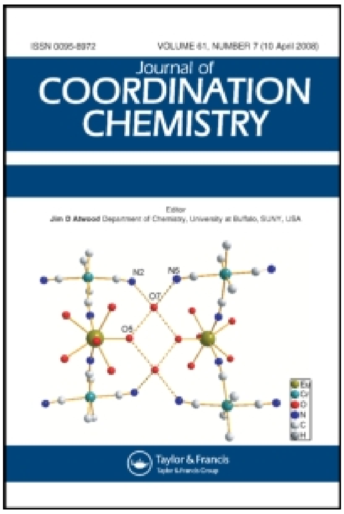


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Self-assembly of ionic triorganotin(IV) complexes of tetrafluorophthalic acid with a tetranuclear macrocyclic or polymeric structure: syntheses, characterization and crystal structures

Chunlin Ma[ab]; Yawen Han[a]; Rufen Zhang[a]
[a] Department of Chemistry, Liaocheng University, Liaocheng, P.R. China [b] Taishan University, Taian 271021, P.R. China

First published on: 25 September 2007

To cite this Article Ma, Chunlin , Han, Yawen and Zhang, Rufen(2008) 'Self-assembly of ionic triorganotin(IV) complexes of tetrafluorophthalic acid with a tetranuclear macrocyclic or polymeric structure: syntheses, characterization and crystal structures', Journal of Coordination Chemistry, 61: 8, 1200 — 1211, First published on: 25 September 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701509750

URL: http://dx.doi.org/10.1080/00958970701509750

Journal of Coordination Chemistry
Vol. 61, No. 8, 20 April 2008, 1200–1211

Taylor & Francis
Taylor & Francis Group

Self-assembly of ionic triorganotin(IV) complexes of tetrafluorophthalic acid with a tetranuclear macrocyclic or polymeric structure: syntheses, characterization and crystal structures

CHUNLIN MA*†‡, YAWEN HAN† and RUFEN ZHANG†

†Department of Chemistry, Liaocheng University, Liaocheng 252059, P.R. China
‡Taishan University, Taian 271021, P.R. China

(*Received 19 December 2006; revised 26 January 2007; in final form 31 January 2007*)

Four triorganotin(IV) complexes constructed from tetrafluorophthalic acid (H_2tfp) with a 1 : 1 : 1 molar ratio of H_2tfp: Et_3N: R_3SnCl gave two of type $\{[R_3Sn\ (tfp)].Et_3NH\}_4$ ($R = Me$ **1**, $R = n$-Bu **2**), and two of type $[R_3Sn\ (tfp).Et_3NH]_n$ ($R = PhCH_2$ **3**, Ph **4**). All the complexes are characterized by elemental, IR, ^1H, ^{13}C and ^{119}Sn NMR analyses. Complexes **1** and **4** were also confirmed by X-ray crystallography. Complex **1** is tetranuclear with a 28-membered $C_{16}O_8Sn_4$ macrocyclic ring system with a cavity. The supramolecular structure of **1** has been found to consist of a three-dimensional network built up by intermolecular N–H···O, C–H···O hydrogen bonds and C–F···F weak interactions. Complex **4** is an infinite polymeric structure. The salient feature of the supramolecular structure of **4** is that of a two-dimensional plane, in which intermolecular N–H···O and C–H···π hydrogen bonds are important.

Keywords: Triorganotin(IV); Tetrafluorophthalic acid; Macrocyclic ring; Polymeric structure

1. Introduction

Metal-directed self-assembly of organic ligands and metal ions or organometallic substances to well-defined structures can be applied for the generation of two different types of chemical substances, both having a range of applications. The first type is compounds with discrete molecular structures and frequently a more or less huge cavity [1] and second is materials with polymeric and microporous structures in the solid state [2]. The most common ligands used for construction of compounds with polymeric and microporous structures in the solid state are dicarboxylic [3] and tricarboxylic acids [4], which permit the preparation of neutral complexes with 2- or 3-fold charged metal ions, respectively, if they are reacted in a 1 : 1 stoichiometric ratio. More recently, noncovalent weak molecular forces capable of connecting these metallic subunits into looser and more intriguing supramolecular infrastructures (such as hydrogen bonds, van der Waals forces, nonbonded contacts, and π–π interactions) have been widely

---

*Corresponding author. Tel.: +86-635-8230660. Fax: +86-538-6715521. Email: macl@lcu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701509750

investigated in structural chemistry, structural biology, and the pharmaceutical sciences [5]. Although considerable advances have been made in the development of self-assembly chemistry, only a relatively small number of organometallic species with main group elements have so far been reported [6]. Among them, organotin(IV) complexes are attracting more and more attention not only for their wide industrial applications and biological activity [7], but also for their interesting and various architectures and topologies [8]. However, little is known with respect to the synthesis of discrete oligomeric macrocyclic complexes with these ligands [9–12]. In our previous work, we reported several organotin(IV) complexes with 1,3,5-benzenetricarboxylic [13], 5-nitroisophthalate [14] and pyridinedicarboxylates [15]. In continuation of our research in this area, we selected another fascinating ligand: tetrafluorophthalic acid (H_2tfp).

