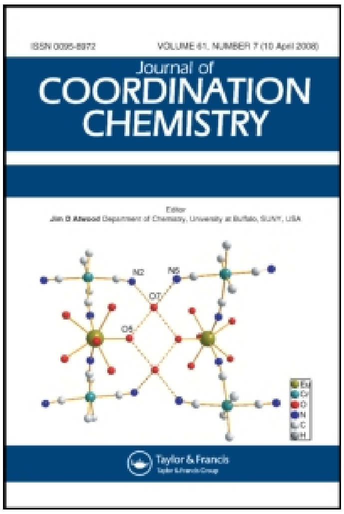

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Drum-shaped mono-organooxotin assembly through solvothermal synthesis with 2,3,4,5-tetrafluorobenzoic acid: crystal structure, hydrogen bonding and π–π stacking interactions

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A drum-shaped organooxotin (IV) complex with 2,3,4,5-tetrafluorobenzoic acid of the type $\{[SnR_2(2,3,4,5\text{-}F_4C_6HCO_2)]O\}_6$ ($R = m\text{-Cl-PhCH}_2$) has been solvothermally synthesized and structurally characterized by elemental, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectra and X-ray crystallography diffraction analysis. This complex exhibits a new structural environment appearing as a "drum" arrangement with hexa-coordinated tin atoms in a four-membered stannoxane ring, $(–Sn–O–)_2$, as a common structural feature. Each tin(IV) displays a distorted octahedral geometry. Weak, but significant, intramolecular C–H $\cdots$ F hydrogen bonds and π–π stacking interactions are shown. These contacts lead to aggregation and supramolecular self-assembly. Cleavage of Sn–C bond occurred in complexes under the influence of strong acid.

Keywords: 2,3,4,5-tetrafluorobenzoic acid; Organooxotin; Solvothermal synthesis; Assembly; Hydrogen bonding; π–π stacking interaction

1. Introduction

Organooxotin clusters have attracted attention because of their novel structures [1], their suitability for construction of supramolecular frameworks [2], and their efficient catalysis of various organic reactions [3]. A large variety of cluster types such as drums, ladders, cubes, football cages, etc., are known [4]. Only a few examples of fluorinated organooxotin clusters were reported [5]. The fluorine (as a good hydrogen bond donor) may help to construct higher dimension structures, but the presence of fluorine (strong electron-withdrawing substituents) on the carboxylic acid can facilitate debenzylation

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reaction [6] (the use of "normal" carboxylic acids and "normal" reaction conditions do not lead to debenzylation [6]). Reaction of R_2SnO (R = *m*-Cl-$PhCH_2$) and 2,3,4,5-tetrafluorobenzoic acid in solvothermal conditions using benzene affords the drum-shaped product, in which one of two benzyl groups was cleavaged from the Sn, consistent with the literature [7]. There is also considerable interest in the preparation of oligomeric units of these clusters by covalent [8] or coordinative interactions [9], which is likely to lead to the formation of well-defined polymeric arrays in the solid state.

Herein we selected 2,3,4,5-tetrafluorobenzoic acid as a ligand and report a drum-shaped mono-organooxotin complex: $\{[SnR_2(2,3,4,5\text{-}F_4C_6HCO_2)]O\}_6$ (R = *m*-Cl-$PhCH_2$), which was solvothermally synthesized and structurally characterized by elemental, IR, ^1H, ^{13}C, ^{119}Sn NMR spectra analysis. This complex exhibits a new structural environment appearing as a "drum" arrangement with hexa-coordinated tin atoms in a four-membered stannoxane ring, $(\text{–Sn–O–})_2$, as a common structural feature. Each tin(IV) atom displays a six-coordinated distorted octahedron geometry. The structure of **1** reveals that formation involves Sn–C bond cleavage under the influence of strong acid; supramolecular structures were formed by intermolecular C–H···F hydrogen bonding and π–π stacking.

2. Experimental

2.1. *Materials and measurements*

2,3,4,5-tetrafluorobenzoic acid was commercially available and used without further purification. *m*-Chlor-dibenzyltin was prepared by a standard method [10]. The melting point was obtained on a Kofler micro-melting point apparatus and was uncorrected. Infrared-spectra were recorded on a Nicolet–460 spectrophotometer using KBr discs and sodium chloride optics. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in ppm relative to Me_4Si in $CDCl_3$ as solvent. Elemental analyses (C, H) were performed with a PE-2400II apparatus.

