Research Article

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Syntheses and crystal structures of ethyltin complexes with ferrocenecarboxylic acid

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Abstract: Three new ethyltin complexes containing ferrocenecarboxylate, $Et_2Sn(OC(O)Fc)_2$ (**1**), $[(Et_2SnOC(O)Fc)_2O]_2$ (**2**), and $[EtSn(O)OC(O)Fc]_6$ (**3**) (Fc = $C_5H_5FeC_5H_4$), have been synthesized by the reaction of diethyltin dichloride with ferrocenecarboxylic acid in the presence of potassium hydroxide and characterized by means of elemental analysis, FT-IR, NMR spectroscopy, and X-ray single crystal diffraction. In solid state, **1** is a weak dimer possessing a cyclic Sn_2O_2 unit formed by the intermolecular Sn···O interaction, and the tin atom has a distorted pentagonal bipyramid geometry. Compound **2** is a four-tin nuclear diethyltin complex with a ladder framework, and each tin atom adopts a distorted trigonal bipyramidal configuration in which two oxygen atoms occupy the axial positions. Compound **3** is a hexa-tin nuclear monoethyltin complex having a drum-shaped structure, and each of the tin atoms possesses a distorted octahedral geometry. The ferrocene units are attached to the tin atoms through the monodentate or bidentate coordinated carboxylates.

Keywords: organotin, ferrocenecarboxylic acid, crystal structure

1 Introduction

Organotins are a kind of widely used main group metal compound, which have more applications than the organic derivatives of any other metal (Davies et al., 2008). They have been used as stabilizers for polyvinyl chloride, ionophores in sensors, insecticides, fungicides, organic synthesis reagents, reaction catalysts, and so on (Davies et al., 2008). Recent studies have shown that organotin carboxylates exhibit high cytotoxic activity and good prospects in cancer therapy (Bantia et al., 2019; Chen et al., 2020; Shang et al., 2011). Ferrocene is an organic transition metal compound, and its derivatives have been used as catalysts for asymmetric reactions and functional materials including photosensitizer, nonlinear optical material, membrane electrode, and smoke agent, and exhibited a variety of biological properties (Braga and Silva, 2013; Cunningham et al., 2020; Xiao et al., 2020). To synthesize organotin carboxylates containing ferrocenyl group is a valuable choice for broadening the use of ferrocene derivatives and searching for highly efficient and low toxic organotin anticancer drugs. Some organotin carboxylates containing ferrocenyl were synthesized in succession and also showed good *in vitro* anticancer activity. Some examples are as follows: $R_3SnOC(O)Fc$ (R = Me, *n*-Bu, Ph, Cy), $R_2Sn(OC(O)Fc)_2$ (R = Me, *n*-Bu, Ph), $[(n\text{-}Bu_2SnOC(O)Fc)_2O]_2$, and $[RSn(O)OC(O)Fc]_6$ (R = *n*-Bu, $PhCH_2$) (Chandrasekhar et al., 2000, 2005a; Chandrasekhar and Thirumoorthi, 2008; Dong et al., 2014; Zhu et al., 2011). Up to now, the reaction of diethyltin dichloride with ferrocenecarboxylic acid (FcCOOH) has not been reported in the literature. In order to continue to expand the chemistry of the ferrocene–organotin compounds, we synthesized three ethyltin ferrocenecarboxylates, $Et_2Sn(OC(O)Fc)_2$ (**1**), $[(Et_2SnOC(O)Fc)_2O]_2$ (**2**), and $[EtSn(O)OC(O)Fc]_6$ (**3**), and determined their crystal structures (Scheme 1).

2 Results and discussion

2.1 Synthesis

In the presence of potassium hydroxide, diethyltin dichloride reacted with ferrocenecarboxylic acid (FcCOOH) to produce compounds **1–3** (Scheme 1). The nature of the product is related to the stoichiometry of the reaction as well as the reaction temperature (solvent reflux temperature). Under