The ligand was chosen for the following reasons: (a) the ligand has two carboxyl groups so it should form strong covalent bonds with a triorganotin(IV) moiety, (b) the orientation of the two groups attached to the same aromatic ring should induce the formation of a polymeric chain or cyclooligomeric ring structure, (c) it presents a number of opportunities for creation of supramolecular arrangements through hydrogen bonds from a Lewis base site (O) and π–π interactions (face-to-face or edge-to-face) between the adjacent aromatic rings, (d) each ligand contains four C–F groups, an "organic fluorine" [16], that has potential opportunities for C–F$\cdots$X (X = F, H, π) weak interactions. (e) triorganotin(IV) ions have high affinity for hard donor atoms, and ligands containing oxygen atoms, especially carboxylic ligands, are usually employed in the architectures for polymeric complexes. Herein we report the syntheses and characterizations of four triorganotin(IV) complexes constructed from H_2tfp with a 1 : 1 : 1 molar ratio of H_2tfp: Et_3N: R_3SnCl, two tetranuclear macrocycle complexes of the type $\{[R_3Sn\ (tfp)]_2.Et_3NH\}_2$ (R = Me **1**, R = n-Bu **2**) and two infinite polymeric complexes of the type $[R_3Sn\ (tfp).Et_3NH]_n$ (R = $PhCH_2$ **3**, Ph **4**).

2. Experimental

2.1. *Materials and measurements*

Trimethyltin chloride, tri-n-butyltin chloride, triphenyltin chloride and tetrafluorophthalic acid (H_2tfp) are commercially available and were used without further purification. Tribenzyltin chloride was prepared by a standard method [17]. Melting points were obtained with Kofler micro-melting point apparatus and were uncorrected. Infrared-spectra are recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{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. The chemical shifts were reported in ppm in $CDCl_3$ solvent. Elemental analyses (C, H) were performed with a PE-2400II apparatus.

2.2. *Syntheses*

2.2.1. Synthesis of $\{[Me_3Sn\ (tfp)].Et_3NH\}_4$ 1. The reaction was carried out under nitrogen. Tetrafluorophthalic acid (0.238 g, 1.0 mmol) and triethylamine

(0.102 g, 1.0 mmol) were added to benzene, and the mixture was stirred for 10 min. Me_3SnCl (0.199 g, 1.0 mmol) was then added and the reaction mixture was stirred for 12 h at 40°C. After cooling to room temperature, the precipitate was filtered off. The solid was then recrystallized from hexane-dichloromethane to give colorless crystals. Yield: 73%. m.p.: 172–174°C. Anal. Calcd for $C_{68}H_{100}F_{16}N_4O_{16}Sn_4$: C 40.67, H 5.02, N 2.79. Found: C 40.31, H 4.89, N 2.52%. IR (KBr, cm^{-1}): ν(N–H) 3435.24, ν_{asym}(COO) 1642.38, 1607.36, ν_{sym} (COO) 1385.64, 1367.09, ν(Sn–C), 545.34, ν(Sn–O), 457.69. ^1H NMR ($CDCl_3$, ppm): δ 3.09 (m, 24H, –N–CH_2), 1.26 (m, 36H, CH_3), 0.9 (s, 36H, Sn–CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 7.7, 9.4 (Sn–CH_3), 52.8, 118.3 (C3, C6), 140.5 (C4, C5), 146.3 (C1, C2), 170.9 (C7, C8). ^{119}Sn NMR ($CDCl_3$, ppm): −112.8 ppm.

2.2.2. Synthesis of {[*n*-Bu_3Sn(tfp)].Et_3NH}$_4$ 2. The synthesis procedure was the same as **1**. The tetrafluorophthalic acid (0.238 g, 1.0 mmol), triethylamine (0.102 g, 1.0 mmol) and *n*-Bu_3SnCl (0.325 g, 1.0 mmol), reaction time 12 h, temperature 40°C. Recrystallized from hexane-dichloromethane. Colorless crystals were formed. Yield: 78%. m.p.: 175–177°C. Anal. Calcd for $C_{104}H_{172}F_{16}N_4O_{16}Sn_4$: C 49.70, H 6.90, N 2.23. Found: C 49.33, H 6.62, N 2.48%. IR (KBr, cm^{-1}): ν(N–H) 3433.89, ν_{asym}(COO) 1646.12, 1657.32, ν_{sym} (COO) 1392.35, 1362.21, ν(Sn–C), 548.64, ν(Sn–O), 452.83. ^1H NMR ($CDCl_3$, ppm): δ 2.98 (m, 24H, –N–CH_2), 1.28–1.76 (m, 72H, –$CH_2CH_2CH_2$–), 0.9–1.13 (s, 72H, –CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 7.9, 26.4, 27.6, 52.8, 121.6 (C3, C6), 141.9 (C4, C5), 147.2 (C1, C2), 171.5 (C7, C8). ^{119}Sn NMR ($CDCl_3$, ppm): −118.5.

2.2.3. Synthesis of [($PhCH_2$)$_3$Sn (tfp).Et_3NH]$_n$ 3. The synthesis procedure was the same as **1**. The tetrafluorophthalic acid (0.238 g, 1.0 mmol), triethylamine (0.102 g, 1.0 mmol) and ($PhCH_2$)$_3$SnCl (0.427 g, 1.0 mmol), reaction time 12 h, temperature 40°C. Recrystallized from hexane-dichloromethane. Colorless crystals were formed. Yield: 78%. m.p.: 160–162°C. Anal. Calcd for $C_{35}H_{37}F_4NO_4Sn$: C 60.55, H 4.63, N 4.15. Found: C 60.29, H 4.81, N 4.34%. IR (KBr, cm^{-1}): ν(N–H) 3435.81, ν_{asym}(COO) 1634.91, 1595.27, ν_{sym} (COO) 1376.94, 1330.84, ν(Sn–C), 555.68, ν(Sn–O), 454.76. ^1H NMR ($CDCl_3$, ppm): δ 3.19 (s, 6H, Ph–CH_2), 2.78 (m, 6H, –N–CH_2), 1.16 (m, 9H, CH_3), 7.48–7.81 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 7.6, 38.5, 52.6, 117.1, 119.2, 127.5, 129.4, 141.5, 142.8, 143.6, 144.6, 168.8 (C7, C8). ^{119}Sn NMR ($CDCl_3$, ppm): −122.6.

