

Structural study of bis(triorganotin(IV)) esters of 4-ketopimelic acid

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Abstract

The set of six bis(triorganotin(IV)) esters of 4-ketopimelic acid was prepared. Their structures were studied using IR, NMR and X-ray crystallographic (cyclohexyl and ethyl derivatives) techniques both in solution and the solid state. Five of these compounds are polymeric in the solid state and depolymerise upon dissolving in non-coordinating and/or addition of coordinating solvent to monomeric species with four-coordinated tin atom or complexes with donor solvent with five-coordinated tin central atom. The tricyclohexyltin derivative is dimeric in the solid state and monomeric in solution.

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1. Introduction

There is a long-standing interest in chemistry of triorganotin(IV) carboxylates both in academia and industry, because of known catalytic and medical activity [1,2].

The structural motifs of these compounds are well established and studied by X-ray [3], Mössbauer and CP MAS NMR techniques in the solid state, and mainly multinuclear NMR techniques in solution [1]. The tin atom in these compounds can be four-coordinated (Fig. 1A) or five-coordinated with major occurrence in the solid state. In this case, the tin atom is surrounded by three carbon atoms originated from organyl groups and two oxygen atoms from one asymmetrically bidentate carboxylate (intramolecularly chelated – Fig. 1B) or two different carboxylate groups (intermolecularly bridging – Fig. 1C). The compounds where the intermolecularly bridging bond fashion

is taking place form the polymeric networks in the solid state [3], which can be often fragmented into oligomeric or monomeric species in solution of various solvents [4]. Another structural motif in polymeric and/or chelate arrangement can be revealed when a further donor atom is implemented as a part of carboxylate ligand into the tin coordination sphere [3].

Only little is known about properties and structure of diesters of dicarboxylic acids. To the best of our knowledge, only six papers are related to the structure of triorganotin diesters of dicarboxylic acids [5] and certain others to the structure of mentioned esters adducts and complex compounds [6].

In our previous work, we have been interested in structure of organotin carboxylates containing mainly one organotin fragment in solution of different solvents [4]. Now we would like to pay much more attention to systems where two or more non-equivalent organotin groups exist, caused by chemical or geometrical (sterical) non-equivalency or dynamic exchange and to study and compare such

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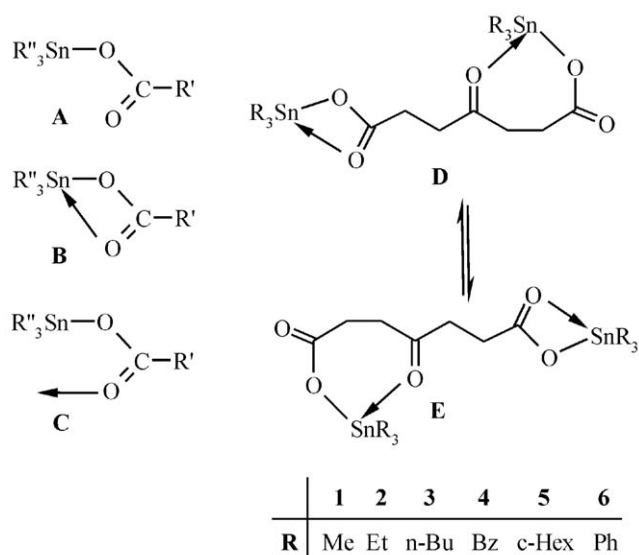


Fig. 1. Possible structural motifs and numbering for studied compounds.

phenomena both in the solid state and solution. For this paper we have selected the triorganotin diesters of ketopimelic acid in order to observe two equivalent or non-equivalent tin fragments depending on sterical hindrance of organyl substituents and the possibility of formation of seven-membered ring through the intramolecular interaction of tin atom with the ketonic oxygen (Fig. 1D and E). This type of coordination is known in organotin chemistry for phosphine oxides [7] or substituted carboxylates [8].

2. Results and discussion

The studied compounds – bis(triorganotin(IV)) esters of 4-ketopimelic (4-oxoheptanedioic) acid **1–6** – were prepared by two different methods; (i) reaction of triorganotin halide with ketopimelic acid and KOH in refluxing isopropanol, (ii) bis(triorganotin)oxide (**3**) or triorganotin hydroxide (**1**) with ketopimelic acid in refluxing toluene. Both reactions gave after purification satisfactory (46% of **6**) to nearly quantitative yields (97% for **2**) of analytically pure products. All attempts to prepare triorganotin monoesters of 4-ketopimelic acid failed. The purity of **1–6** was checked by elemental analysis, ESI-MS spectrometry and NMR measurements. Only broad and unresolved resonances were found in ^1H NMR spectrum of **4**, much more clear spectrum was obtained when **4** was crystallized from methanol, but the molecules of coordinated methanol were detected in this spectrum. A decomposition of **4** to benzaldehyde and a yellow insoluble solid was observed upon standing of sample on the air for a couple of days. The rest of compounds studied is stable under these conditions.

The results of electrospray ionisation (ESI) mass spectrometry measurements the both in positive- and negative-ion modes are summarized in Section 5. The typical feature of ESI mass spectra of organotin carboxylates consists in the cleavage of the most labile Sn–O bond in the

molecules yielding two complementary ions, where the cationic part (“Cat”) of the molecule is measured in the positive-ion mode and the anionic part (“An”) in the negative-ion mode [9]. The cationic part $[\text{SnR}_3]^+$ (base peak for $\text{R} = \text{Me}$) and subsequent fragment ions $[\text{HSnR}_2]^+$ and $[\text{H}_2\text{SnR}]^+$ (base peak for $\text{R} = \text{Bz}$) were observed in the first-order positive ESI mass spectra. Moreover, the adduct ions of fragment $[\text{SnR}_3]^+$ with water, methanol or molecule are observed: $[\text{HOSnR}_3 + \text{SnR}_3]^+$ (base peak for $\text{R} = c\text{-Hex, Ph}$), $[\text{CH}_3\text{OSnR}_3 + \text{SnR}_3]^+$ and $[\text{M} + \text{SnR}_3]^+$ (base peak for $\text{R} = \text{Et, } n\text{-Bu}$). The formation of adducts $[\text{M} + \text{K}]^+$ and $[\text{M} + \text{Na}]^+$ is also observed but with a lower relative intensity in most cases. The proposed structures of individual ions are supported by tandem mass spectrometric experiments. Ions $[\text{M} - \text{SnR}_3]^-$ or $[\text{M} + \text{H} - 2 * \text{SnR}_3]^-$ are the base peaks of all first-order negative-ion spectra. CO_2 , alkene, alkane, H_2O , toluene, benzene, etc. are the characteristic neutral losses in MS/MS spectra.