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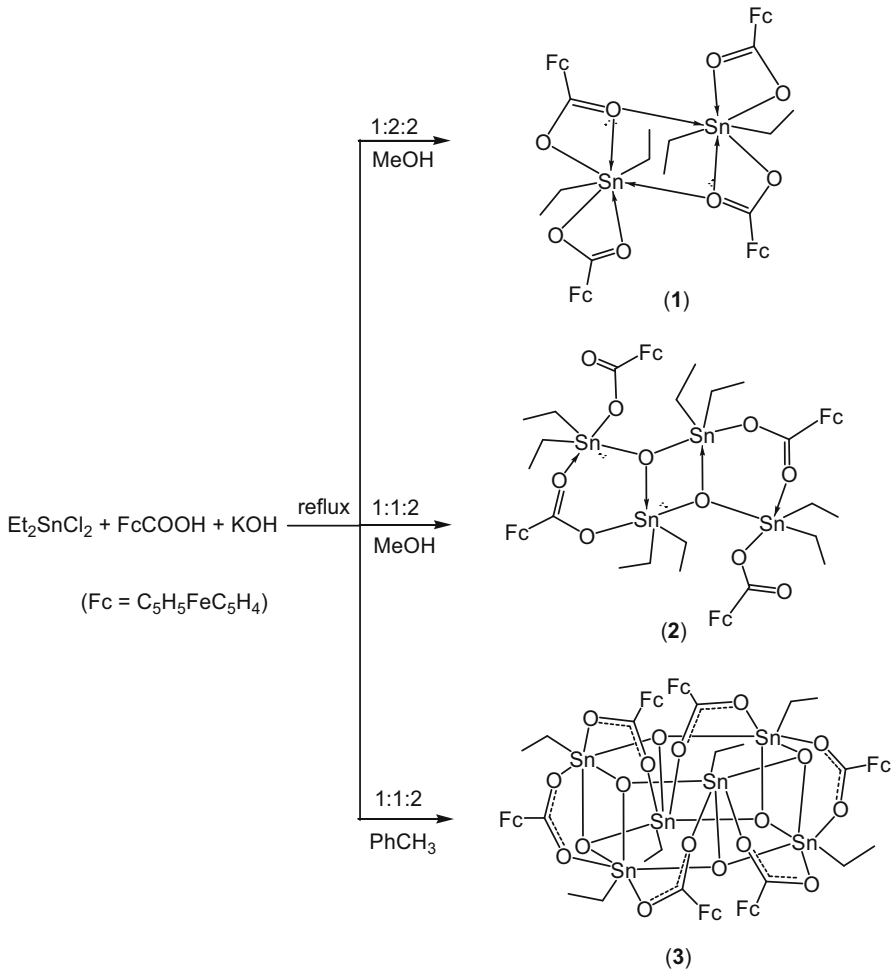

Scheme 1: Synthesis of compounds **1–3**.

reflux conditions, diethyltin bis(ferrocenecarboxylate) (**1**) and bis[oxo-bis(diethyltin ferrocenecarboxylate)] (**2**) were formed in good yields (isolated yield >80%) in a methanolic solution, and hexakis(oxo-ethyltin ferrocenecarboxylate) (**3**) was isolated in a low yield (31%) in toluene. Compound **3** was formed by a Sn–C bond cleavage of diethyltin in the reaction process. A wide range of Sn–C bonds are cleaved by carboxylic acids leading to Sn–O bond formation (Chandrasekhar et al., 2005b). Although the Sn–C bond cleavage is a common reaction in phenyl-, benzyl-, allyl-, and methyl-tin compounds, very few examples of Sn–ethyl and Sn–butyl bonds cleavage are known. The cleavage of the alkyl-tin bond may involve an S_E2 mechanism (Chandrasekhar et al., 2005b; Davies, 2004; Gopal et al., 2014; Shankar et al., 2010). Compounds **1–3** are orange red crystals and stable in air. **1** and **2** are soluble in benzene, methanol, chloroform, and acetone, while **3** is not (Chandrasekhar and Thirumoorthi, 2008; Mairychova et al., 2014).

2.2 Spectroscopic analysis

Ferrocenecarboxylic acid displays a broad band at 3,200–2,500 cm^{-1} and a strong band at 1,658 cm^{-1}, which are assigned to the ν(OH) and ν_{as}(COO) stretching vibrations, respectively. In **1–3**, the absorption band at 3,200–2,500 cm^{-1} disappears, and the ν_s(COO) and ν_{as}(COO) bands shift considerably, indicating the formation of the ethyltin complexes by the carboxyl (COO) oxygen atom coordination to tin (Shang et al., 2011; Zhu et al., 2011). The difference between the ν_{as}(COO) and ν_s(COO) of carboxylate moiety, $\Delta\nu$(COO), has been used to determine its bidentate or monodentate coordination mode (Chen et al., 2020; Deacon and Phillips, 1980; Shang et al., 2011; Tian et al., 2020). In **1–3**, FcCOO is bidentate, which is evidenced by the small $\Delta\nu$(COO) value (179 cm^{-1} for **1**, 160 cm^{-1} for **2**, 192 cm^{-1} for **3**). In **2**, there is also a carboxyl group of monodentate coordination to tin because of a large $\Delta\nu$(COO) value of 285 cm^{-1} (Tian et al., 2020;

Wang et al., 2010), which is in agreement with the below X-ray structure of **2**.