2.2.4. Synthesis of Ph_3Sn (tfp).Et_3NH 4. The procedure was the same as **1**. The tetrafluorophthalic acid (0.238 g, 1.0 mmol), triethylamine (0.102 g, 1.0 mmol) and Ph_3SnCl (0.385 g, 1.0 mmol), reaction time 12 h, temperature 40°C. Recrystallized from hexane-dichloromethane. Colorless crystals were formed. Yield: 78%. m.p.: 160–162°C. Anal. Calcd for $C_{32}H_{31}F_4NO_4Sn$: C 55.84, H 4.54, N 8.14. Found: C 55.58, H 4.79, N 8.36%. IR (KBr, cm^{-1}): ν(N–H) 3436.38, ν_{asym}(COO) 1636.80, 1594.17, ν_{sym} (COO) 1375.87, 1331.18, ν(Sn–C), 556.88, ν(Sn–O), 456.96. ^1H NMR ($CDCl_3$, ppm): δ 2.86 (m, 6H, –N–CH_2), 1.12 (m, 9H, CH_3), 7.40–7.79 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 7.9, 52.6, 117.9, 120.2, 128.9, 130.4, 134.5, 136.8, 137.2, 142.8, 173.8 (C7, C8). ^{119}Sn NMR ($CDCl_3$, ppm): −129.1.

Table 1. Crystal, data collection and structure refinement parameters for **1** and **4**.

Complexes	**1**	**4**
Empirical formula	$C_{68}H_{100}F_{16}N_4O_{16}Sn_4$	$C_{32}H_{31}F_4NO_4Sn$
Formula weight	2008.28	688.27
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	8.338(5)	25.951(11)
b (Å)	16.745(10)	14.364(6)
c (Å)	16.777(10)	19.628(8)
α (°)	98.132(10)	90
β (°)	100.145(9)	121.921(6)
γ (°)	98.934(9)	90
V (Å^3)	2243(2)	6210(5)
Z	1	8
D_{Calcd} (Mg m^{-3})	1.487	1.472
$F(000)$	1008	2784
μ(mm^{-1})	1.191	0.883
Crystal size (mm^{-3})	$0.45 \times 0.31 \times 0.26$	$0.48 \times 0.45 \times 0.33$
θ Range	2.50 to 25.01	1.78 to 25.01
Index ranges	$-9 \le h \le 9$, $-19 \le k \le 17$, $-19 \le l \le 16$	$-26 \le h \le 30$, $-17 \le k \le 17$, $-23 \le l \le 23$
Reflections collected	11813	16022
Unique reflections	7781	5458
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max/min transmission	0.7471/0.6164	0.7594/0.6766
Data, restraints, parameters	7781/1323/506	5458/190/388
GOF	1.003	1.007
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0527$, $wR_2 = 0.1147$	$R_1 = 0.0401$, $wR_2 = 0.1006$
R indices (all data)	$R_1 = 0.1077$, $wR_2 = 0.1404$	$R_1 = 0.0747$, $wR_2 = 0.1322$

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 semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS–97 and refined against F^2 by full matrix least-squares using SHELXL–97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations of **1** and **4** are listed in table 1.

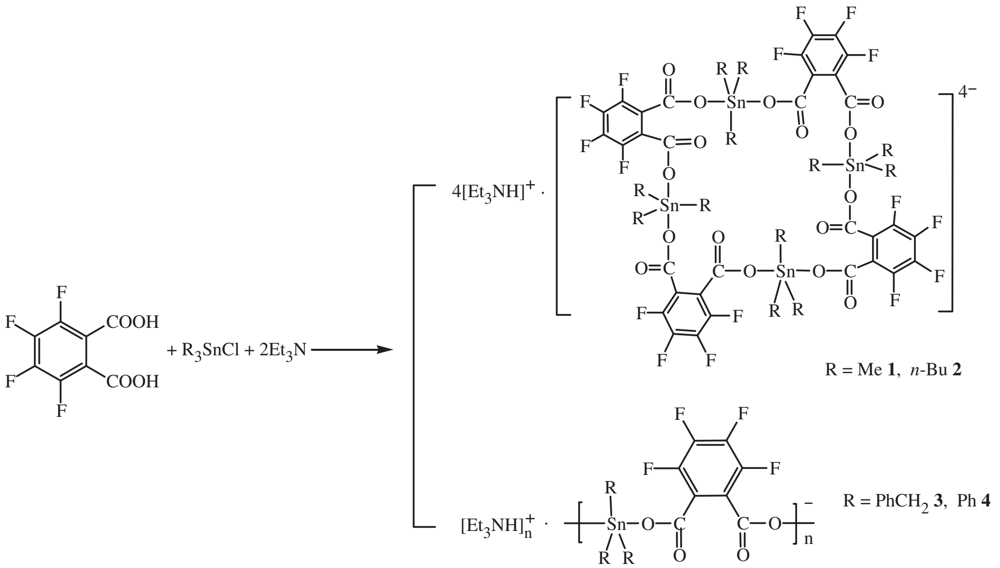
3. Results and discussion

3.1. *Syntheses aspect*

The synthesis procedure is shown in the scheme 1.

3.2. *Spectroscopic studies*

In the IR spectra, the stretching frequencies of interest are those associated with the acid COO, Sn–C, Sn–O and Sn–O-Sn groups. The spectra of all the complexes **1-4** show



Scheme 1. The synthesis procedure of complexes **1**–**4**.

some common features. The explicit feature in the infrared spectra of all complexes **1**–**4** is the absence of the band at 3422.20 cm^{-1}, which appears in the free ligand as the ν(O–H) vibration, indicating metal-ligand bond formation through this site. Strong absorption at 452–457 cm^{-1} in the respective spectra of the **1**–**4**, which is absent in the spectra of the free ligand, is assigned to the Sn–O stretching. The absorption in the region 545–557 cm^{-1} is assigned to the Sn–C stretch.

