Structural chemistry of organotin ferrocenecarboxylic esters II. The crystal structure of dibutyltin ferrocenecarboxylate oxide

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Abstract

The X-ray analysis confirms dibutyltin ferrocenecarboxylate oxide (IA) adopts an oxo-bridging dimer structure mode with four anisobidentate bridging carboxylate groups as ligands and has a planar tortuous ladder geometry. IA crystallizes in the monoclinic space group $P2_1/c$ with $a = 1403.2(3)$ pm, $b = 1309.3(3)$ pm, $c = 2786.0(6)$ pm, $\beta = 102.49(3)°$ and $Z = 2$. The structure was refined to $R = 0.0508$ and $WR = 0.0564$.

Keywords: Tin; Ferrocene; Carboxylate; Oxide; Crystal structure; X-ray difraction

1. Introduction

The compounds dibutyltin ferrocenecarboxylate oxide (IA) and dioctyltin ferrocenecarboxylate oxide (IB) have been synthesized and their possible structures deduced [1]. However, the final exact structure must be determined by mono-crystal X-ray diffraction. IA can be obtained as a crystal, but IB as a solid powder or like glass. This report represents the results of the X-ray diffraction of IA and detailed analyses of its structure.

2. Experimental section

The red-orange crystal for IA, grown from benzene–ethanol solution, degrades fairly rapidly when exposed to ambient conditions; this behavior is due to loss of benzene of solvation. So, a crystal of IA (0.15 mm × 0.20 mm × 0.50 mm) sealed by epoxy glue was used for the X-ray study.

Intensity data for compound IA were performed on a Rigaku AFC6S diffractometer fitted with highly oriented graphite monochromated Mo Kα radiation, $\lambda = 70.073$ pm at ambient temperature of 296 K. 8816 independent reflections $(+h, +k, \pm l)$ were collected using the ω scan mode for $4° \leq 2\theta \leq 50°$. During collection

of the diffraction data, the standard reflection intensity decreased by 10%, so the diffraction intensities were corrected using a decay coefficient, Lp factor and absorption.

The structure was solved by direct methods using the Siemens SHELXTL PLUS (VMS) system and refined by a full-matrix least squares procedure. All Fe, Sn, O atoms were refined with anisotropic temperature factors. Owing to the flexibility of the butyl chains and easy loss of benzene molecules from the crystal, all of the C atoms were refined with isotropic thermal parameters. The positions of the H atoms were according to theoretical calculations, without least squares correction. The semiempirical method was made for absorption corrections.

3. Results

Crystal data for IA uniquely determined that empirical formula $C_{100}H_{132}Fe_4O_{10}Sn_4 \cdot 4C_6H_6$ or $\{[FeC_{10}H_9-COOSn(C_4H_9)_2O]_2 \cdot 4C_6H_6;$ formula weight 2192.2; space group $P2_1/c$; unit cell dimensions $a = 1403.2(3)$ pm, $b = 1309.3(3)$ pm, $c = 2786.0(6)$ pm, $\alpha = 90°$, $\beta = 102.49(3)°$, $\gamma = 90°$; volume $= 4998(2) \times 10^3$ nm^3; $Z = 2$; density (calc.) 1.457 Mg m^{-3}; $F(000) = 2232$; numbers of observed reflections 2305 $(I \geq 4.0\sigma(i))$; min./max. transmission faction =
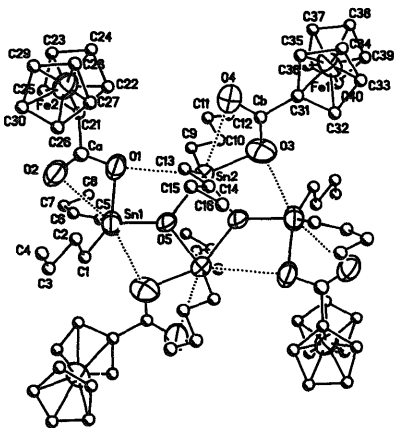
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Fig. 1. ORTEP plot of **IA**. The intermediate and the longer Sn–O interactions (271.0, 274.0, 288.8, 312.2 pm) are shown as dashed lines. The benzene molecules and hydrogen atoms are omitted for the purpose of clarity.