The ^{1}H NMR spectra of **1–3** exhibit the expected integration and multiplicities of the resonance absorption peaks. The chemical shifts of the protons of Cp-rings (C_5H_5 and C_5H_4) appear at ~4.20, 4.40, and 4.80 ppm, respectively. The ^{13}C chemical shift of carboxyl carbon in **1** and **2** is 182.1 and 177.6 ppm, respectively, and the resonance absorptions of carbon atoms of Cp-rings appear in the region of 69–75 ppm. In **2**, the $(CH_3CH_2)_2Sn$ moiety displays two sets of ^{1}H and ^{13}C NMR signals (see Section 4), which is consistent with the NMR spectra of the other diorganooxotin carboxylates $[(R_2SnOOCR')_2O]_2$, such as $[(n\text{-}Bu_2SnOOCFc)_2O]_2$ (Tao and Xiao, 1996) and $[(Et_2SnOOCC_6H_3N_2S)_2O]_2$ (Wang et al., 2010). The ^{119}Sn chemical shifts primarily depend on the coordination number and the type of the donor atoms bonded to tin atom (Davies, 2004; Holecek et al., 1986). Compound **1** displays a single ^{119}Sn resonance at –149.5 ppm, suggesting that the tin atom in **1** is five-coordinated in the $CDCl_3$ solution (Holecek et al., 1986). In solution, there may be the following situations: one of the two carboxyl groups of the ligands is monodentate coordination, and the other is bidentate chelation coordination (Chandrasekhar and Thirumoorthi, 2007). In compound **2**, a pair of ^{119}Sn resonances is observed at –189.0 and –199.2 ppm due to the presence of endo- and exo-cyclic tin atoms. These values are comparable with those reported in other dimeric distannoxanes (Chandrasekhar et al., 2005a; Wang et al., 2010; Zhu et al., 2011) and correspond to a five-coordinated or weakly six-coordinated tin atom (Holecek et al., 1986). Due to the poor solubility of **3**, the ^{13}C and ^{119}Sn NMR cannot be obtained for identification.

2.3 Structure analysis

The molecular structures of **1–3** are presented in Figures 1–3, respectively. The selected bond lengths and bond angles are shown in Table 1. The structure of compound **1** is similar to that of the reported diorganotin dicarboxylates, such as $n\text{-}Bu_2Sn(OOCFc)_2$ (Chandrasekhar et al., 2005a), $Me_2Sn(OOCFc)_2$ (Chandrasekhar and Thirumoorthi, 2008), and $Et_2Sn(OOCCH_2C_6H_4Cl\text{-}4)_2$ (Muhammad et al., 2014), and the central tin atom is also six-coordinated and adopts a skew-trapezoidal geometry. Two ferrocenecarboxylate ligands are chelated to a tin atom with anisobidentate coordination mode, which leads to two different Sn–O bonds (short Sn(1)–O(1) (2.114(3) Å) and Sn(1)–O(3) (2.115(2) Å), and long Sn(1)–O(2) (2.499(3) Å) and Sn(1)–O(4) (2.550(3) Å)). The O(2)–Sn(1)–O(4) (168.33(9)°) and C(1)–Sn(1)–C(3) (152.03(17)°) angles are larger than those found in its analogues $n\text{-}Bu_2Sn(OOCFc)_2$ (166.93(2)° and 145.0(3)°)