The ^{1}H NMR spectra show the expected integration and peak multiplicities. In the spectrum of the free ligand, the resonance observed at about $\delta = 11.0$ ppm, which is absent in the spectra of the complexes indicates the replacement of the carboxylic acid proton on complex formation. The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonances compared with the free ligand because of an electron density transfer from the ligand to the acceptor. The ^{119}Sn NMR shifts of complexes **1**–**4** show resonances -112.8, -118.5, -122.6 and -129.1 ppm, respectively. As reported in the literature [18], values of δ (^{119}Sn) in the ranges -210 to -400, -90 to -190 and 200 to -60 have been associated with six-, five- and four-coordinate tin centers, respectively. On this basis we can conclude that complexes **1**–**4** are five-coordinate. This is confirmed by the X-ray crystal structures of complexes **1** and **4**.

3.3. *Molecular structure*

3.3.1. Crystal structure of {[Me_3Sn (tfp)]$_2$.Et_3NH}$_2$ 1. The molecular structure and supramolecular structures of **1** are illustrated in figures 1–3. Selected bond lengths and angles are shown in table 2. Complex **1** is a tetranuclear complex and characterized by a 28-membered $C_{16}O_8Sn_4$ macrocyclic ring with a cavity, which can be evaluated by the Sn$\cdots$Sn transannular distances [Sn(1)$\cdots$Sn(1)# 10.966 Å and

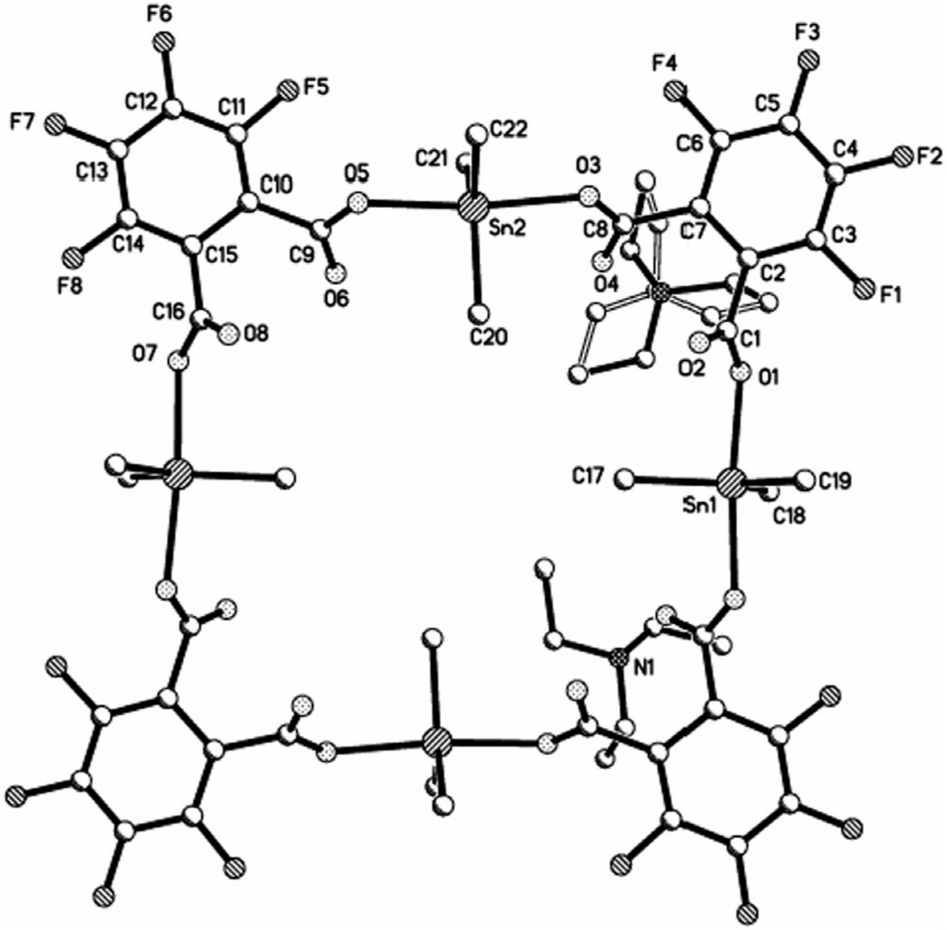


Figure 1. The molecular structure of **1**. Probability ellipsoids are drawn at the 50% level and the hydrogen atoms have been omitted for clarity.

Sn(2) $\cdots$ Sn(2#) 10.788 Å]. There are some differences from the tetranuclear structures in our previous work [13, 15]. One is that each carboxyl group is coordinated monodentate to the tin atom and the other O atom lies with above and below alternation to the phenyl plane; the other difference is the four tin atoms are not in the same plane. Sn(1) and Sn(1)#1 are in the same plane, but Sn(2) and Sn(2)#1 occupy another plane. This monodentate coordination and non-planarity give a number of opportunities to form intermolecular hydrogen bonds.

