

Structural chemistry of organotin ferrocenecarboxylic esters I. Synthesis and spectroscopic studies on dialkyltin esters of ferrocenecarboxylic acid FcCOOH and 1,1'-ferrocenedicarboxylic acid Fc(COOH)₂

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Abstract

Dibutyltin and dioctyltin esters of ferrocenecarboxylic acid and dibutyltin ester of 1,1'-ferrocenedicarboxylic acid have been synthesized and characterized by IR and NMR (¹H, ¹³C, ¹¹⁹Sn) spectral data. Spectroscopic data suggest that the esters of ferrocenecarboxylic acid adopt an oxygen-bridge dimer structure mode. The structure features four anisobidentate bridging carboxylate ligands. The ester of 1,1'-ferrocenedicarboxylic acid is five-coordinate monomer in solution.

Keywords: Tin; Ferrocene; Carboxylate; Nuclear magnetic resonance; Infrared spectroscopy; Polyoxometallate

1. Introduction

Organotin carboxylic esters have biocidal activity [1–3]. Many dialkyltin(IV) carboxylic esters are useful thermal stabilizers for PVC plastic [4,5]. In recent years more and more reports of the synthesis and structural elucidation of various organotin carboxylic esters have appeared, revealing various new structural possibilities. In particular, diorganotin(IV) esters attract considerable interest in structural studies because there are many possible bonding modes between the oxygen atoms in the carboxyl group (COO) and the tin atom. Spectroscopic data, such as IR, NMR and ¹¹⁹Sn-Mössbauer spectroscopy, X-ray crystallography, etc., tell us that, in general, the 1:1 (tin:ligand) complexes show the dicarboxylate tetraorganodistannoxane structure mode and the 1:2 (tin:ligand) complexes have six-coordinate trans-skew octahedral structure [6–13]. A special structure will be possible if the acid has special structure [9]. We have studied a series of dialkyltin esters of ferrocenecarboxylic acids. In this paper we describe the synthesis and IR and NMR spectroscopic characterization of three dialkyltin esters of ferrocenecarboxylic

acid or 1,1'-ferrocenedicarboxylic acid and their presumable structures.

2. Experimental section

2.1. Materials and methods

All reactants were reagent grade. Ferrocene and CH₃COCl were pretreated before use by sublimating and distilling respectively.

Elemental analyses (C and H) were performed on a Carlo Erba 1106 elemental analyzer. Infrared spectra were recorded as KBr discs on a Perkin-Elmer FT-IR 1600 spectrophotometer. The ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on a JEOL FX90Q spectrometer. The chemical shifts were determined relative to external standard (CH₃)₄Si for ¹H, to internal standard solvents for ¹³C, and to external standard (n-Bu)₄Sn (–6.6 ppm) for ¹¹⁹Sn NMR respectively.

2.2. Synthesis

Firstly, FcCOOH and Fc(COOH)₂ (Fc = ferrocenyl group) were synthesized from ferrocene [14–16]. Then, the compound {[(n-Bu)₂SnOOCFc₂O]₂ (1) or {[(n-

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$(\text{Oct})_2\text{SnOOCFe}_2\text{O})_2$ (**2**) was prepared by refluxing FeCOOH and dibutyltin oxide or dioctyltin oxide in 1:1 molar ratio in a dry benzene ethanol mixture (3:1, v/v) with azeotropic removal of water [13]. The mixture was filtered and the solvent removed. The compound $(n\text{-Bu})_2\text{Sn}(\text{OOC})_2\text{Fc}$ (**3**) was prepared with $\text{Fe}(\text{COOH})_2$ using the same procedure. All compounds were obtained as solids.

3. Results and discussion

3.1. Physical properties

Physical data for compounds **1–3** are listed in Table 1. The obtained compound **1** is a needle crystal and **2, 3** are power states. Their solubilities in many organic solvents, such as CCl_4 , CHCl_3 , C_6H_6 , $(\text{CH}_3)_2\text{CO}$ and petroleum ether, are very poor.

Table 1
Physical data for **1, 2** and **3**

Compound	Colour	M.p. (°C)	Component (%) ^a	
			C	H
$\{[(n\text{-Bu})_2\text{SnOOCFe}]_2\text{O}\}_2$ (1)	orange	129–130	47.90 (48.52)	5.89 (5.74)
$\{[(n\text{-Oct})_2\text{SnOOCFe}]_2\text{O}\}_2$ (2)	orange	85–87	55.27 (55.71)	7.82 (7.40)
$(n\text{-Bu})_2\text{Sn}(\text{OOC})_2\text{Fc}$ (3)	orange	> 70 (decomp.)	47.36 (47.57)	5.23 (5.19)

^a Theoretical value in brackets.