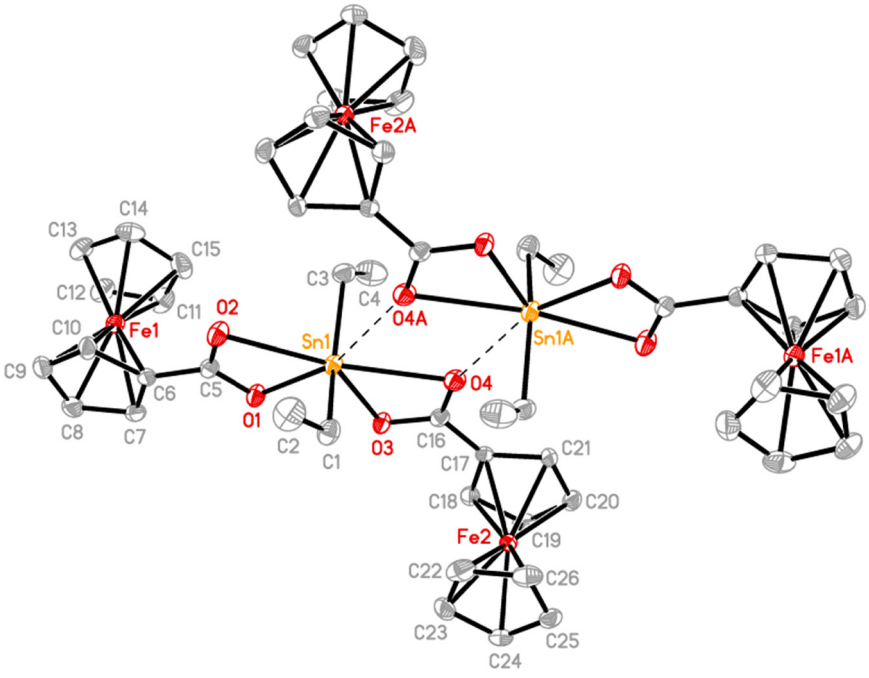

Figure 1: The molecular structure of **1**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry code *A*: 1/2 – *x*, 1/2 – *y*, 1 – *z*.

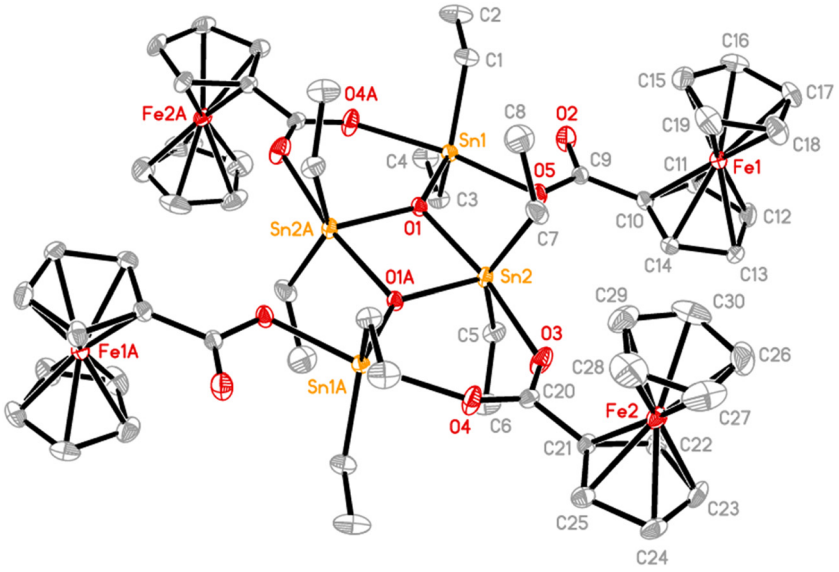

Figure 2: The molecular structure of **2**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry code *A*: 2 – *x*, 1 – *y*, 1 – *z*.

(Chandrasekhar et al., 2005a) and $Me_2Sn(OOCFc)_2$ (165.6(1)° and 146.9(4)°) (Chandrasekhar and Thirumoorthi, 2008) due to the intermolecular Sn(1)···O(4)$^{\#1}$ (2.851(3) Å) interaction (symmetry code #1: 1/2 – *x*, 1/2 – *y*, 1 – *z*) between Sn(1) atom and the carbonyl O(4) atom of the neighboring ligand. This Sn···O separation (2.851(3) Å) is much shorter than the sum of the van der Waals radii of the two atoms (3.73 Å), but longer than the O→Sn coordination bond (~2.50 Å) (Hu et al., 2003). If the intermolecular contact was considered, the coordination geometry of tin atom can be described as a distorted pentagonal bipyramid, and a centrosymmetric dimer with a four-membered Sn_2O_2 ring complex **1** was formed (Figure 1).

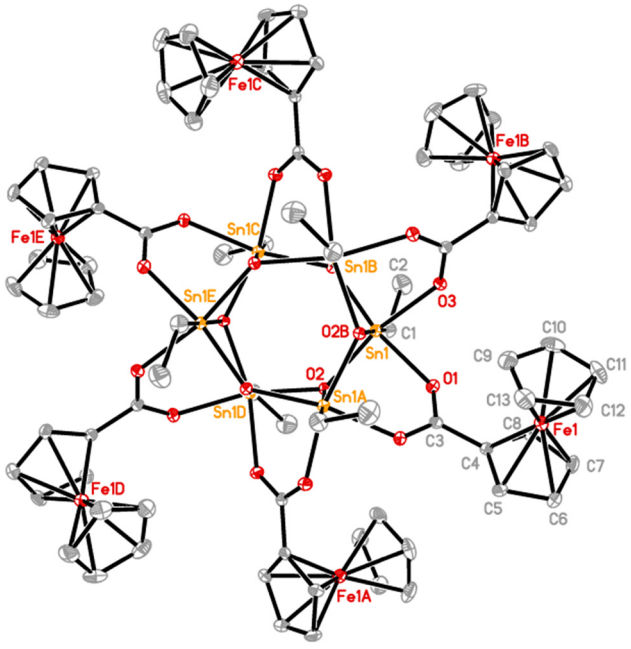

Figure 3: The molecular structure of **3**. Ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Symmetry code *A*: –*y*, *x* – *y*, *z*; B: *x* – *y*, *x*, 2 – *z*.