All the tin atoms possess the same ligand environments, with only minor differences in bond lengths and bond angles. Each tin atom in **1** is pentacoordinate (figure 1), bound to three methyl groups and two carboxylate oxygens. The geometry of each tin is distorted trigonal bipyramidal in which the apical positions are occupied by the oxygen atoms from two carboxylates. The angles O(1)–Sn(1)–O(7)#1 174.53(17)° and O(5)–Sn(2)–O(3) 170.08(18)° are close to linear. The sum of the angles subtended at the tin atom in the trigonal plane are all 360° for Sn(1) and Sn(2), so that the

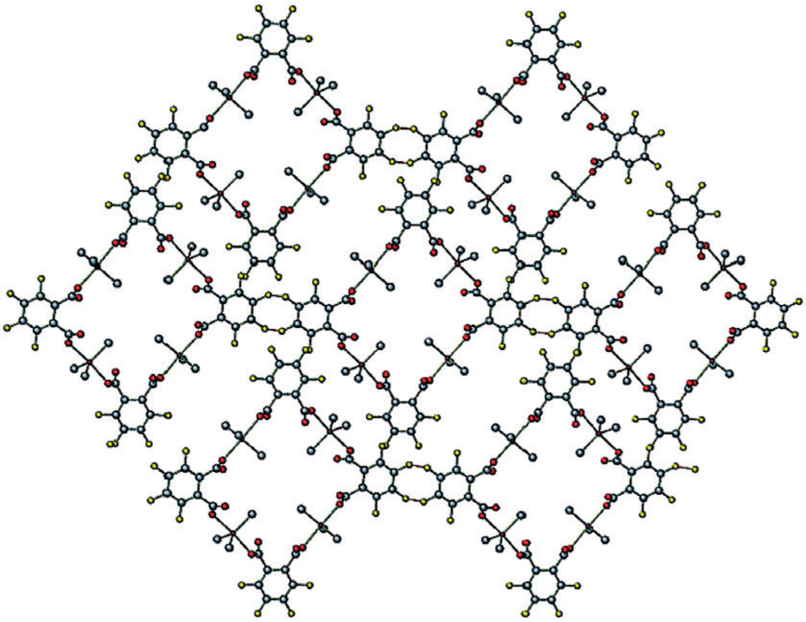


Figure 2. The two-dimensional network connected by F···F interactions in the *bc* plane.

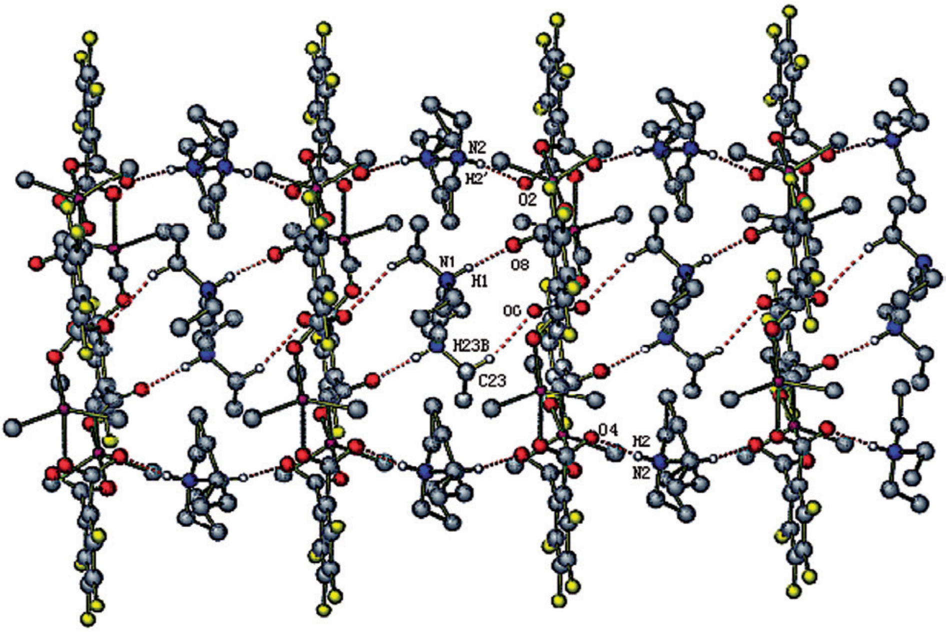


Figure 3. The tube formed by intermolecular N–H···O, C–H··· O hydrogen bonds along the *a* axis.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths			
Sn(1)–C(17)	2.116(7)	Sn(1)–C(19)	2.119(7)
Sn(1)–C(18)	2.121(6)	Sn(1)–O(1)	2.259(4)
Sn(1)–O(7)#1	2.262(5)	Sn(2)–C(20)	2.101(8)
Sn(2)–C(21)	2.116(8)	Sn(2)–C(22)	2.130(7)
Sn(2)–O(5)	2.250(4)	Sn(2)–O(3)	2.253(5)
Bond angles			
C(17)–Sn(1)–C(19)	121.8(3)	C(17)–Sn(1)–C(18)	120.2(3)
C(19)–Sn(1)–C(18)	118.0(3)	C(17)–Sn(1)–O(1)	93.1(3)
C(19)–Sn(1)–O(1)	90.7(2)	C(18)–Sn(1)–O(1)	86.5(2)
C(17)–Sn(1)–O(7)#1	92.3(3)	C(19)–Sn(1)–O(7)#1	85.8(2)
C(18)–Sn(1)–O(7)#1	91.4(2)	O(1)–Sn(1)–O(7)#1	174.53(17)
C(20)–Sn(2)–C(21)	122.7(4)	C(20)–Sn(2)–C(22)	118.0(4)
C(21)–Sn(2)–C(22)	119.3(4)	C(20)–Sn(2)–O(5)	93.6(3)
C(21)–Sn(2)–O(5)	91.9(2)	C(22)–Sn(2)–O(5)	84.9(2)
C(20)–Sn(2)–O(3)	92.2(3)	C(21)–Sn(2)–O(3)	91.7(2)
C(22)–Sn(2)–O(3)	85.3(2)	O(5)–Sn(2)–O(3)	170.08(18)

Symmetry code: 1 $-x$, $-y+1$, $-z+1$.

atoms Sn(1), C(17), C(18), and C(19) and Sn(2), C(20), C(21), and C(22) are in an ideal plane. The Sn–O distance (av 2.256 Å) is a litter shorter than another reported macrocycle structure (av 2.278 Å) [19]. The Sn–C distances [2.101(8)–2.130(7) Å] are equal within experimental error and close to the single-bond value for trigonal bipyramidal tin [20].