2.1. Structure of 1–6

2.1.1. IR spectroscopy

The significant tool for evaluation of organotin carboxylate structure is IR spectroscopy, especially the values of ν_{as} and ν_{s} for CO_2 group [10]. These values and $\nu(\text{C}=\text{O})$ for **1–6** in chloroform solution, nujol mulls and KBr pellets, respectively, are collected in Table 1. The $\nu(\text{C}=\text{O})$ values, similar to the same parameter of free 4-ketopimelic acid (1695 cm^{-1}) [10c], for all compounds and media were found in the narrow interval which indicate no interaction of ketonic function and tin. The $\nu_{\text{as}}(\text{CO}_2)$ ($1530\text{--}1570\text{ cm}^{-1}$) and $\nu_{\text{s}}(\text{CO}_2)$ ($\sim 1400\text{ cm}^{-1}$) values reported earlier for a polymeric structure with bridging bidentate carboxylic groups were found for all compounds in the solid state spectra except for **5**. The increase of $\nu_{\text{as}}(\text{CO}_2)$ values for **2** and **3** in chloroform solution, compared to the same parameter in nujol or KBr, corresponds to the fact that a solid state polymeric structure is broken up into the monomers upon dissolving of these compounds in chloroform.

Table 1
Selected parameters of IR spectra for **1–6** (cm^{-1})

Compound (R)	Medium	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{CO}_2)$	$\nu_{\text{s}}(\text{CO}_2)$
1 (Me)	Nujol	1720	1570, 1550	–
	CHCl ₃	1720	1645	1360
2 (Et)	Nujol	1725	1570, 1550	–
	CHCl ₃	1720	1645	1360
3 (<i>n</i> -Bu)	Nujol	1730	1555, 1575	–
	CHCl ₃	1722	1650	1350
4 (Bz)	Nujol	1705	1570	–
	CHCl ₃	1705	1560, 1550	1380, 1360
5 (<i>c</i> -Hex)	Nujol	1725, 1715	1635	–
		1725 ^a	1645 ^a , 1575 ^a	1405 ^a , 1350 ^a
	CHCl ₃	1720	1645	1350
6 (Ph)	Nujol	1720, 1700	1530	–

^a KBr disc.

The $\nu_{\text{as}}(\text{CO}_2)$ in nujol suspension for **1** and **6** were found in the range typical for a polymeric structure and these compounds are insoluble in chloroform. This confirms the fact that chloroform is not able to break up these polymers. On the other hand, the band $\nu_{\text{as}}(\text{CO}_2)$ in chloroform solution for **4** is split into two at 1560 and 1550 cm^{-1} as well as the $\nu_{\text{s}}(\text{CO}_2)$ one (1380 and 1360 cm^{-1}), indicating that a polymeric network of **4** is not completely dissociated into the monomers and/or is sufficiently soluble in chloroform. In order to break up these polymers, 1–10 molar equivalents of methanol were added. During this addition, additional bands appeared at 1640 and 1345 cm^{-1} , which can be assigned as bands of monomeric **4**, indicate the progressive dissociation of polymeric network bind with an addition of coordinating solvent. Rather interesting phenomenon has been observed in the case of **5** where the $\nu_{\text{as}}(\text{CO}_2)$ values were found in region at about 1640 cm^{-1} in all media, indicating a monomeric structure, but an additional band at 1575 cm^{-1} was found in spectrum in KBr pellet, probably caused by two different coordination fashions of CO_2 groups, evoking the presence of two different types of tin atoms, a tetrahedral and a trigonal bipyramidal ones, and an oligomeric structure. The fact that this band is not present in nujol spectrum could be caused by a disintegration of solid state structure in this media.

2.1.2. NMR spectroscopy

The structure of **1–6** was studied in solution of CDCl_3 and $\text{DMSO}-d_6$ by multinuclear NMR approach (Table 2). Although only compound **2** was sufficiently soluble in both solvents (compounds **1** and **6** were insoluble in chloroform and **3**, **4**, and **5** in DMSO, respectively), significant information about their structure was obtained. Compounds **1–3**, **5**, and **6** reveal one set of sharp and resolved signals in proton NMR spectra indicating the geometrical equivalency of organotin moieties and the both parts of acid at room temperature, respectively (at least on the NMR time scale). The decrease of temperature (the lowest reachable temperature for samples of **2** and **5** in dichloromethane/deuteriochloroform mixture 3:1 was 220 K) led in a broadening of resonances only.

Only one signal was observed for **1–6** in ^{119}Sn NMR spectrum at room temperature in the appropriate solvents. The values (see Table 2) of these signals for **2**, **3** and **5** are in accord with the values found for four-coordinated tin in solution of non-coordinating solvent [11] which confirms the results of IR spectra that organotin carboxylates depolymerize on going from the solid state to solution. For **4**, the signal at -124.3 ppm was observed in chloroform solution in ^{119}Sn NMR spectrum, when crystallized from methanol (see above) the only detectable signal at -13.18 ppm was determined. This fact, analogously to IR measurements, can be explained by presumption that a polymeric structure of **4** is only partially dissociated in CDCl_3 and the complete dissociation is possible when a donor solvent is added. Compounds **1** and **6** are insoluble in common organic non-coordinating solvents and the ^{119}Sn NMR spectra were obtained only for DMSO solutions. The values of $\delta(^{119}\text{Sn})$ indicate the five-coordinated tin atom and are consistent with values reported for another organotin carboxylates in the same solvent [4b,11b,11c].

In order to explore the further complexation of tin centre by the nitrogen donor, the amount of approximately 50 mg of each compound was suspended or dissolved in CDCl_3 and the appropriate volume of pyridine was added. The addition of 3.5 μl of pyridine to **1** (0.5 mol. equiv.) caused the dissolution of entire amount of **1** and the well resolved ^1H NMR spectrum was obtained. After the addition of further 0.5 mol. equiv. also the ^{119}Sn NMR spectrum was measured and the $\delta(^{119}\text{Sn})$ determined to be 113.7 ppm. This value has been changed after the addition of next 3.5 μl of pyridine to 106.9 and to 96.6 ppm after completing the second molar equivalent (one pyridine donor nitrogen fall on one tin atom). The same procedure with similar results (see Table 2) was made for **2–6**. This led us to conclusion that the pyridine addition increased the polarity and the “coordination” ability of solvent system and caused here-with the progressive dissociation of either oligo- or polymeric chains or nets into the monomeric species with nearly four-coordinated tin atoms. To determine the contradictory tin coordination behaviour – five-coordination – we added an excess (10% by volume) of much more stronger coordinating agent – HMPA – to the samples of **1–6** in

Table 2
 ^{119}Sn chemical shifts (ppm) of compounds **1–6**

R	$\text{CDCl}_3/\text{DMSO}-d_6$	0.5 mol. eq. pyridine	1 mol. eq. pyridine	1.5 mol. eq. pyridine	2 mol. eq. pyridine	ex. HMPA
1 (Me)	-8.8^{a}	^c	113.7	106.9	96.6	-33.1
2 (Et)	-17.8^{a}					
		106.6	104.2	101.9	99.3	-28.3
3 (<i>n</i> -Bu)	108.2^{b}	110.1	109.4	108.8	108.0	-23.6
4 (Bz)	-13.2^{c}	-12.7	-14.9	^c	-15.4	^c
5 (<i>c</i> -Hex)	13.5^{b}	13.76	14.2	14.1	14.2	-22.9^{d}
6 (Ph)	-272.9^{a}	^c	^c	^c	-117.1	-257.3

^a $\text{DMSO}-d_6$.