0.8606/1.0000; final agreement factors (obs. data) $R = 5.08\%$, $WR = 5.64\%$.

The atom labeling scheme for **IA** is given in the ORTEP plot of Fig. 1 and in its unit cell plot of Fig. 2, while atomic coordinates are given in Table 1. The selected bond lengths and angles are given in Table 2.

4. Discussion

The compound **IA** has a dimeric formulation. **IA** exists as a planar tortuous ladder structure which con-

tains pseudo-six and pseudo-seven coordinated tin atoms. **IA** can be viewed as a centrosymmetric dimer, where one half of the molecule comprises the crystallographic asymmetric unit and other half is generated by an inversion center located at the center of the oxo-bridging parallel quadrilateral $(SnO)_2$ ring. **IA** has a ladder structure rather than a staircase arrangement, as evidenced by the coplanarity of the atoms comprising the fused ring system. The atoms Sn1, Sn2, Sn1A, Sn2A, O5 and O5A are coplanar to within ± 2.38 pm. The atoms Sn1, O3A, O5, Sn2A are coplanar to within ± 1.89 pm. The dihedral angle between the central and terminal four atom rings is 3.2°. So, the atoms Sn1, Sn2, O3, O5, Sn1A, Sn2A, O3A and O5A are coplanar (to within ± 1.90 pm).

As to the atoms of tin, there are apparently two types: bridging tin atoms Sn2, Sn2A and side tin atoms Sn1, Sn1A. The bridging tin atoms adopt a pseudo-seven coordination structure, in which the five stronger coordination bonds, Sn2–C9 211(2) pm, Sn2–C13 207(2) pm, Sn2–O5 219.5(8) pm, Sn2–O5A 205.6(9) pm, Sn2–O3 223(1) pm, consist of a distorted trigonal bipyramid. The atoms Sn2, O5A, C9 and C13 are coplanar (to within ± 1.76 pm). The plane composed of them may be viewed as an equatorial plane of a trigonal-bipyramid. In addition, the atoms Sn2, O1, O3, O4, O5, O5A are coplanar (to within ± 1.62 pm) and is nearly perpendicular to the equatorial plane (their dihedral angle is 89.5°). However, from the two directions facing the faces composed of C9, C13, O3 and of C9, C13, O3 and O1 approach the Sn2 atom with a weaker long-range interaction (the distances between the two atoms are 289 pm and 312 pm respectively). The axial angle O3–Sn2–O5 is closed to 150.6°; the angle C9–Sn2–C13 in the equatorial plane is opened up to 133.3°.
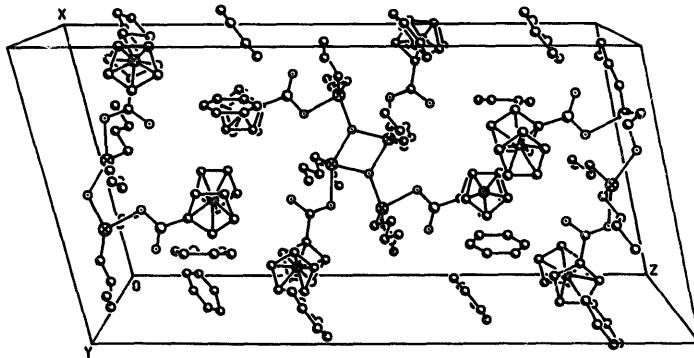