Analysis of the supramolecular infrastructure in the crystal lattice of **1** reveals that intermolecular N–H ⋯ O and C–H ⋯ O hydrogen bonds and C–F ⋯ F non-bonded interactions play important roles in supramolecular arrangements. The C–F ⋯ F interaction has been identified in previous studies [21]. While F ⋯ F interactions are ubiquitous their exact structural role is not clear, but it plays an important role in molecular self-asssembly [21]. In **1**, a series of parallel chains of rings connected by intermolecular C–F ⋯ F non-bonded interactions and spread along the *bc* plane (figure 2) have been found. Because the macrocycle is centrosymmetric (symmetry code: $-x$, $y+1$, $-z+1$), similar molecular chains have also been found along the [011] direction. This gives rise to an interesting and loose two-dimensional network in the *bc* plane. A series of intermolecular N–H ⋯ O and C–H ⋯ O hydrogen bonds have been found running along the *a* axis and the triethylamine as bridges interlink the parallel discrete molecular rings into a tube (figure 3). According to the above description, the loose two-dimensional network formed a third-dimensional network by intermolecular N–H ⋯ O and C–H ⋯ O hydrogen bonds. The values for the N–H ⋯ O, C–H ⋯ O hydrogen bonds and C–F ⋯ F non-bonded interactions are listed in table 3. The values for C–H ⋯ O hydrogen bonds suggest that it is equivalent to the C–H ⋯ O hydrogen bonds in $\{[(n\text{-Bu})_2\text{Sn}(2,5\text{-pdc})(\text{H}_2\text{O})]_3 \cdot 3\text{H}_2\text{O}.3\text{EtOH}\}_n$ (2.45 Å, 3.33 Å, 154°) [22], whilst the F ⋯ F distances are a little longer than the literature (2.80 Å) [20], but shorter than the sum of the van der Walls radii of the two fluorine atoms (2.94 Å) [18].

3.3.2. Crystal structure of $[\text{Ph}_3\text{Sn (tfp).Et}_3\text{NH}]_n$ 4.

The molecular structure, polymeric structure and supramolecular structure are illustrated in figures 4–6. Selected bond lengths and angles are list in table 4.

Table 3. Hydrogen bonds and weak interactions for **1** and **4**.

Complex	D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
1	N1–H1···O8#1	0.910	1.839	2.748	176.81
	N2–H2_a···O4	0.910	1.948	2.853	172.26
	N2'–H2'_b···O2#2	0.910	1.891	2.792	170.62
	C23–H23B···O6	0.970	2.492	3.404	156.73
	C4–F2···F8	1.322	2.911	3.111	85.29
	C13–F7···F6	1.322	2.906	3.524	106.2
4	N1–H1_a···O2	0.910	1.764	2.654	165.37
	C27–H27B···π	0.970	3.149	3.925	138.18

#1 $-x$, $-y+1$, $-z+1$, #2 $x+1$, y, z.

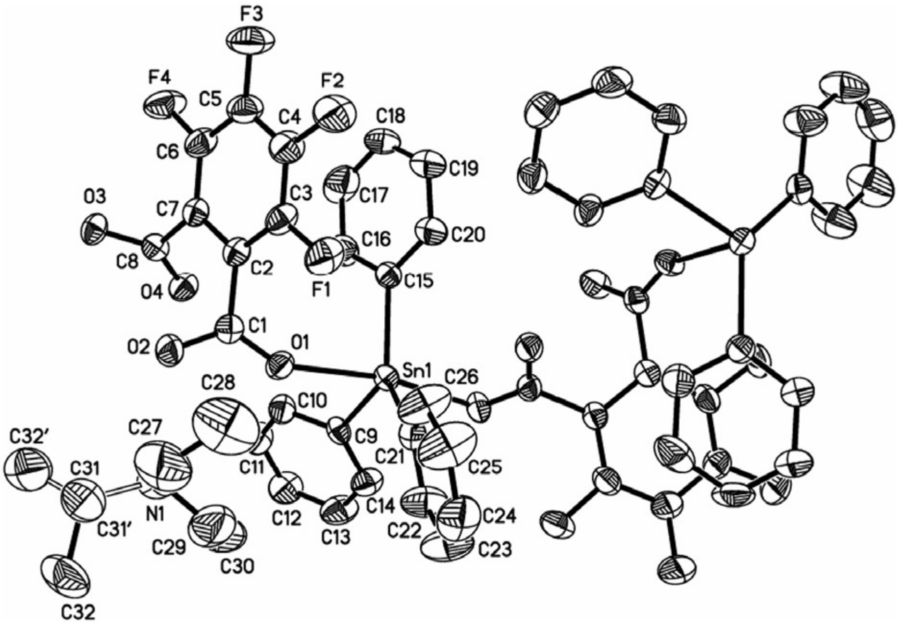


Figure 4. The molecular structure of **2**.

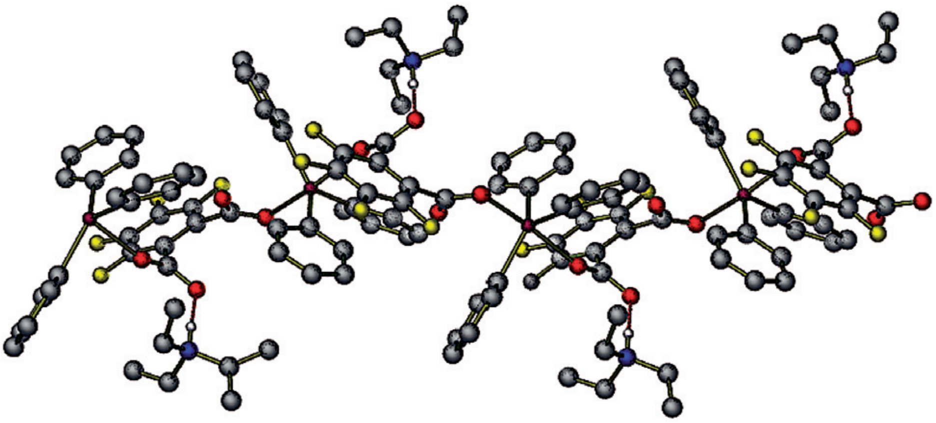


Figure 5. The polymeric structure of **4**.