Table 2
Selected IR data^a (470–4000 cm^{-1}) for **1–3** and their parent acids

Compound	$\nu_{\text{as}}(\text{COO})$	$\Delta\nu_1$ ^b	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu_2$ ^c	$\nu(\text{Sn-O-Sn})$	$\nu(\text{Sn-O})$
FeCOOH	1657 s	—	1232 s	—	—	—
$\text{Fe}(\text{COOH})_2$	1675 s	—	1300 s	—	—	—
$\{[(n\text{-Bu})_2\text{SnOOCFe}]_2\text{O}\}_2$ (1)	1543 s	114	1326 s	-94	639 s	—
$\{[(n\text{-Oct})_2\text{SnOOCFe}]_2\text{O}\}_2$ (2)	1547 s	110	1323 s	-91	636 s	—
$(n\text{-Bu})_2\text{Sn}(\text{OOC})_2\text{Fc}$ (3)	1555 s	120	1337 s	-37	—	684 m

^a Measured as KBr discs: s, strong; m, medium.

^b $\Delta\nu_1 = \nu_{\text{as}}(\text{COO})[\text{acid}] - \nu_{\text{as}}(\text{COO})[\text{ester}]$.

^c $\Delta\nu_2 = \nu_{\text{s}}(\text{COO})[\text{acid}] - \nu_{\text{s}}(\text{COO})[\text{ester}]$.

Table 3
¹H NMR (δ , ppm) data for **1–3** and their parent acids

Compound	δ (ppm)				
	Ferrocenyl ^a			Sn-R ^b	
	<i>o</i>	<i>m</i>	un	$(\text{CH}_2)_n$	CH_3
FeCOOH	4.70 s	4.37 s	4.19 s	—	—
$\text{Fe}(\text{COOH})_2$	4.70 s	4.39 s	—	—	—
$\{[(n\text{-Bu})_2\text{SnOOCFe}]_2\text{O}\}_2$ (1)	4.69 s	4.32 s	4.16 s	1.1–2.2 mb	0.99 t
$\{[(n\text{-Oct})_2\text{SnOOCFe}]_2\text{O}\}_2$ (2)	4.72 s	4.36 s	4.22 s	1.1–2.4 mb	0.84 t
$(n\text{-Bu})_2\text{Sn}(\text{OOC})_2\text{Fc}$ (3)	4.84	4.35 s	—	1.2–2.4 mb	1.00 t

^a *o*, *ortho*-H in substituted Cp ring; *m*, *meta*-H; un, H in unsubstituted Cp ring; s, singlet; q, quartet.

^b $n = 3, 7$ for Bu, Oct; mb, multiplet broad; t, triplet.

3.2. Analysis of spectroscopies

3.2.1. IR

IR data for the three compounds with their parent acids together are listed in Table 2.

A broad O–H absorption band at 2500–3500 cm^{-1} which shows the feature of the hydrogen bonded acids is absent in the IR spectra of **1–3**, implying the deprotonation and coordination of the carboxyl groups, and the additional strong absorptions of alkyl groups prove the existence of alkyltin groups. However, the bands of the ferrocenyl group apparently do not change from the hydrogen bonded acid to the esters **1–3**.

Table 2 indicates that **1–3** and their parent acids have strong bands of $\nu(\text{COO})_{\text{as}}$ and $\nu(\text{COO})_{\text{s}}$. $\nu_{\text{as}}(\text{ester})$ is 100 cm^{-1} lower than $\nu_{\text{as}}(\text{acid})$, and $\nu_{\text{s}}(\text{ester})$ is higher than $\nu_{\text{s}}(\text{acid})$. The IR data show the fall in $\nu(\text{COO})_{\text{s}}$ into the range of carboxylic metal salts. This generally denotes the formation of a bidentate carboxylic complex

Table 4
¹³C NMR (δ, ppm) data for 1–3

Compound	δ (ppm)					
	COO	Ferrocenyl ^a			Sn-R ^b	
		s	o	m		un
[(n-Bu) ₂ SnOOCFc] ₂ O ₂ (1)	176.62	74.95	70.44	69.23	27.02(1–3), 13.84(4)	
[(n-Oct) ₂ SnOOCFc] ₂ O ₂ (2)	176.42	75.12	70.44	69.23	25.63(1), 34.37(2), 29.27(3–5), 31.87(6), 22.65(7), 14.10(8)	
(n-Bu) ₂ Sn(OOC) ₂ Fc (3)	180.18	75.12	72.44	71.50	—	26.26(1–3), 13.58(4)

^a s, quaternary carbon; o, m, ortho, meta carbon in substituted Cp ring; un, carbons in unsubstituted Cp ring.

^b CH₂–CH₂–CH₂–CH₃, for R = n-Bu; CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₃, for R = n-Oct.