Fig. 2. The packing plot of **IA** in its unit cell.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^3$) for **IA**

	x	y	z	U_{eq} [a]
Sn(1)	2819(1)	4477(1)	168(1)	65(1)
Sn(2)	5496(1)	5068(1)	611(1)	56(1)
Fe(1)	9240(2)	6786(2)	1680(1)	75(1)
Fe(2)	3689(2)	3208(2)	2161(1)	71(1)
O(1)	3552(8)	4500(9)	919(4)	79(5)
O(2)	2023(10)	4193(10)	962(4)	91(6)
O(3)	7086(9)	5427(9)	803(4)	90(6)
O(4)	6863(9)	5299(12)	1542(6)	114(7)
O(5)	4152(7)	4751(8)	63(3)	56(4)
Ca	2863(16)	4335(14)	1167(7)	69(6)
Cb	7417(15)	5394(15)	1248(8)	78(6)
C(1)	2454(16)	2943(15)	−31(8)	107(7)
C(2)	2773(22)	2224(25)	312(11)	181(12)
C(3)	2329(27)	1097(30)	131(14)	221(16)
C(4)	2619(51)	515(59)	412(25)	495(53)
C(5)	1947(20)	5826(19)	67(10)	143(10)
C(6)	1195(41)	5992(43)	174(19)	343(28)
C(7)	505(33)	7083(38)	157(17)	281(23)
C(8)	1065(33)	7697(36)	203(15)	283(23)
C(9)	4976(13)	6447(13)	853(7)	77(6)
C(10)	5504(18)	7335(19)	821(9)	139(9)
C(11)	5077(22)	8353(23)	1053(11)	166(11)
C(12)	5426(40)	9179(45)	984(20)	397(34)
C(13)	5627(14)	3594(13)	889(7)	82(6)
C(14)	6287(20)	2914(22)	703(10)	160(11)
C(15)	6300(26)	1735(28)	867(13)	217(15)
C(16)	7031(40)	1253(46)	665(19)	398(32)
C(21)	3226(13)	4404(13)	1704(6)	68(5)
C(22)	4168(14)	4595(14)	1970(7)	82(6)
C(23)	3187(14)	4376(14)	2524(7)	85(6)
C(24)	4150(14)	4574(14)	2481(7)	86(6)
C(25)	2611(14)	4261(13)	2059(7)	78(6)
C(26)	3658(16)	1905(15)	1778(8)	95(7)
C(27)	4595(17)	2125(16)	2001(8)	112(8)
C(28)	4622(16)	2116(15)	2495(8)	101(7)
C(29)	3691(15)	1913(14)	2552(8)	95(7)
C(30)	3049(19)	1789(16)	2089(9)	116(8)
C(31)	8500(13)	5485(13)	1445(6)	64(5)
C(32)	9195(14)	5638(13)	1154(8)	95(7)
C(33)	10107(16)	5652(15)	1515(8)	100(7)
C(34)	9990(14)	5528(14)	1962(7)	81(6)
C(35)	8963(14)	5431(14)	1958(7)	87(6)
C(36)	8371(18)	8003(15)	1611(8)	107(7)
C(37)	8882(17)	7917(16)	2097(9)	114(8)
C(38)	9845(17)	8004(16)	2076(9)	110(8)
C(39)	9886(17)	8142(15)	1598(8)	103(7)
C(40)	8937(18)	8119(16)	1308(9)	115(8)
C(41)	2648(16)	7182(20)	1866(9)	118(8)
C(42)	2617(16)	7245(21)	2349(10)	126(9)
C(43)	2735(18)	8163(22)	2564(10)	138(9)
C(44)	2907(15)	8973(19)	2330(9)	107(7)
C(45)	2910(18)	8978(19)	1831(9)	122(8)
C(46)	2789(18)	7999(22)	1622(10)	139(9)
C(51)	8987(27)	1797(31)	1648(12)	212(15)
C(52)	9609(23)	925(25)	1581(10)	169(11)
C(53)	10327(25)	960(28)	1371(11)	188(13)
C(54)	10592(22)	2009(26)	1227(10)	166(11)
C(55)	10073(22)	2775(23)	1329(10)	141(10)
C(56)	9361(26)	2706(28)	1502(11)	177(12)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The side tin atoms adopt a pseudo-six coordination structure, in which the atoms Sn1, O1, O3A and O5 are coplanar to within ±2.10 pm; its geometry, for example for the Sn1 atom, can be seen as four coordination (with distances 198.7(10) ~ 213.3(26) pm) to the nearby tetrahedron of atoms O1 O5 C1 C5, where the atoms O2, O3A coordinate to the side tin Sn1 facing the faces shared by the edge defined by the atoms C1 and C5. There is stronger long-range interaction between the capped O2, O3A atoms and the side tin (Sn1) with distances 271.0 pm and 274.0 pm respectively.