^b CDCl_3 .

^c Not found.

^d Broad signal.

^e See text.

CDCl_3 . The shift of $\delta(^{119}\text{Sn})$ values (Table 2) in this media to higher field is in line with the increase of tin coordination number to five. In compound **5**, there is only slight difference (~ 35 ppm) between the values of $\delta(^{119}\text{Sn})$ in solution of pure chloroform and chloroform with an excess of HMPA (usually ~ 130 ppm). The reason for this fact seems to be the disinclination of tin atom to five coordination because steric demand of cyclohexyl groups.

There is no concentration dependence of $\delta(^{119}\text{Sn})$ value for all compounds dissolved in chloroform or DMSO. The ^{119}Sn NMR spectra of **2** and **5** were measured in chloroform solution at lower temperature (220 K) and only a few ppm shift with respect to the values obtained at room temperature was detected.

The ^{13}C NMR spectra revealed three parameters useful for a structural study, (i) the $\delta(^{13}\text{C}(\text{C}=\text{O}))$ value in all solvents for all compounds was found in the narrow range (207.7–209.5 ppm) typical for non-coordinated ketonic group, (ii) $\delta(^{13}\text{C}(\text{CO}_2))$ are typical for a bidentate carboxylic group (175.4–178.9 ppm), and (iii) the average angle $\text{C}-\text{Sn}-\text{C} = 110.9^\circ$ common for tetrahedral vicinity of tin

atom was estimated from the value of $^1J(^{119}\text{Sn}, ^{13}\text{C})$ for **3** in chloroform [12].

The ^{119}Sn CP/MAS NMR of **2** and **5** (Fig. 2) were measured in order to explore the differences between these two compounds in the solid state. The spectrum for **2** reveals two spinning frequency independent resonances (-56.7 and -62.1 ppm) shifted upfield compared to values of $\delta(^{119}\text{Sn})$ in solution (108.9 ppm in CDCl_3 and -17.8 ppm with the presence of HMPA) to the range typical of trialkyltin(IV) five-coordinated compounds. This shift is most probably caused by much stronger association of species of **2** in the solid state. The slight difference between two resonances corresponds to the presence of two tin centres in the asymmetric unit of the crystal structure. The compound **5** reveal four resonances (-0.7 , -5.7 , -11.4 and -20.9 ppm) in the same type of spectra in the range defined by values found for **5** in solution of non-coordinating and coordinating solvents (13.5 and -22.9 ppm (see Table 2)). These values document the presence of four geometrically non-equivalent tin atoms, coordinated by four or five other atoms, which is inconsistent with the X-ray crystal structure where only two geometrically different tin atoms are present in the asymmetric unit. This is probably caused by two different phase in the polycrystalline material.

3. X-ray diffraction

The solid state structures of **2** and **5** were determined by diffraction techniques. The supramolecular organisation of **2** can be described as a S-shape (Fig. 3) layered two-dimensional polymer. Each layer is assembled of the twenty eight-membered rings, made up of four triorganotin fragments and four carboxylic acids (Fig. 4), where two of them are incorporated in the core of the ring and other two are bridging and participating in the ring system by three atoms of CO_2 group only. Based on slightly different angles and distances around tin atom, there are two slightly different types of tin atoms in the polymeric network of **2**, both are five-coordinated, with distorted trigonal bipyramidal environment (Σ of $\text{C}-\text{Sn}-\text{C}$ angles is 360.0° and 359.5°), by three alkyls and two oxygen atoms originated from two different asymmetrically bridging carboxylate fragments, in addition one these groups is able to interact weakly via the second oxygen to the tin centre. Second carboxylate group interact in similar manner with another tin atom. Similar structures were found for diesters of terephthalic [5c], succinic [5d] and acetylenedicarboxylic [5c] acids. The selected structural parameters are collected in Table 3.

On the other hand, the structure of **5** can be described as a centrosymmetric dimer formed by two weak intermolecular contacts $\text{Sn}-\text{O}$ (Fig. 5), throughout these connections the 20-member ring is formed. The rings are placed in parallel layers in the crystal system (Fig. 6). Two types of tin atoms are present in the dimeric structure of **5**, first one bound to three carbon atoms and asymmetrically bidentate carboxylic group ($\text{Sn1}-\text{O1}$ 2.077(2) Å; $\text{Sn1}-\text{O2}$ 2.924(3) Å;