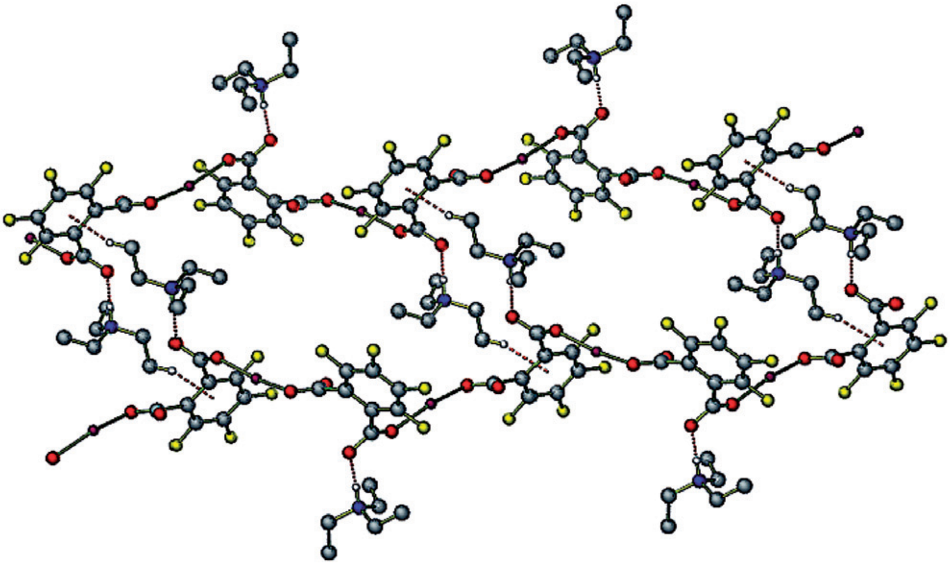


Figure 6. The 2D network connected by intermolecular C–H···O and C–H···π interactions. The hydrogen atoms and phenyl rings have been omitted for clarity.

Table 4. Selected bond lengths (Å) and angles (°) for **2**.

Bond lengths		Bond angles	
Sn(1)–C(15)	2.128(8)	C(15)–Sn(1)–C(21)	130.2(3)
Sn(1)–C(9)	2.148(7)	C(21)–Sn(1)–C(9)	116.6(3)
Sn(1)–C(21)	2.132(8)	C(21)–Sn(1)–O(3)#1	90.1(2)
Sn(1)–O(3)#1	2.189(5)	C(15)–Sn(1)–O(1)	89.8(2)
Sn(1)–O(1)	2.336(5)	C(9)–Sn(1)–O(1)	88.1(2)
O(2)–C(1)	1.244(9)	C(15)–Sn(1)–C(9)	112.5(3)
O(1)–C(1)	1.242(8)	C(15)–Sn(1)–O(3)#1	100.5(2)
O(3)–C(8)	1.278(9)	C(9)–Sn(1)–O(3)#1	87.3(2)
O(4)–C(8)	1.219(8)	C(21)–Sn(1)–O(1)	83.8(2)
		O(3)#1–Sn(1)–O(1)	169.69(18)

Symmetry code: 1 $-x+1/2$, $y+1/2$, $-z+1/2$.

The X-ray diffraction investigation of **4** shows that it is an infinite polymeric chain (figures 4 and 5). Each tetrafluorophthalic acid dianion bridges two tin centers via only one O atom of the monodentate carboxylate. As a result of the bidentate mode of coordination of the dicarboxylic acid, each Sn atom center is five-coordinate in a trigonal bipyramidal geometry with the O atoms occupying the axial sites [Sn(1)–O(1) 2.336(5), Sn(1)–O(3)#1 2.189(5) Å and O(3)#1–Sn(1)–O(1) 169.69(18)°]. The intramolecular Sn(1)···O(4) separations of 2.968 Å are considerably longer than the normal Sn–O covalent bond length, in the range of Sn···O distances of 2.61–3.02 Å which have been reported for intramolecular bonds [23, 24]. As oxygen atoms of the carboxylate are involved in a weak coordinative interaction with tin along one of the trigonal bipyramidal geometry faces, the structure distortion for the Sn (1) atom is best described as capped trigonal bipyramidal geometry. Despite the rather high estimated standard deviations in the C–O bond distances, a clear trend in these parameters may be discerned. It is different from the previous reported structure in that all C–O bond distances associated with the non-coordinating O atoms are significantly shorter than the other two C–O bond distances. As expect, the O(3)–C(8) [1.278(9) Å] bond distance is significantly shorter than the O(4)–C(8) [1.219(8) Å] bond distance. But the O(2)–C(1) [1.244(9) Å] and O(1)–C(1) [1.242(8) Å] distances are almost the same perhaps from the hydrogen bond between triethylamine and the non-coordinated O(2) atom.

Analysis of the supramolecular structure in the crystal lattice of **4** reveals that a series of N1–H1_a $\cdots$ O and C27–H27B $\cdots \pi$ (C9–C14) hydrogen bonds link these polymeric structures together running along the *c* axis, and thus **4** is a two-dimensional plane in the *bc* plane. The value for C–H $\cdots \pi$ (see table 4) is close to that found in $[\alpha\text{-NaiEtH}]^+[PF_6]^-$ (C-centroid = 4.090 Å, H-centroid = 3.149 Å, C–H-centroid = 167.088°) [25].