2.2. *Syntheses*

2.2.1. Synthesis of $[(2,3,4,5\text{-}F_4C_6HCO_2)RSnO]_6$ (R = *m*-Cl-$PhCH_2$). The reaction was carried out under nitrogen atmosphere. Di-*m*-*chlor*-benzyltin oxide (0.301 g, 1 mmol) and 2,3,4,5-tetrafluorobenzoic acid (0.194 g, 1 mmol) were added to dry benzene in a sealed vessel for 3 days. After filtration, the solvent was evaporated *in vacuo*. The solid was then recrystallized from ethanol giving colorless crystals. Yield, 82%. m.p. 162–164°C; Anal. Calcd for $C_{84}H_{42}Cl_6F_{24}O_{18}Sn_6$: C, 37.09; H, 1.56. Found: C, 37.32; H, 1.41%. IR (KBr, cm^{-1}): $\nu(C{=}O)$ 1696; $\nu(COO)_{as}$ 1618; $\nu(COO)_s$

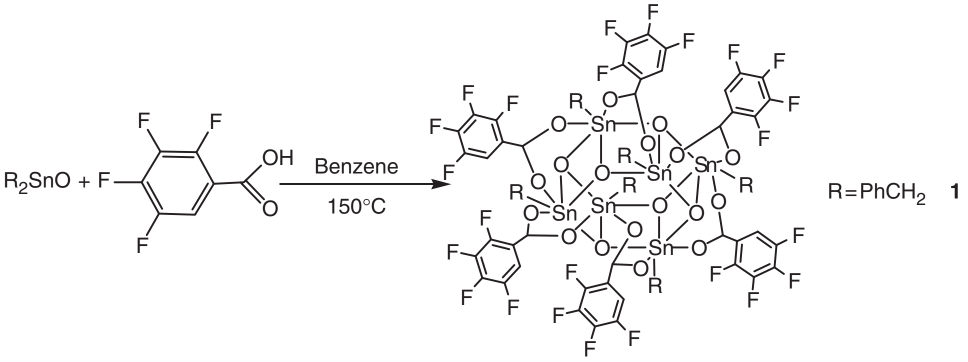
1472, 1352; ν(Sn–O–Sn) 631; ν(Sn–O) 473 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): 3.12–3.28 (m, 12H) 7.36–7.90 (m, 24H), 7.70–7.88 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 178.4 (COO), 151.6, 148.5, 142.8, 134.8, 129.0, 128.6, 125.7, 110.0, 19.9. ^{13}C NMR ($CDCl_3$): δ 174.6 (COO), 150.5, 148.2, 143.8, 139.2, 131.0, 129.1, 126.8, 115.3, 21.3. ^{119}Sn NMR ($CDCl_3$, 298 K): −610.8 ppm.

2.3. *X-ray crystallography studies*

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart-1000 CCD area-detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXLS-97 and refined against F^2 by full matrix least squares using SHELXL-97. A fluorine atom is disordered from the F4Ph group, showing half F atoms at two sites. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determination are listed in table 1.

Table 1. Crystal data and structure refinements for the complex.

Empirical formula	$C_{84}H_{36}Cl_6F_{24}O_{18}Sn_6$
Formula weight	2713.97
Wavelength (Å)	0.71073
Crystal system	Trigonal
Space group	$R\bar{3}$
a (Å)	20.201(4)
b (Å)	20.201(4)
c (Å)	20.294(8)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	7172(3)
Z	1
D_{Calcd} (Mg m^{-3})	1.885
F(000)	3906
Absorption coefficient (mm^{-1})	1.821
Crystal size (mm^3)	0.45 × 0.38 × 0.32
θ range for data collection (°)	3.01–25.00
Index ranges	$-24 \le h \le 23$; $-21 \le k \le 24$; $-14 \le l \le 24$
Reflections collected	12412
Unique reflections	2774 ($R_{\text{int}} = 0.0889$)
Absorption correction	Semi-empirical from equivalents
Max/min transmission	0.5934, 0.4945
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2774/0/217
Goodness-of-fit on F^2	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0615$, $wR_2 = 0.1503$
R indices (all data)	$R_1 = 0.1079$, $wR_2 = 0.1857$



Scheme 1. Synthesis of an organooxotin(IV) cluster.