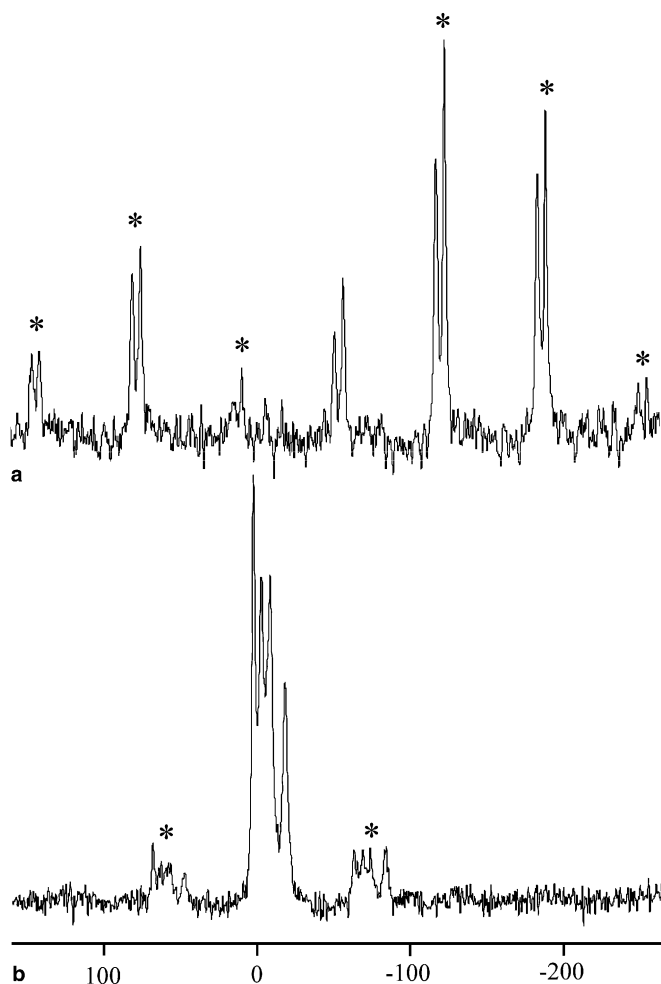
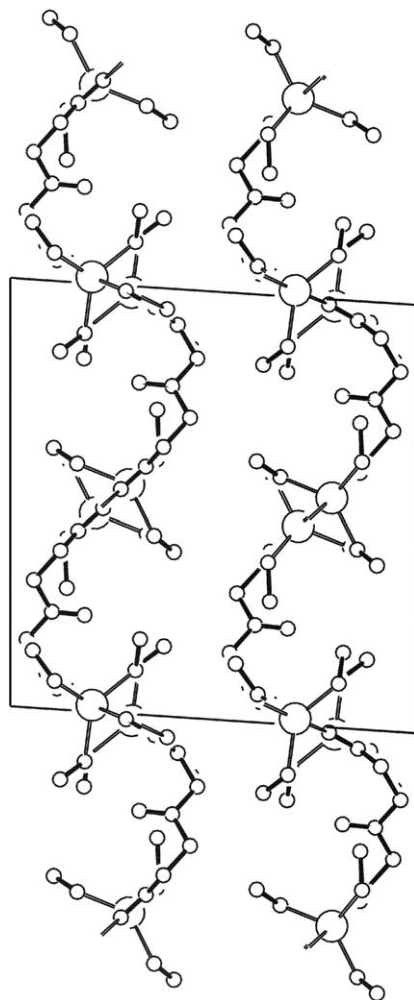
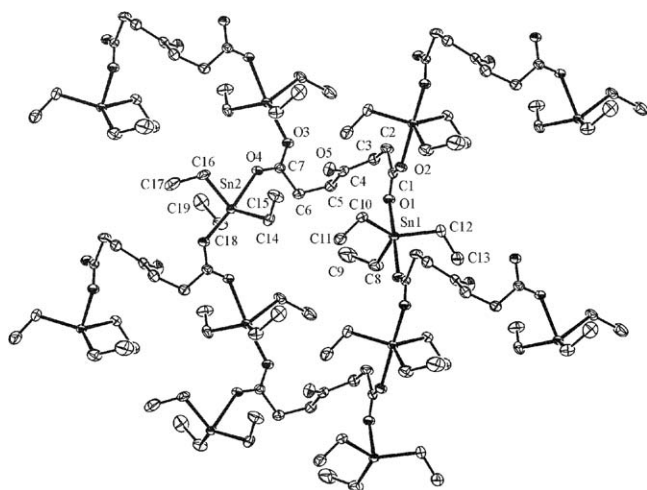


Fig. 2. ^{119}Sn CP/MAS NMR spectra of **2** (a) and **5** (b), spinning side bands are marked with * symbols.

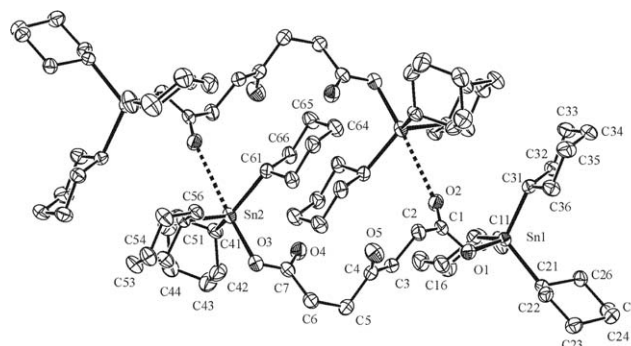
Fig. 3. Crystal unit cell of **2**. View along *b*-axis.Fig. 4. Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

$\Sigma C_{eq.}-Sn1-C_{eq.} = 350.4^\circ$), the second one, where similar ($Sn2-O3$ 2.109(3) Å; $Sn2-O4$ 2.877(3) Å; $\Sigma C_{eq.}-Sn2-C_{eq.} = 344.0^\circ$) coordination sphere is completed with the weak intermolecular interaction to oxygen atom from

Table 3
Selected geometrical parameters (distances [Å] and angles [°]) for **2** and **5**

2		5	
Sn1–C12	2.150(5)	Sn1–O1	2.077(2)
Sn1–C10	2.143(5)	Sn1–O2	2.924(3)
Sn1–C8	2.142(5)	Sn1–C11	2.148(4)
Sn1–O1	2.248(3)	Sn1–C31	2.158(3)
Sn1–O2 ⁱ	2.312(3)	Sn1–C21	2.163(4)
Sn2–C14	2.137(5)	Sn2–O3	2.109(3)
Sn2–C18	2.127(5)	Sn2–O4	2.877(3)
Sn2–C19	2.146(5)	Sn2–O2 ⁱ	3.020(3)
Sn2–O3 ⁱⁱ	2.213(3)	Sn2–C61	2.153(4)
Sn2–O4	2.351(3)	Sn2–C51	2.161(4)
O2–C1	1.258(6)	Sn2–C41	2.171(4)
O1–C1	1.262(6)	C1–O2	1.234(5)
O5–C4	1.210(6)	C1–O1	1.302(4)
O3–C7	1.276(6)	C4–O5	1.208(5)
O4–C7	1.249(6)	C7–O4	1.223(5)
O4 ⁱⁱ –Sn2	3.160(4)	C7–O3	1.306(4)
O2–Sn1	3.174(3)	O1–Sn1–C11	109.47(13)
C8–Sn1–C12	116.0(2)	O1–Sn1–C31	104.36(12)
C10–Sn1–C12	130.0(2)	C11–Sn1–C31	113.69(15)
C8–Sn1–O1	114.0(2)	O1–Sn1–C21	96.61(12)
C12–Sn1–O1	88.20(18)	C11–Sn1–C21	117.21(15)
C10–Sn1–O1	90.08(18)	C31–Sn1–C21	113.18(14)
C8–Sn1–O2 ⁱ	87.60(18)	O3–Sn2–C61	102.92(13)
C10–Sn1–O2 ⁱ	90.78(16)	O3–Sn2–C51	91.63(12)
C12–Sn1–O2 ⁱ	90.97(18)	C61–Sn2–C51	111.24(14)
O1–Sn1–O2 ⁱ	175.71(12)	O3–Sn2–C41	104.98(12)
C14–Sn2–C18	129.5(2)	C61–Sn2–C41	125.55(15)
C14–Sn2–C16	116.6(2)	C51–Sn2–C41	113.64(14)
C18–Sn2–C16	113.5(2)	O2–C1–O1	122.0(4)
C16–Sn2–O4	84.87(18)	O4–C7–O3	122.9(4)
C18–Sn2–O4	87.10(17)	O3–Sn2–O2 ⁱ	172.41(9)
C14–Sn2–O4	90.83(17)		
C18–Sn2–O3 ⁱⁱ	94.15(18)		
C14–Sn2–O3 ⁱⁱ	92.58(17)		
C16–Sn2–O3 ⁱⁱ	89.63(18)		
O3 ⁱⁱ –Sn2–O4	174.40(12)		
O2–C1–O1	122.5(4)		
O4–C7–O3	122.3(4)		
O1–Sn1–O2 ⁱ	175.71(14)		
O4–Sn2–O3 ⁱⁱ	174.40(12)		