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article (**1** and **4**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-623896 and 623897. 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 www:http://www. ccdc.cam.ac.ck).

Acknowledgements

We thank the National Nature Science Foundation of China (20271025) for financial support.

References

[1] (a) B. Linton, A.D. Hamilton, *Chem. Rev.* **97**, 1669 (1997); (b) P.J. Stang, *Chem. Eur. J.*, **4**, 19 (1998); (c) D.L. Caulder, K.N. Raymond, *Acc. Chem. Res.*, **32**, 975 (1999); (d) G.F. Swiegers, T.J. Malefetse, *Chem. Rev.*, **1000**, 3483 (2000); (e) B.J. Holliday, C.A. Mirkin, *Angew. Chem., Int. Ed.*, **40**, 2022 (2001).

[2] (a) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, *Acc. Chem. Res.*, **31**, 474 (1998); (b) G. Férey, *Chem. Mater.*, **13**, 3084 (2001).

[3] (a) T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O.M. Yaghi, *J. Am. Chem. Soc.*, **121**, 1651 (1999); (b) H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Nature*, **402**, 276 (1999); (e) K. Seki, S. Takamizawa, W. Mori, *Chem. Lett.*, 332 (2000).

[4] (a) O.M. Yaghi, G. Li, H. Li, *Nature*, **378**, 703 (1995); (b) O.M. Yaghi, C.E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.*, **119**, 2861 (1997); (h) D. Sun, R. Cao. J. Weng, M. Hong, Y. Liang, *J. Chem. Soc., Dalton Trans.*, 291 (2002).

[5] (a) J.M. Lehn, Supramolecular Chemistry. *Concepts and Perspectives*, VCH, Weinheim, 139 (1995); (b) M. Nishio, *CrystEngComm.*, **6**, 130 (2004); (c) K. Biradha, *CrystEngComm.*, **5**, 74 (2003).

[6] (a) M.J. Plater, A.J. Roberts, J. Marr, E.E. Lachowski, R.A. Howie, *J.Chem. Soc. Dalton Trans.*, 797 (1998); (b) C.Y. Chen, P.P. Chu, K.H. Lii, *Chem. Commun.*, 1473 (1999); (c) G. Prabusankar, R. Murugavel, *Organometallics*, **23**, 5644 (2004); (d) C.L. Ma, F.L, D.Q. Wang, H.D. Yin, *J. Organomet. Chem.*, **667**, 5 (2003); (e) C.L. Ma, Q. Jiang, R.F. Zhang, D.Q. Wang, *Dalton Trans.*, 2975 (2003); (f) C.L. Ma, J.F. Sun, *Dalton Trans.*, 1 (2004); (g) C.L. Ma, Y.F. Han, R.F. Zhang, D.Q. Wang, *Dalton Trans.*, 1832 (2004).

[7] P. Yang, M.L. Guo. *Coord. Chem. Rev.*, **185**, 189 (1999).
[8] V. Chandrasekhar, S. Nagendran, V. Baskar. *Coord. Chem. Rev.*, **235**, 1 (2002).
[9] R. García-Zarracino, H. Höpfl. *J. Am. Chem. Soc.*, **127**, 3120 (2005).
[10] V. Chandrasekhar, V. Baskar, A. Steiner, S. Zacchini. *Organometallics*, **23**, 1390 (2004).
[11] R. García-Zarracino, J. Ramos-Quiñones, H. Höpfl. *Inorg. Chem.*, **42**, 3835 (2003).
[12] R. García-Zarracino, H. Höpfl. *Angew. Chem. Int. Edn.*, **43**, 1507 (2004).
[13] C.L. Ma, Y.F. Han, R.F. Zhang, D.Q. Wang. *Eur. J. Chem.*, **60**, 3024 (2005).
[14] C.L. Ma, J.K. Li, R.F. Zhang, D.Q. Wang. *Inorg. Chimi. Acta*, **359**, 2407 (2006).
[15] C.L. Ma, J.K. Li, R.F. Zhang, D.Q. Wang. *J. Organomet. Chem.*, **691**, 1713 (2006).
[16] V.R. Thalladi, H.C. Weiss, D. Bla1ser, R. Boese, A. Nangia, G.R. Desiraju. *J. Am. Chem. Soc.*, **120**, 8702 (1998).
[17] K.A. Koreschkow. *Chem. Ber.*, **66**, 1935 (1961).
[18] J. Holeĕek, M. Nadvornik, K. Handlir, A. Lycka. *J. Organomet. Chem.*, **315**, 299 (1986).
[19] C.L. Ma, Q.F. Zhang, R.F. Zhang, D.Q. Wang. *Chem. Eur. J.*, **12**, 420 (2006).
[20] A. Bondi. *J. Phys. Chem.*, **68**, 441 (1964).
[21] (a) V.R. Vangala, A. Nangia, V.M. Lynch *Chem. Commun.*, 1304 (2002); (b) J. Kowalik, D. Van Derveer, C. Clower, L.M. Tolbert, *Chem. Commun.*, 2007 (1999).
[22] R. García-Zarracino, H. Höpfl. *Angew. Chem. Int. Ed.*, **43**, 1507 (2004).
[23] K.C. Molly, T.G. Purcell, K. Quill, I.W. Nowell. *J. Organomet. Chem.*, **267**, 237 (1984).
[24] A.R. Forrester, S.J. Garden, R.A. Howie, J.L. Wardell. *J. Chem. Soc., Dalton Trans.*, 2615 (1992).
[25] J. Dinda, K. Bag, C. Sinha, G. Mostafa, T.H. Lu. *Polyhedron*, **22**, 1367 (2003).