3. Results and discussion

3.1. *Synthesis*

An organooxotin(IV) cluster was obtained by reacting stoichiometric amounts of the 2,3,4,5-tetrafluorobenzoic acid and benzyltin oxide. The synthesis procedure is given in scheme 1.

3.2. *Spectroscopic studies*

The explicit feature in the infrared spectra of complexes is the absence of the ν(O–H) between 2600–3436 cm^{-1}, indicating metal-ligand bond formation through this site. All IR values are consistent with a number of organotin(IV)-oxygen derivatives [11, 12].

In organotin(IV) carboxylate complexes, IR spectroscopy can provide useful information concerning bonding of carboxylate. Based on previous reports, it is possible to distinguish the coordination mode of the COO$^-$ group [13]. A symmetrical doublet for the carboxylate stretching frequency, ν_{COO}, is centered near 1550 cm^{-1} and a single Sn–O stretch, $\nu_{Sn–O}$, near 600 cm^{-1}. The magnitude of $\Delta\upsilon$ of about 168 cm^{-1}, compared with those for the corresponding sodium salts, revealed that the carboxylate is bidentate. A strong band in the 640–620 cm^{-1} region is assigned to ν(Sn–O–Sn), indicating a Sn–O–Sn bridged structure.

The ^{1}H NMR spectra show the expected integration and peak multiplicities. In the spectrum of the free ligand, the resonance observed at about $\delta = 10.114$ ppm, which is absent in the spectra of the complexes, indicates the replacement of the carboxylic acid proton on complex formation. The chemical shifts for the benzyl group are observed at 3.17–3.26 and 7.32–7.86 ppm, upfield shifts compared with the precursor. The $^2J_{SnH}$ of dibenzyltin derivative **1** has a value of 95.6 Hz, comparable with those previously reported for six-coordinate octahedral tin(IV) adducts [14].

The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonances, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor. There is only a single resonance in the region 168–182 ppm for the carboxyl group.

The ^{119}Sn NMR data show only one triplet at −610.8 ppm, typical of a six-coordinate species, in accord with the solid state structure [15]. The ^{119}Sn chemical shift is especially diagnostic of the structure.

3.3. *Molecular structure*

3.3.1. Crystal structure of $\{[SnR_2(2,3,4,5\text{-}F_4C_6HCO_2)]O\}_6$ (R = *m*-Cl-PhCH$_2$). The molecule structure and unit cell of the complex are shown in figures 1 and 2 and selected bond lengths and angles are listed in table 2. The reported phenyltin cyclohexanoate analogue [16], has idealized S_6 molecular symmetry (symmetry modes: #1: $1-y$, $x-y$, z; #2: $0.33+x-y$, $-0.33+x$, $0.67-z$). The geometry of the stannoxane framework is shown in figure 1, where it can be seen that the six-membered rings have a chair conformation. Each Sn atom is bonded to three framework oxygen atoms, where the Sn–O bonds have lengths ranging from 2.071(5) to 2.094(5) Å. The oxygen atoms of the framework are trivalent and have a distorted pyramidal geometry. The sum of the three Sn–O–Sn angles about these oxygen atoms ranges from 331.8 to 333.9°.

The six tin atoms are chemically equivalent, as are the six trivalent oxygen atoms. The Sn–O framework of the molecule can be described as a drum with top and bottom faces each being comprised of a six-membered $(–Sn–O–)_3$ tri-stannoxane ring. The drum faces are joined together by six Sn–O bonds containing tri-coordinated oxygen atoms. The sides of the drum are thus comprised of six four-membered $(–Sn–O–)_2$ distannoxane rings, each of which is spanned by a carboxylate group that forms a symmetrical bridge between two tin atoms. The Sn–O bonds to the bridging carboxylate atoms are longer than the core bonds and range from 2.103(6) to 2.155(6) Å. The sides of the structure are reminiscent of the ladder arrangement in dimeric distannoxanes recently found for aryl [17] and alkyl [18] derivatives, e.g., $[Ph_2(Cl)SnOSnPh_2(Cl)]_2$. Concomitant with the