Symmetry codes. For **2**: (i) $-x + 1, y - 1/2, -z + 1/2$; (ii) $-x, y - 1/2, -z + 1/2$. For **3**: (i) $-x + 2, -y, -z$.

Fig. 5. Molecular structure of **5**, hydrogen atoms are omitted for clarity.

another molecule ($Sn2-O2^i$ 3.020(3) Å). The different aggregation of **2** and **5** in the solid state is due to different sterics of Et and *c*-Hex groups.

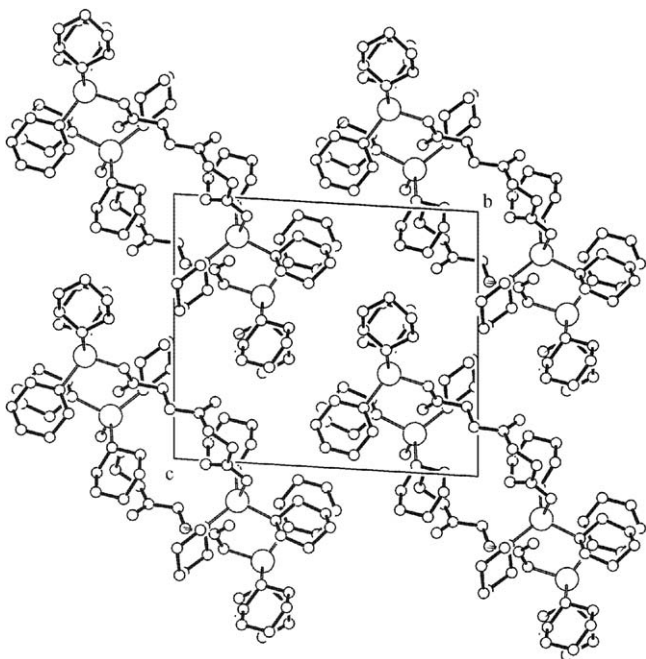


Fig. 6. Crystal packing of **5**, view along *a*-axis.

4. Conclusion

The bis(triorganotin(IV)) esters of **4** – ketopimelic acid (**1–4** and **6**) have polymeric structure in the solid state as a result of tin fragments association by means of bidentate bridging carboxylate groups. Some of these compounds (**2** and **3**) depolymerise upon dissolving in chloroform to monomeric species. Compound **4** is oligo- or polymeric in chloroform solution and these associates can be split when a trace of donor solvent such as methanol or pyridine is added. Compounds **1** and **6** are insoluble in chloroform and the progressive addition of coordinating solvent to their suspensions caused the monomerisation to species with four-coordinated tin and the further addition of donor solvent led to formation of complexes with five-coordinated tin atoms. On the other hand, **5** crystallize as weakly connected dimer probably due to averseness of tricyclohexyl compounds to increase the coordination number of tin atom to five. Also the formation of complex of **5** with HMPA in solution is incomplete. The ^{119}Sn CP/MAS NMR spectra were found to be very sensitive to the coordination vicinity of tin atom and the information about the coordination number of tin atom and the number of non-equivalent tin atoms in the solid state has been obtained.

5. Experimental

5.1. General remarks

The syntheses were carried out on the air. 4-Ketopimelic acid (4-oxoheptanedioic acid) and triorganotin chlorides, oxide or hydroxide were obtained from commercial sources (Sigma–Aldrich). Toluene and isopropanol were dried over

and distilled from sodium and Na_2SO_4 , respectively, and stored under argon.

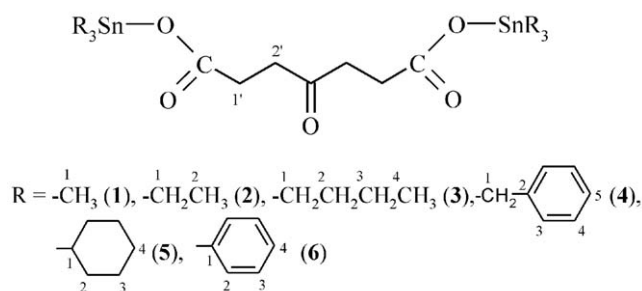
5.2. NMR spectroscopy

The solution state ^1H (500.13 MHz), $^{119}\text{Sn}\{^1\text{H}\}$ (186.50 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (125.67 MHz) NMR spectra of the studied compounds were measured on a Bruker Avance 500 spectrometer equipped with 5 mm probes with *z*-gradient in the temperature range of 220–300 K. The solutions were obtained by dissolving of 50 mg of each compound in 0.6 ml of deuterated solvents. The ^1H chemical shifts were calibrated relative to the signal of residual CHCl_3 ($\delta = 7.25$ (^1H); 77.0 (^{13}C)) and DMSO ($\delta = 2.50$ (^1H); 39.6 (^{13}C)). The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$). Positive chemical shifts values denote shifts to the higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. The numbering system for the NMR spectral data is shown in Scheme 1.

All CP/MAS NMR spectra were measured using Bruker Avance 500 WB/US NMR spectrometer in 4-mm ZrO_2 rotor at frequencies of 186.49 and 500.18 MHz (for ^{119}Sn , and ^1H , respectively). Magic angle spinning (MAS) speed was 8–12 kHz, nutation frequency of $B_1(^{13}\text{C})$ field was 62.5 kHz and repetition delay was 4–10 s. Intensity of $B_1(^1\text{H})$ field of TPPM (two-pulse phase-modulated) decoupling corresponds to $\omega_1/2\pi = 89.3$ kHz. The ^{119}Sn chemical shifts were calibrated indirectly by external tetracyclohexyltin ($\delta = -97.35$ ppm).