In **IA**, all of the carboxylate ligands are anisobidentate. The ester oxygen atoms as a bridge-oxygen coordination atom have a normal linkage (Sn–O; 212.1(10) ~ 222.8(12) pm), simultaneously coordinating to an adjacent tin atom with long-range interaction (distances 274.0 pm, 312.2 pm), while each of the carbonyl oxygen atoms, as terminal-oxygen coordination atoms, coordinates to the same tin atom with long-range interaction (271.0 pm, 288.8 pm; the van der Waals sum $r_{vdw}(Sn-O) = 368$ pm [2]). However, the ester bond and carbonyl bond in carboxylate ligand bonding to the bridging tin atom are more averaged ($\Delta = Cb-O4 = Cb-O3 = 2$ pm) than to the side tin atom ($\Delta = Ca-O1 = Ca-O2 = 11$ pm).

The Cp rings in the same ferrocenyl group are eclipsed and parallel to each other, between which the dihedral angles are 0.7 ~ 1.4°. The Cp rings in different ferrocenyl groups are nearly parallel to each other, between which the dihedral angles are 8.6 ~ 10.7°.

The solvate benzene molecules embed in the unit cell with dihedral angles to the Sn_2O_2 core of 113.6° for C41 ~ C46 and 89.5° for C51 ~ C56. The dihedral angle between the planes of two kinds of benzene molecule is 53.7°.

Since the atoms Sn1, Sn1A, Sn2, O1 ~ O5, O5A, Ca, Cb, C21 ~ C23 and C31 ~ C33 are coplanar to within ±9.24 pm, the main skeleton of **IA**, in general, has a planar structure, except for the butyl groups. The oxo-bridging core in **IA** has a parallel quadrilateral geometry with two unequal length Sn–O bonds: 219.5(8) pm, 205.6(9) pm; their difference $\Delta = 13.9$ pm, $\angle O–Sn–O$ 74.1(4)°, is similar to many other dialkyltin oxides (Sn–O 217 pm [11] and 199 pm [6,11], $\Delta \sim 3$ pm [12] to 16 pm [6,11], $\angle O–Sn–O 71.8°$ [11], ca. 77.5° [7]). However, the geometric positions about the side-tin atoms may differ with different coordinating groups; also, they may be out of the oxo-bridging core or become tortured in some degree in the core plane. Therefore, the molecular geometry of the main skeleton about this kind of compound may transform from ladder mode into a tortuous ladder mode [3–12] or into staircase mode [13].

The ^{119}Sn NMR spectrum of **IA** has two signals; this shows that the structures of the two types of tin atom in