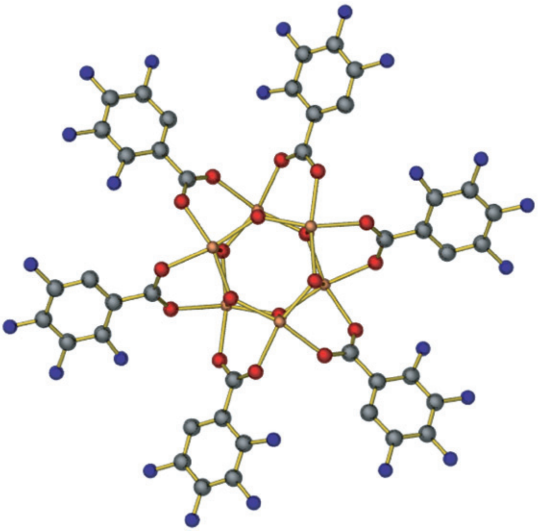


Figure 1. The molecular structure of the complex, showing a drum-shaped framework (the benzyl groups and the disordered F atoms have been omitted for clarity).

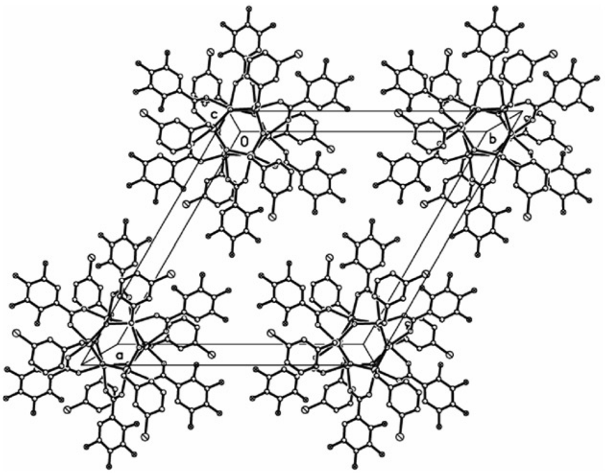


Figure 2. Unit cell of the complex.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Sn(1)–O(3)	2.071(5)
Sn(1)–O(3)#2	2.103(6)
Sn(1)–O(1)	2.155(6)
Sn(1)–Sn(1)#2	3.2005(13)
Sn(1)–O(3)#1	2.094(5)
Sn(1)–C(8)	2.135(10)
Sn(1)–O(2)#3	2.148(6)
Sn(1)–Sn(1)#3	3.2005(12)
O(2)–Sn(1)#2	2.148(6)
O(3)–Sn(1)–O(3)#1	104.1(3)
O(2)#3–Sn(1)–O(1)	77.8(3)
O(3)–Sn(1)–O(1)	157.8(3)
O(3)#2–Sn(1)–O(1)	86.5(3)
O(3)–Sn(1)#3	2.103(6)
O(3)–Sn(1)–O(3)#2	78.6(2)
O(3)–Sn(1)–O(2)#3	85.5(3)
O(3)#1–Sn(1)–O(1)	88.6(2)
O(3)–Sn(1)–O(1)	157.8(3)

Symmetry operations: 1: $-x+y+1$, $-x+1$, $z-x+y+1$, z; #2: $y+1/3$, $-x+y+2/3$, $-z+2/3$; #3: $x-y+1/3$, $x-1/3$, $-z+2/3$.

equivalence of the Sn–O bonds to a particular carboxylate group is the corresponding equivalence of the pairs of C–O carboxylate bond lengths.

The distannoxane ring units of the sides of the drum are not planar but are folded along the Sn–Sn vectors so that the oxygen atoms are directed towards the interior of the cavity. Similarly, the tristannoxane ring faces of the drum are not planar but have the oxygen atoms directed toward the interior of the cavity, relative to the Sn atoms. Thus, the interior of the cavity is defined by a crown of six oxygen atoms, in a

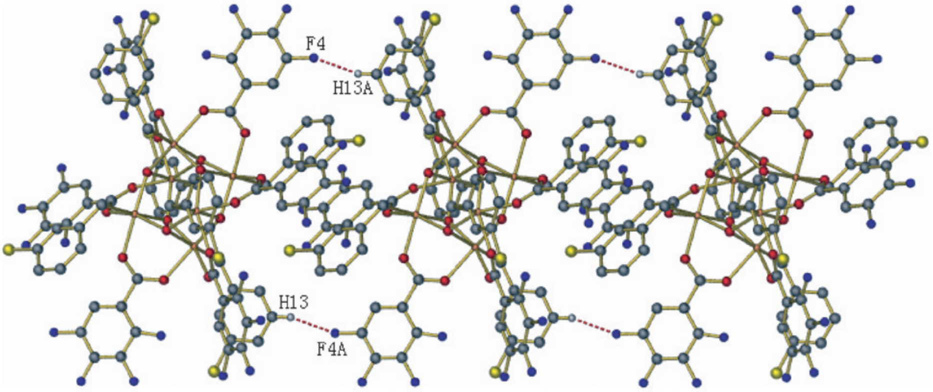


Figure 3. The supramolecular assembly showing a 1D infinite chain structure via intermolecular C–H···F hydrogen bonding.