Complex **2** exists as a centrosymmetric dimer (Figure 2) and possesses a ladder framework built up around the planar cyclic Sn_2O_2 unit (Sn(2)O(1)Sn(2)$^{\#2}$O(1)$^{\#2}$, #2: 2 – *x*, 1 – *y*, 1 – *z*) in which Sn(2)–O(1) and Sn(2)–O(1)$^{\#2}$ distances are 2.157(3) and 2.033(2) Å, respectively. On both sides of the central Sn_2O_2 ring, there are two six-membered rings formed by the bridging bidentate coordination of ferrocenecarboxylate (O(3)C(20)O(4)) to the endo- and exo-cyclic tin atoms (Sn(2) and Sn(1)). The Sn(2)–O(3) and Sn(1)$^{\#2}$–O(4) bond lengths are 2.238(3) and 2.243(3) Å, respectively. The other ferrocenecarboxylate (O(2)C(9)O(5)) acts as a monodentate ligand to coordinate to exocyclic Sn(1) atom with a Sn(1)–O(5) distance of 2.164(3) Å. Each of the tin atoms is five-coordinated and has a distorted trigonal bipyramidal configuration in which two oxygen atoms occupy the axial positions. The axial O(5)–Sn(1)–O(4)$^{\#2}$ and O(1)–Sn(2)–O(3) angles are 168.89(11)° and 170.23(10)°, respectively. Distortions from the ideal geometry are partly due to the intramolecular Sn···O interactions (Sn(1)···O(2) 2.785(3) Å and Sn(2)···O(5) 2.752(3) Å), which make the C(1)–Sn(1)–C(3) and C(5)–Sn(1)–C(7) angles on the equatorial plane expand to 134.68(17)° and (145.0(2))°, respectively, from the ideal value of 120°. The