5.3. Mass spectrometry

Positive-ion and negative-ion electrospray ionisation (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–1500. The samples were dissolved in methanol (in acetonitrile is low signal) and analyzed by direct infusion at the flow rate 5 $\mu\text{l}/\text{min}$. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: the isolation width $m/z = 8$ for ions containing one tin atom and $m/z = 12$ for ions containing more tin atoms, the collision amplitude in the range 0.7–



Scheme 1.

1.0 V depending on the precursor ion stability, the ion source temperature 300 °C, the tuning parameter compound stability 100%, the flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively.

5.4. IR spectroscopy

IR spectra were recorded on Perkin–Elmer 684 spectrophotometer in nujol mulls, KBr pellets or in CHCl₃ solution, respectively, at laboratory conditions.

5.5. X-ray crystallography

The single crystals of **2** and **5** were grown from ca 5% CH₂Cl₂ solution of the appropriate compound, into which hexane was charged via slow vapour diffusion.

The X-ray data were collected on a Nonius KappaCCD diffractometer fitted with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150(2) K. The absorption correction was performed using a gaussian procedure (Coppens [13]), the structure was solved by direct methods (SIR92 [14]) and full-matrix least-squares refinements on F^2 were carried out using the program SHELXL97 [15].

Crystallographic data for 2. C₁₉H₃₈O₅Sn₂, $M = 583.87$, monoclinic, $P2_1/c$, $a = 15.8060(4) \text{ \AA}$, $b = 10.1540(2) \text{ \AA}$, $c = 15.0020(4) \text{ \AA}$, $\beta = 93.8170(12)^\circ$, $Z = 4$, $V = 2402.39(10) \text{ \AA}^3$, $D_c = 1.614 \text{ g cm}^{-3}$, $\mu = 2.102 \text{ mm}^{-1}$, $T_{\min} = 0.656$, $T_{\max} = 0.896$; 32899 reflections measured ($\theta_{\max} = 27.5^\circ$), 5484 independent ($R_{\text{int}} = 0.043$), 4679 with $I > 2\sigma(I)$, 241 parameters, $S = 1.322$, R_1 (obs. data) = 0.0388, wR_2 (all data) = 0.0855; max, min residual electron density = 0.718, $-0.904 \text{ e \AA}^{-3}$. CCDC Deposition number: 287932.

Crystallographic data for 5. C₄₃H₇₄O₅Sn₂, $M = 908.40$, triclinic, $P\bar{1}$, $a = 10.5120(4) \text{ \AA}$, $b = 13.3400(7) \text{ \AA}$, $c = 15.2700(8) \text{ \AA}$, $\alpha = 86.568(2)^\circ$, $\beta = 89.205(3)^\circ$, $\gamma = 85.549(3)^\circ$, $Z = 2$, $V = 2130.94(18) \text{ \AA}^3$, $D_c = 1.416 \text{ g cm}^{-3}$, $\mu = 1.213 \text{ mm}^{-1}$, $T_{\min} = 0.810$, $T_{\max} = 0.944$; 27586 reflections measured ($\theta_{\max} = 25.1^\circ$), 7515 independent, 5756 with $I > 2\sigma(I)$, 475 parameters, $S = 1.046$, R_1 (obs. data) = 0.0347, wR_2 (all data) = 0.0774. max, min residual electron density = 0.915, $-0.912 \text{ e \AA}^{-3}$. CCDC Deposition number: 287933.

5.6. Bis(trimethyltin)-4-oxoheptanedioate (1)

The compound **1** was prepared from 4-ketopimelic acid (0.1 g; 0.575 mmol) and Me₃SnOH (0.21 g; 1.149 mmol) in refluxing toluene (30 ml) for 2 h at 125 °C. The mixture gave the pure product after filtration (0.26 g; 90%), m.p.: 192–194 °C.

¹H NMR (DMSO-*d*₆, 300 K, ppm): 2.49 (4H, t, H-2'), 2.18 (4H, t, H-1'), 0.33 (18H, s, Me), ²J(¹¹⁹Sn, ¹H) = 68.4 Hz. ¹³C{¹H} NMR (DMSO-*d*₆, 300 K, ppm): 209.44 (C=O), 176.31 (COOSn), 38.25 (C-2'), 30.15 (C-1'), 0.27 (Me), ¹J(¹¹⁹Sn, ¹³C) = 514.6 Hz. ¹¹⁹Sn {¹H} NMR (DMSO-*d*₆, 300 K, ppm): -8.8 . Positive-ion MS: m/z 1027 [$2 * M + Na$]⁺, 4%; m/z 667 [M + SnMe₃]⁺,

24%; m/z 541 [M + K]⁺, 2%; m/z 525 [M + Na]⁺, 9%; m/z 503 [M + H]⁺, 1%; m/z 487 [M + H – methane]⁺, 2%; m/z 361 [CH₃OSnMe₃ + SnMe₃]⁺, 3%; m/z 347 [HOSnMe₃ + SnMe₃]⁺, 6%; m/z 165 [SnMe₃]⁺, 100%; m/z 151 [HSnMe₂]⁺, 8%; m/z 135 [SnMe]⁺, 25%. MS/MS of 1027: m/z 525 [M + Na]⁺. MS/MS of 667: m/z 487 [M + H – methane]⁺; m/z 305 [M + H – SnMe₄ – H₂O]⁺; m/z 259 [M + H – H₂O – CO₂ – HOSnMe₃]⁺. MS/MS of 541: m/z 359 [M + K – HOSnMe₃]⁺; m/z 343 [M + K – CH₄ – HOSnMe₃]⁺. MS/MS of 525: m/z 343 [M + Na – HOSnMe₃]⁺; m/z 315 [LSn + Na]⁺. MS/MS of 503: m/z 487 [M + H – methane]⁺; m/z 347 [HOSnMe₃ + SnMe₃]⁺; m/z 323 [M + H – SnMe₄]⁺; m/z 305 [M + H – SnMe₄ – H₂O]⁺; m/z 277 [M + H – CO₂ – HOSnMe₃]⁺; m/z 259 [M + H – H₂O – CO₂ – HOSnMe₃]⁺; m/z 165 [SnMe₃]⁺. MS/MS of 487: m/z 469 [M + H – methane – H₂O]⁺; m/z 305 [M + H – SnMe₄ – H₂O]⁺; m/z 259 [M + H – H₂O – CO₂ – HOSnMe₃]⁺; m/z 165 [SnMe₃]⁺. MS/MS of 347: m/z 165 [SnMe₃]⁺; m/z 135 [SnMe]⁺. MS/MS of 165: m/z 135 [SnMe]⁺. MS/MS of 151: m/z 135 [SnMe]⁺. Negative-ion MS: m/z 839 [$2 * M - SnMe_3$]⁻, 10%; m/z 337 [M – SnMe₃]⁻, 91%; m/z 173 [LH]⁻, 100%; m/z 155 [LH – H₂O]⁻, 38%; m/z 137 [LH – 2 * H₂O]⁻, 18%; m/z 129 [LH – CO₂]⁻, 14%; m/z 111 [LH – H₂O – CO₂]⁻, 26%. MS/MS of 839: m/z 337 [M – SnMe₃]⁻. MS/MS of 337: m/z 321 [M – SnMe₃ – CH₄]⁻; m/z 155 [LH – H₂O]⁻; m/z 137 [LH – 2 * H₂O]⁻; m/z 111 [LH – H₂O – CO₂]⁻. MS/MS of 173: m/z 155 [LH – H₂O]⁻; m/z 137 [LH – 2 * H₂O]⁻; m/z 129 [LH – CO₂]⁻; m/z 111 [LH – H₂O – CO₂]⁻. MS/MS of 155: m/z 137 [LH – 2 * H₂O]⁻; m/z 111 [LH – H₂O – CO₂]⁻. MS/MS of 137: m/z 93 [LH – 2 * H₂O – CO₂]⁻. MS/MS of 129: m/z 111 [LH – H₂O – CO₂]⁻. MS/MS of 111: m/z 93 [LH – 2 * H₂O – CO₂]⁻; m/z 83 [LH – H₂O – CO – CO₂]⁻; m/z 67 [LH – H₂O – 2 * CO₂]⁻. IR analysis: 1720 (ν(CO), s), 1570 – 1550 (ν_{as}(CO₂), vs), 1455 (nujol), 1430, 1370 (nujol), 1090 (m), 775 (m), 680 (m), 550–540 (w) cm⁻¹. Elemental analysis found: C, 31.2%; H, 5.2%. Calculated: C, 31.25%; H, 5.24%.