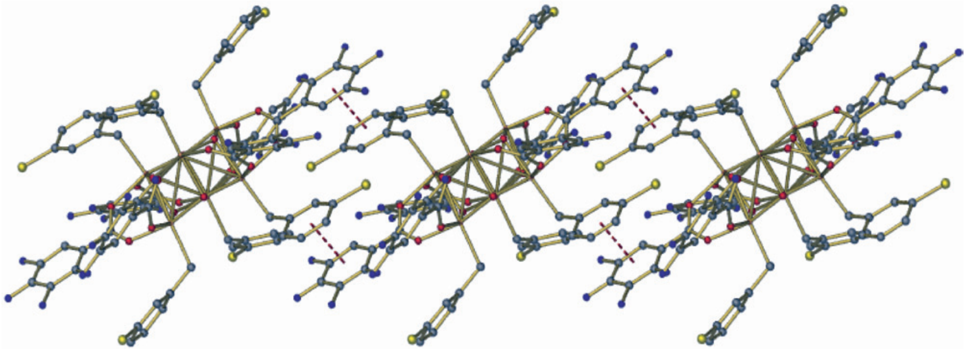


Figure 4. The supramolecular assembly showing a 1D infinite chain structure via intermolecular offset π–π stacking interaction.

trigonal-antiprismatic arrangement, and the entrance to the cavity is defined by three oxygen atoms from three μ3-atoms arranged as an equilateral triangle. The coordination geometry about each Sn atom is completed by a C atom of the phenyl 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.

In figure 3, the supramolecule exhibits a 1D infinite chain structure, formed by intermolecular C–H···F hydrogen bonding. The C–F group acts as a bifurcated acceptor. The H13A···F3 distance and the angle C13A–H13A···F3 are 2.512 Å and 161.49°, respectively. In figure 4 the distance of the phenyl rings centroids from each pair of neighboring molecules is 3.738 Å. The mean derivation angle of planes and the centroids are 4.7° and 68.5°, respectively, showing the presence of significant offset π–π stacking interactions. The molecules were further linked into a 2D framework via inter-chain π–π stacking interactions along the *b*-axis direction (figure 5).

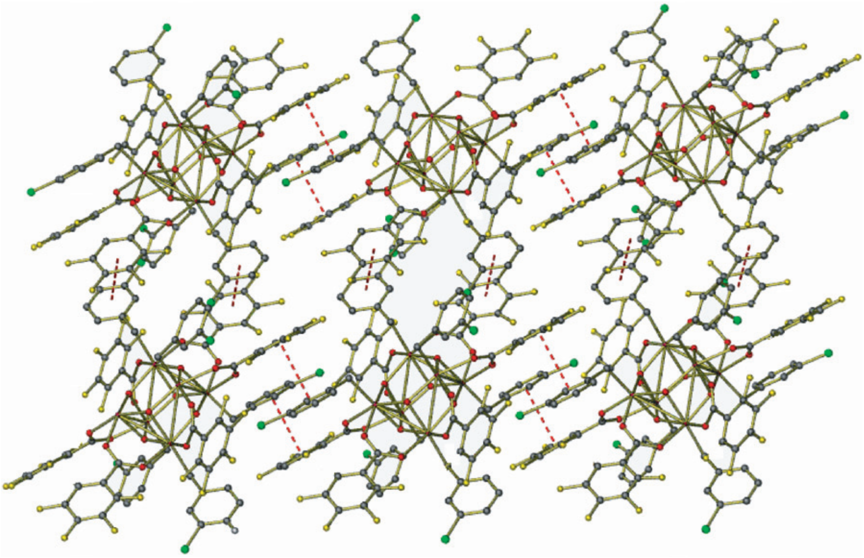


Figure 5. The supramolecular assembly showing a 2D framework via interchain offset π–π stacking interaction.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper **1** have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC: 615050 for **1**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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