[10,11]. For 1 and 2, an anisodentate, chelating carboxylic group is inferred, while for 3 a bidentate bridging carboxylic group. The strong band in the range 630–650 cm⁻¹ for 1 and 2 is attributed to ν(Sn–O–Sn), which indicates the existence of an oxygen-bridge[–Sn–O–]₂ skeleton [13]. However, in 3 there is a middle intensity absorption at 684 cm⁻¹ designated as a vibration about the Sn–O bond.

3.2.2. NMR

The chemical shift data from ¹H and ¹³C NMR spectra are given in Tables 3 and 4.

In the ¹H NMR spectra of 1–3, the proton peaks of carboxylic acids disappear and the alkyl group peak appears, which presents a triplet peak and broad multiplet peak owing to the terminal CH₃ of the long alkyl chain and the (CH₂)_n chain respectively. From the integration curves, it is easily seen that the three compounds are expected to be 1:1 compounds. In addition to the results of elemental analysis data (see Table 1), all of these data are consistent with the suggested molecular formation and are in agreement with data for other organotin esters [11,17].

In ¹H NMR spectra, the proton peaks of the ferrocenyl group in 1 and 2 are similar to those in their parent acids, but that in 3 becomes a more complex spin system with AA'BB' coupling peaks, indicating that the peaks of o-Hs and m-Hs are close when the carboxyl groups bond with the tin atom (see Table 5). Because two carboxyl groups, which belong to each of two Cp rings in the same ferrocenyl group, simultaneously coordinate to one tin atom, the interaction between the tin atom and the Cp rings increases through two carboxyl groups. Furthermore, the introduction of the alkyltin chain from the same side of the ferrocene leads to a

Table 5

The difference in chemical shifts between o-H and m-H in the substituted Cp ring for 1–3 and their parent acids [Δ(δ_{o-H} – δ_{m-H}), ppm]

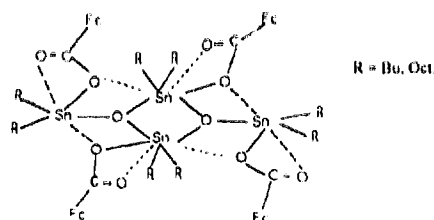
FcCOOH	1	2	Fc(COOH) ₂	3
0.33	0.37	0.36	0.31	0.25

tension between two Cp rings, breaking their parallel, so the ferrocenyl group would be a wedge-shaped structure, like many ferrocenophanes [18].

In ¹³C NMR spectra of 1–3, only one COO group peak is observed, implying that there is only one type of COO group, or some unresolvable COO groups or COO groups in dynamic equilibrium in solution at room temperature.

¹¹⁹Sn NMR spectroscopic data are very useful for determining the coordination number of tin, its molecular geometry and stereochemistry. In the dialkyltin esters, four-coordinate tin has δ(¹¹⁹Sn) values ranging from about +200 to –60 ppm, five-coordinate tin from –90 to –190 ppm, and six-coordinate tin from –210 to –400 ppm [11,19,20].

The ¹¹⁹Sn NMR data for compounds 1 and 2 (see Table 6) indicate that two signals appear at –213 to –223 ppm, showing that there are two non-equivalent tin atoms in one molecule, and the δ(¹¹⁹Sn) values suggest that the coordination number of both tin atoms should be six. So, the structures of the compounds 1 and 2 are deduced to be as below:



In the structure, all of the carboxylate ligands are

Table 6

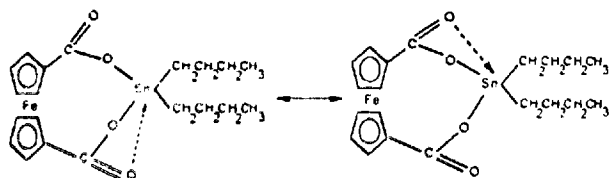
¹¹⁹Sn NMR (δ, ppm) data^a for 1–3

Compound	δ (ppm)
[(n-Bu) ₂ SnOOCFc] ₂ O ₂ (1)	–217.3, –222.3
[(n-Oct) ₂ SnOOCFc] ₂ O ₂ (2)	–213.8, –227.7
(n-Bu) ₂ Sn(OOC) ₂ Fc (3)	–148.8

^a Relative to (n-Bu)₄¹¹⁹Sn = –6.6 ppm.

anisobidentate and the two tin atoms are in pseudo-six-coordination.

As to compound **3**, the ^{119}Sn NMR spectrum shows that there is only one type of five-coordinate tin atom. This supports the structure in dynamic equilibrium shown below:



There are Sn–O σ bonds and one weak Sn \cdots O coordination bond. Because of the special spatial structure of ferrocene, the two carboxylic groups cannot coordinate equivalently to the tin atom.

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