Table 1: Selected bond lengths (Å) and angles (°) for **1–3**

1			
Sn(1)–O(1)	2.114(3)	Sn(1)–C(3)	2.102(4)
Sn(1)–O(2)	2.499(3)	C(5)–O(1)	1.288(4)
Sn(1)–O(3)	2.115(2)	C(5)–O(2)	1.232(5)
Sn(1)–O(4)	2.550(3)	C(16)–O(3)	1.281(4)
Sn(1)–O(4)$^{\#1}$	2.851(3)	C(16)–O(4)	1.240(4)
Sn(1)–C(1)	2.114(4)	C(3)–Sn(1)–O(1)	99.22(14)
C(3)–Sn(1)–C(1)	152.03(17)	C(1)–Sn(1)–O(2)	88.43(13)
O(1)–Sn(1)–C(1)	100.77(15)	O(3)–Sn(1)–O(2)	137.14(9)
C(3)–Sn(1)–O(3)	104.24(14)	C(3)–Sn(1)–O(4)	90.18(14)
O(1)–Sn(1)–O(3)	81.39(10)	O(1)–Sn(1)–O(4)	135.84(9)
C(1)–Sn(1)–O(3)	97.96(14)	C(1)–Sn(1)–O(4)	88.99(13)
C(3)–Sn(1)–O(2)	86.78(14)	O(3)–Sn(1)–O(4)	54.53(9)
O(1)–Sn(1)–O(2)	55.83(9)	O(2)–Sn(1)–O(4)	168.33(9)
2			
Sn(1)–O(1)	2.020(2)	Sn(2)–O(1)	2.157(3)
Sn(1)–O(5)	2.164(3)	Sn(2)–O(3)	2.238(3)
Sn(1)–O(4)$^{\#2}$	2.243(3)	Sn(2)–O(1)$^{\#2}$	2.033(2)
Sn(1)–C(1)	2.115(4)	Sn(2)–C(5)	2.107(4)
Sn(1)–C(3)	2.115(4)	Sn(2)–C(7)	2.125(5)
C(9)–O(2)	1.219(5)	C(20)–O(3)	1.243(5)
C(9)–O(5)	1.292(5)	C(20)–O(4)	1.247(5)
O(1)–Sn(1)–C(3)	112.30(14)	C(5)–Sn(2)–C(7)	145.0(2)
O(1)–Sn(1)–C(1)	111.67(15)	C(5)–Sn(2)–O(1)	95.98(15)
C(3)–Sn(1)–C(1)	134.68(17)	C(7)–Sn(2)–O(1)	98.51(15)
O(1)–Sn(1)–O(5)	79.86(10)	C(5)–Sn(2)–O(3)	86.65(16)
C(3)–Sn(1)–O(5)	98.85(15)	C(7)–Sn(2)–O(3)	84.41(16)
C(1)–Sn(1)–O(5)	99.01(16)	O(1)–Sn(2)–O(3)	170.23(10)
O(1)–Sn(1)–O(4)$^{\#2}$	89.05(11)	O(1)$^{\#2}$–Sn(2)–O(3)	93.83(11)
C(3)–Sn(1)–O(4)$^{\#2}$	84.69(16)	O(1)$^{\#2}$–Sn(2)–O(1)	76.40(10)
C(1)–Sn(1)–O(4)$^{\#2}$	85.62(17)	O(1)$^{\#2}$–Sn(2)–C(5)	107.92(15)
O(5)–Sn(1)–O(4)$^{\#2}$	168.89(11)	O(1)$^{\#2}$–Sn(2)–C(7)	106.42(17)
3			
Sn(1)–C(1)	2.122(7)	Sn(1)–O(2)$^{\#4}$	2.094(4)
Sn(1)–O(1)	2.144(4)	Sn(1)–O(3)	2.164(4)
Sn(1)–O(2)	2.087(3)	C(3)–O(1)	1.271(7)
Sn(1)–O(2)$^{\#3}$	2.079(3)	C(3)–O(3)	1.261(7)
O(2)–Sn(1)–O(2)$^{\#3}$	103.78(19)	O(1)–Sn(1)–O(2)$^{\#4}$	88.71(16)
O(2)–Sn(1)–O(2)$^{\#4}$	77.60(16)	C(1)–Sn(1)–O(1)	92.5(2)
O(2)$^{\#3}$–Sn(1)–O(2)$^{\#4}$	77.78(16)	O(2)$^{\#4}$–Sn(1)–O(3)	86.33(15)
C(1)–Sn(1)–O(2)	99.5(2)	O(2)–Sn(1)–O(3)	160.17(16)
C(1)–Sn(1)–O(2)$^{\#3}$	101.7(2)	O(2)$^{\#4}$–Sn(1)–O(3)	88.18(15)
C(1)–Sn(1)–O(2)$^{\#4}$	176.8(2)	C(1)–Sn(1)–O(3)	94.9(2)
O(1)–Sn(1)–O(2)$^{\#3}$	160.53(16)	O(1)–Sn(1)–O(3)	79.22(16)
O(1)–Sn(1)–O(2)	86.62(15)		

Symmetry code: $^{\#1}1/2 - x, 1/2 - y, 1 - z$; $^{\#2}\ 2 - x, 1 - y, 1 - z$; $^{\#3}\ -y, x - y, z$; $^{\#4}\ x - y, x, 2 - z$.

structural features of **2** are consistent with Type I among the structures of $[(R_2SnOOCR')_2O]_2$ summarized by Tiekink (1991). In the molecular structure of **2**, the central Sn_2O_2 ring, carboxylates, and substituted cyclopentadiene rings are essentially in the same plane, and the maximum deviation (O(3)) from the mean plane is 0.248(3) Å. The ferrocenyls are located in the upper and lower sides of this plane, respectively.

Compound **3** crystallizes in a trigonal space group $R\bar{3}$ and is a hexa-tin nuclear organotin complex possessing the drum-shaped structure. Although many of such drum compounds have been reported (Basu Baul et al., 2017; Chandrasekhar et al., 2007; Shang et al., 2011; Tiekink, 1991; Xiao et al., 2019), to our knowledge, **3** is the first example of structural determined hexameric ethyloxotin carboxylate $[EtSn(O)OC(O)R]_6$. In the central stannoxane Sn_6O_6 core, two six-membered Sn_3O_3 drum faces display a chair-like conformation with the two different Sn–O bonds (Sn(1)–O(2) 2.087(3) Å and Sn(1)–O(2)$^{\#3}$ 2.079(3) Å (#3: $-y, x - y, z$)), and six four-membered Sn_2O_2 rings in the sides of the drum present butterfly-like conformation with the three different Sn(1)–O(2), Sn(1)–O(2)$^{\#3}$, and Sn(1)–O(2)$^{\#4}$ (#4: $x - y, x, 2 - z$) (2.094(4) Å) bonds. Each O(2) atom as a tridentate ligand links three tin centers, and ferrocenecarboxylate bridges two tin centers by anisobidentate coordination mode with the Sn–O distances of 2.144(4) and 2.164(4) Å. Each tin atom is six-coordinated and adopts a distorted octahedral geometry. The three bond angles in the *trans* position of octahedron are C(1)–Sn(1)–O(2)$^{\#4}$ 176.8(2)°, O(1)–Sn(1)–O(2)$^{\#3}$ 160.53(16)°, and O(2)–Sn(1)–O(3) 160.17(16)°, respectively. These structural parameters in **3** are similar to those of $[RSn(O)OCOFc]_6$ (R = *n*-Bu, $PhCH_2$) reported by Chandrasekhar and coauthors (Chandrasekhar et al., 2000; Chandrasekhar and Thirumoorthi, 2008), indicating that R bound to tin has little effect on the drum structure.