5.7. Bis(triethyltin)-4-oxoheptanedioate (2)

Mixture of 4-ketopimelic acid (1 g; 5.747 mmol) with KOH (0.55 g; 12.643 mmol, 10% excess) and Et₃SnCl (2.77 g; 11.494 mmol) was refluxed in isopropanol (50 ml) for 3 h. The cooled mixture was filtered and after evaporating of volatiles the pure **2** was obtained (3.28 g; 97%), mp: 143–146 °C. ¹H NMR (CDCl₃, 300 K, ppm): 2.73 (4H, t, H-2'), 2.59 (4H, t, H-1'), 1.23 (30H, m, Et). ¹H NMR (DMSO-*d*₆, 300 K, ppm): 2.53 (4H, t, H-2'), 2.25 (4H, t, H-1'), 1.12 (12H, t, H-1), 0.96 (18H, m, H-2). ¹³C{¹H} NMR (CDCl₃, 300 K, ppm): 207.97 (C=O), 178.35 (COOSn), 38.38 (C-2'), 28.67 (C-1'), 9.97 (C-1), ²J(¹¹⁹Sn, ¹³C) = 25.2 Hz, 7.99 (C-2), ¹J(¹¹⁹Sn, ¹³C) = 350.5 Hz. ¹¹⁹Sn{¹H} NMR (CDCl₃, 300 K, ppm): 108.87. ¹¹⁹Sn{¹H} NMR (DMSO-*d*₆, 300 K, ppm): -17.8 .

Positive-ion MS: m/z 1195 $[2 * M + Na]^+$, 6%; m/z 793 $[M + SnEt_3]^+$, 100%; m/z 625 $[M + K]^+$, 38%; m/z 609 $[M + Na]^+$, 64%; m/z 587 $[M + H]^+$, 6%; m/z 557 $[M + H - ethane]^+$, 6%; m/z 445 $[CH_3OSnEt_3 + SnEt_3]^+$, 4%; m/z 431 $[HOSnEt_3 + SnEt_3 + H]^+$, 8%; m/z 207 $[SnEt_3]^+$, 7%; m/z 179 $[HSnEt_2]^+$, 7%; m/z 151 $[H_2SnEt]^+$, 18%; m/z 123 $[H_3Sn]^+$, 12%. MS/MS of 1195: m/z 609 $[M + Na]^+$. MS/MS of 793: m/z 557 $[M + H - ethane]^+$; m/z 333 $[M + H - SnEt_4 - H_2O]^+$. MS/MS of 609: m/z 549 $[M + Na - 2 * ethane]^+$; m/z 385 $[M + Na - HOSnEt_3]^+$; m/z 315 $[LSn + Na]^+$. MS/MS of 587: m/z 557 $[M + H - ethane]^+$; m/z 351 $[M + H - SnEt_4]^+$; m/z 333 $[M + H - SnEt_4 - H_2O]^+$. MS/MS of 431: m/z 225 $[SnEt_3 + H_2O]^+$; m/z 207 $[SnEt_3]^+$; m/z 197 $[HSnEt_2 + H_2O]^+$; m/z 179 $[HSnEt_2]^+$; m/z 151 $[H_2SnEt]^+$; m/z 123 $[H_3Sn]^+$. MS/MS of 207: m/z 225 $[SnEt_3 + H_2O]^+$; m/z 197 $[HSnEt_2 + H_2O]^+$; m/z 179 $[HSnEt_2]^+$; m/z 151 $[H_2SnEt]^+$; m/z 123 $[H_3Sn]^+$. MS/MS of 179: m/z 197 $[HSnEt_2 + H_2O]^+$; m/z 169 $[H_2SnEt + H_2O]^+$; m/z 151 $[H_2SnEt]^+$. MS/MS of 151: m/z 169 $[H_2SnEt + H_2O]^+$; m/z 141 $[H_3Sn + H_2O]^+$; m/z 123 $[H_3Sn]^+$. Negative-ion MS: m/z 965 $[2 * M - SnEt_3]^-$, 3%; m/z 729 $[M - Et + L]^-$, 3%; m/z 645, 2%; m/z 379 $[M - SnEt_3]^-$, 100%; m/z 173 $[LH]^-$, 9%; m/z 155 $[LH - H_2O]^-$, 7%; m/z 137 $[LH - 2 * H_2O]^-$, 5%; m/z 111 $[LH - H_2O - CO_2]^-$, 6%. MS/MS of 965: m/z 379 $[M - SnEt_3]^-$. MS/MS of 729: m/z 379 $[M - SnEt_3]^-$; m/z 349 $[M - SnEt_3 - ethane]^-$. MS/MS of 379: m/z 349 $[M - SnEt_3 - ethane]^-$; m/z 155 $[LH - H_2O]^-$; m/z 137 $[LH - 2 * H_2O]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 173: m/z 155 $[LH - H_2O]^-$; m/z 137 $[LH - 2 * H_2O]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 155: m/z 137 $[LH - 2 * H_2O]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 137: m/z 93 $[LH - 2 * H_2O - CO_2]^-$. MS/MS of 129: m/z 111 $[LH - H_2O - CO_2]^-$. IR analysis (nujol mulls): 1725 ($\nu(CO)$, s), 1570–1550 ($\nu_{as}(CO_2)$, vs), 1450 (nujol), 1430 (vs), 1400 (s), 1370 (nujol), 1090 (m), 880 (m), 670 (m), 520 (w); ($CHCl_3$ solution): 1720 ($\nu(CO)$, s), 1640 ($\nu_{as}(CO_2)$, vs), 1360 ($\nu_s(CO_2)$, s), 1270 (s), 1100 (m), 1010 (s), 660 (m), 520 (m) cm^{-1} . Elemental analysis found: C, 39.0%; H, 6.5%. Calculated: C, 39.08%; H, 6.56%.