Table 2
Selected bond bond lengths (pm) and bond angles (deg) for **IA**

Bond lengths							
Sn1–O1	212.1(10)	Sn2–O3	222.8(12)	O1–Ca	132(3)	Cb–C31	151(3)
Sn1–O5	198.7(10)	Sn2–O5	219.5(8)	O2–Ca	121(2)	Sn1–O2	271.0(14)
Sn1–Cl	212(2)	Sn2–C9	211.2(18)	Ca–C21	148(3)	Sn1–O3A	274.0(13)
Sn1–C5	213(3)	Sn2–C13	207.2(17)	O3–Cb	123(2)	Sn2–O1	312.2(12)
		Sn2–O5A	205.6(9)	O4–Cb	125(3)	Sn2–O4	288.8(12)
C1–C2	135(4)	C2–C3	164(5)	C3–C4	110(8)	C5–C6	118(7)
C6–C7	172(8)	C7–C8	111(7)	C9–C10	139(3)	C10–C11	165(4)
C11–C12	122(7)	C13–C14	146(4)	C14–C15	161(5)	C15–C16	142(7)
C–C							
in Cp		$C_{21\sim25}$	138(2) ~ 146(3)	$C_{26\sim30}$	135(4) ~ 141(3)		
		$C_{31\sim35}$	130(3) ~ 145(3)	$C_{36\sim40}$	129(4) ~ 140(3)		
in benzene		$C_{41\sim46}$	130(4) ~ 140(4)	$C_{51\sim56}$	120(5) ~ 150(5)		
Fe1–$C_{31\sim40}$	199 ~ 203(2)	Fe2–$C_{21\sim30}$	201 ~ 206(2)				

Bond angles					
O1–Sn1–O5	82.4(4)	O3–Sn2–O5	150.6(4)	O1–Sn2–O3	150.9(4)
O1–Sn1–O3A	148.9(4)	O3–Sn2–C9	98.1(6)	O1–Sn2–O4	103.2(3)
O1–Sn1–Cl	108.1(6)	O3–Sn2–C13	96.0(6)	O1–Sn2–O5A	132.4(3)
O1–Sn1–C5	105.1(7)	C9–Sn2–C13	133.3(8)	O4–Sn2–C9	80.3(5)
O5–Sn1–O3A	66.3(3)	O5–Sn2–C9	94.5(5)	O4–Sn2–C13	77.0(6)
O5–Sn1–C5	111.3(8)	O5–Sn2–C13	94.4(5)	O4–Sn2–O3	47.7(4)
C1–Sn1–C5	130.7(9)	O5–Sn2–O5A	74.1(4)	O4–Sn2–O5	161.5(4)
C1–Sn1–O3A	81.1(7)	O3–Sn2–O5A	76.6(4)	O4–Sn2–O5a	124.3(4)
C5–Sn1–O3A	88.9(8)	O9–Sn2–O5A	111.1(6)	Sn1–O1–Ca	105(1)
O2–Sn1–C5	84.0(8)	C13–Sn2–O5A	115.4(6)	Sn1–O5–Sn2	128.8(4)
O2–Sn1–O3A	158.2(4)	O1–Sn2–C9	74.5(6)	Sn1–O5–Sn2A	125.1(4)
O2–Sn1–O5	135.4(4)	O1–Sn2–C13	71.8(6)	Sn2–O5–Sn2A	105.9(4)
O2–Sn1–O1	52.8(4)	O1–Sn2–O5	58.3(3)	Sn2–O3–Cb	112(1)
O1–Ca–O2	122(2)	O1–Ca–C21	113(2)	O2–Ca–C21	125(2)
O3–Cb–O4	121(2)	O3–Cb–C31	120(2)	O4–Cb–C31	119(2)
Sn1–C1–Cl	117(2)	C1–C2–C3	111(2)	C2–C3–C4	110(5)
Sn1–C5–C6	130(3)	C5–C6–C7	133(5)	C6–C7–C8	103(4)
Sn2–C9–C10	118(2)	C9–C10–C11	114(2)	C10–C11–C12	118(4)
Sn2–C13–C14	117(2)	C13–C14–C15	117(3)	C14–C15–C16	106(4)
C31–Fe1–C32	40.0(8)	C32–C31–C36	90.3(9)	Ca–C21–C22	129(2)
Ca–C21–C23	124(2)	Cb–C31–C32	125(2)	Cb–C31–C35	124(2)
C21–C22–C24	108(2)	C42–C41–C46	120(2)		

Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figs. 1 and 2.

the solid state are still retained in solution. The signal at −222.3 ppm is assigned to the pseudo-seven coordination bridging tin (or bicapped trigonal bipyramid tin) and at −217.3 ppm to the pseudo-six coordination side tin (or bicapped tetrahedron tin).

Acknowledgements

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