3 Conclusions

Under different conditions, diethyltin dichloride reacts with ferrocenecarboxylic acid to produce compounds **1–3**. In solid state, **1**, **2**, and **3** are weak dimers possessing a cyclic Sn_2O_2 unit, a four-tin nuclear diethyltin complex with a ladder framework, and a hexa-tin nuclear monoethyltin complex having a drum-shaped structure, respectively. The ferrocenyl moieties are appended to the tin atoms by the monodentate or bidentate coordinated carboxylate ligands.

Experimental

All chemical reagents and solvents were purchased from Sinopharm Chemical Reagents Company (Shanghai, China) and used directly without further purification. The instruments used for the characterization of compounds are as follows: a Perkin Elmer 2400 Series II elemental analyzer (carbon and hydrogen analyses), a Nicolet 470 FT-IR spectrophotometer (IR spectra), and a Bruker Avance III HD500 NMR spectrometer (^{1}H and ^{13}C NMR spectra).

Synthesis of diethyltin bis (ferrocenecarboxylate) (1)

Ferrocenecarboxylic acid (0.460 g, 2 mmol), potassium hydroxide (0.112 g, 2 mmol), and methanol (25 mL) were added into a 50 mL round bottom flask and stirred for 10 min. Diethyltin dichloride (0.248 g, 1 mmol) was added, and then the reaction mixture was refluxed for 4 h. The orange red solution was cooled to room temperature and filtered. The solvent was removed from the filtrate by a rotary evaporator. The orange yellow solid obtained was recrystallized from the mixed solvents of *n*-hexane and trichloromethane (2:1, volume ratio). Yield 0.52 g (82%), m.p. 164.5–165.3°C. Anal. found: C, 49.08; H, 4.32. Calcd for $C_{26}H_{28}Fe_2O_4Sn$: C, 49.19; H, 4.45%. Selected IR (KBr) cm^{-1}: 1,564 [ν_{as}(COO)], 1,545, 1,470, 1,385 [ν_s(COO)], 1,335, 1,181. ^{1}H NMR ($CDCl_3$, δ): 4.89 (t, J = 2.0 Hz, 2H, 2CH), 4.44 (t, J = 2.0 Hz, 2H, 2CH), 4.25 (s, 5H, C_5H_5), 1.74 (q, J = 8.0 Hz, 2H, CH_2), 1.44 (t, J = 8.0 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 182.11 (COO), 71.61, 71.03, 70.70 (C_5H_4), 69.89 (C_5H_5), 17.86 (CH_2), 9.18 (CH_3). ^{119}Sn NMR ($CDCl_3$, δ): −149.5.

Synthesis of bis[oxo-bis(diethyltin ferrocenecarboxylate)] (2)

The preparation process of compound **2** is the same as that of compound **1**. Ferrocenecarboxylic acid (0.230 g, 1 mmol), potassium hydroxide (0.112 g, 2 mmol), and diethyltin dichloride (0.248 g, 1 mmol) were used. The crude product was recrystallized from cyclohexane–benzene (2:1, volume ratio), and 0.36 g orange crystal was obtained in 87% yield. M.p. 183.0–184.0°C. Anal. found: C, 43.59; H, 4.58. Calcd for $C_{60}H_{76}Fe_4O_{10}Sn_4$: C, 43.53; H, 4.63%. Selected IR (KBr) cm^{-1}: 1,606 [ν_{as}(COO)], 1,550 [ν_{as}(COO)], 1,476, 1,390 [ν_s(COO)], 1,321 [ν_s(COO)], 1,172. ^{1}H

Table 2: Crystallographic and refinement data of **1–3**

Compound	1	2	3
Empirical formula	$C_{26}H_{28}Fe_2O_4Sn$	$C_{60}H_{76}Fe_4O_{10}Sn_4$	$C_{78}H_{84}Fe_6O_{18}Sn_6$
Formula weight	634.87	1,655.36	2,356.69
Crystal system	Monoclinic	Triclinic	Trigonal
Space group	$C2/c$	$P\bar{1}$	$R\bar{3}$
a (Å)	25.808(4)	10.4492(14)	24.3910(18)
b (Å)	10.3801(17)	11.5889(15)	24.3910(18)
c (Å)	20.476(3)	13.7870(18)	11.8608(18)
α (°)	90	100.453(2)	90
β (°)	117.389(2)	102.373(1)	90
γ (°)	90	103.892(2)	120
Volume (Å^3)	4,870.6(14)	1,534.6(3)	6,110.9(13)
Z	8	1	3
D_c (g·cm^{-3})	1.732	1.791	1.921
μ (mm^{-1})	2.223	2.572	2.903
F(000)	2,544	820	3,456
Crystal size (mm)	0.42 × 0.36 × 0.24	0.16 × 0.12 × 0.10	0.16 × 0.10 × 0.06
θ range (°)	1.8–26.0	1.6–26.0	2.0 to 25.5
Tot. reflections	18,379	11,980	12,667
Uniq. reflections (R_{int})	4,772 (0.047)	5,940 (0.026)	2,534 (0.063)
Reflections ($I > 2\sigma(I)$)	3,805	4,988	1,893
GOF on F^2	1.015	1.017	1.015
R indices [$I > 2\sigma(I)$]	R = 0.037, wR = 0.079	R = 0.035, R = 0.079	R = 0.046, wR = 0.101
R indices (all data)	R = 0.051, wR = 0.084	R = 0.044, wR = 0.084	R = 0.066, wR = 0.109
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e·Å^{-3})	−0.347, 0.704	−0.487, 0.962	−0.457, 1.427

NMR ($CDCl_3$, δ): 4.76 (s, 2H, 2CH), 4.40 (s, 2H, 2CH), 4.25 (s, 5H, C_5H_5), 1.68 (q, J = 7.5 Hz, 2H, CH_2), 1.58 (q, J = 7.5 Hz, 2H, CH_2), 1.49 (t, J = 7.5 Hz, 3H, CH_3), 1.44 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 177.60 (COO), 75.05, 70.73, 70.58 (C_5H_4), 69.54 (C_5H_5), 22.28, 20.86 (CH_2), 10.27, 9.98 (CH_3). ^{119}Sn NMR ($CDCl_3$, δ): –189.0, –199.2.

Synthesis of hexakis(oxo-ethyltin ferrocenecarboxylate) (3)

Ferrocenecarboxylic acid (0.230 g, 1 mmol), potassium hydroxide (0.112 g, 2 mmol), and diethyltin dichloride (0.248 g, 1 mmol) were mixed and ground in an agate mortar, then transferred to a 50 mL round bottom flask. After 20 mL of toluene was added, the mixture was refluxed under stirring for 3 h. The brown solution was filtered when hot, and the filtrate was left to slow evaporation at room temperature. Orange crystals were formed from the solution after 3 days. Yield 0.12 g (31%), m.p. >200°C. Anal. found: C, 39.66; H, 3.48. Calcd for $C_{78}H_{84}Fe_6O_{18}Sn_6$: C, 39.75; H, 3.59%. Selected IR (KBr) cm^{-1}: 1,574 [ν_{as}(COO)], 1,542, 1,469, 1,382 [ν_s(COO)], 1,329, 1,177. ^{1}H NMR (DMSO-d_6, δ): 4.71 (s, 2H, 2CH), 4.43 (t, J = 2.0 Hz, 2H, 2CH), 4.25 (s, 5H, C_5H_5), 1.43 (q, J = 7.5 Hz, 2H, CH_2), 1.23 (t, J = 7.5 Hz, 3H, CH_3).

X-ray crystallography

The orange-red single crystals of **1** and **2** were obtained from cyclohexane–benzene (1:1, v/v), and compound **3** was obtained by slow evaporation of toluene solution, respectively. Diffraction data were collected at room temperature on a Bruker Smart Apex imaging-plate area detector fitted with graphite monochromatized Mo-Kα radiation (0.71073 Å). Structure solution and refinement were completed using SHELXS-97 (Sheldrick, 2008) and SHELXL-2018 (Sheldrick, 2015), respectively. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions. In **2**, the ethyl group was disordered over two positions, and the site occupancy was refined to 0.736(16):0.264(16). Crystal data and refinement parameters are summarized in Table 2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre with supplementary publication numbers CCDC 2094054–2094056.

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Data availability statement: Crystallographic data (CCDC 2094054–2094056) of this article can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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