5.8. Bis(tributyltin)-4-oxoheptanedioate (3)

The mixture of ketopimelic acid (1 g; 5.747 mmol) and $(Bu_3Sn)_2O$ (3.08 g; 5.72 mmol) was refluxed in toluene (50 ml) for 2 h. The mixture was cooled and filtered. The mother liquor was evaporated to give **3** as pure crystalline product (3.78 g; 87%), mp: 92–95 °C.

1H NMR ($CDCl_3$, 300 K, ppm): 2.67 (4H, t, H-2), 2.52 (4H, t, H-1), 1.56 (12H, m, Bu), 1.29 (12H, m, Bu), 1.18 (12H, m, Bu), 0.87 (18H, t, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): 207.86 ($C=O$), 178.02 ($COOSn$), 38.42 (C-2'), 28.81 (C-1'), 27.95 (C-2), $^2J(^{119}Sn, ^{13}C) = 20.17$ Hz; 27.2 (C-3), $^3J(^{119}Sn, ^{13}C) = 64.6$ Hz; 16.6 (C-1), $^1J(^{119}Sn, ^{13}C) = 361.4$ Hz; 13.78 (C-4). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): 108.2. Positive-ion MS: m/z 1045 $[M + SnBu_3]^+$, 100%; m/z 793 $[M + K]^+$, 3%; m/z 777 $[M + Na]^+$, 6%; m/z 755 $[M + H]^+$, 1%; m/z 613 $[CH_3OSnBu_3 + SnBu_3]^+$,

m/z 599 $[HOSnBu_3 + SnBu_3]^+$, 100%; m/z 291 $[SnBu_3]^+$, 39%; m/z 235 $[HSnBu_2]^+$, 31%; m/z 179 $[H_2SnBu]^+$, 67%; m/z 123 $[SnH_3]^+$, 36%. MS/MS of 1045: m/z 697 $[M + H - butane]^+$; m/z 389 $[M + H - H_2O - SnBu_4]^+$; m/z 291 $[SnBu_3]^+$. MS/MS of 793: m/z 677 $[M + K - 2 * butane]^+$; m/z 621 $[M + K - 2 * butane - butene]^+$. MS/MS of 777: m/z 607 $[M + Na - 2 * butene - butane]^+$; m/z 487 $[M + Na - Bu=SnBu_2]^+$; m/z 469 $[M + Na - HOSnBu_3]^+$; m/z 441 $[M + Na - HSnBu_3 - CO_2]^+$; m/z 315 $[LSn + Na]^+$. MS/MS of 755: m/z 697 $[M + H - butane]^+$; m/z 407 $[M + H - SnBu_4]^+$; m/z 389 $[M + H - H_2O - SnBu_4]^+$; m/z 291 $[SnBu_3]^+$. MS/MS of 599: m/z 291 $[SnBu_3]^+$; m/z 253 $[HSnBu_2 + H_2O]^+$; m/z 235 $[HSnBu_2]^+$; m/z 197 $[H_2SnBu + H_2O]^+$; m/z 179 $[H_2SnBu]^+$. MS/MS of 291: m/z 235 $[HSnBu_2]^+$; m/z 179 $[H_2SnBu]^+$. MS/MS of 235: m/z 179 $[H_2SnBu]^+$. Negative-ion MS: m/z 1217 $[2 * M - SnBu_3]^-$, 8%; m/z 785 $[M - H + CH_3OH]^-$, 3%; m/z 463 $[M - SnBu_3]^-$, 100%; m/z 379 $[SnBu_4 - H + CH_3OH]^-$, 7%; m/z 173 $[LH]^-$, 6%; m/z 155 $[LH - H_2O]^-$, 8%; m/z 137 $[LH - 2 * H_2O]^-$, 4%; m/z 129 $[LH - CO_2]^-$, 1%; m/z 111 $[LH - H_2O - CO_2]^-$, 3%. MS/MS of 1217: m/z 463 $[M - SnBu_3]^-$. MS/MS of 785: m/z 463 $[M - SnBu_3]^-$; m/z 405 $[M - SnBu_3 - butane]^-$; m/z 379 $[SnBu_4 - H + CH_3OH]^-$. MS/MS of 463: m/z 405 $[M - SnBu_3 - butane]^-$; m/z 155 $[LH - H_2O]^-$; m/z 137 $[LH - 2 * H_2O]^-$. MS/MS of 173: m/z 155 $[LH - H_2O]^-$; m/z 137 $[LH - 2 * H_2O]^-$; m/z 129 $[LH - CO_2]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 155: m/z 137 $[LH - 2 * H_2O]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 137: m/z 93 $[LH - 2 * H_2O - CO_2]^-$. MS/MS of 129: m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 111: m/z 93 $[LH - 2 * H_2O - CO_2]^-$; m/z 83 $[LH - H_2O - CO - CO_2]^-$; m/z 67 $[LH - H_2O - 2 * CO_2]^-$. IR analysis (nujol mulls): 1730 ($\nu(CO)$, s), 1575–1555 ($\nu_{as}(CO_2)$, vs), 1455 (nujol), 1420, 1390 (nujol), 1090 (w), 880 (m), 660 (m); ($CHCl_3$ solution): 1720 ($\nu(CO)$, s), 1650 ($\nu_{as}(CO_2)$, vs), 1470 (s), 1380 ($\nu_s(CO_2)$, s), 1270 (s), 1100 (m), 870 (m), 660 (m) cm^{-1} . Elemental analysis found: C, 49.5%; H, 8.3%. Calculated: C, 49.50%; H, 8.31%.

5.9. Bis(tribenzyltin)-4-oxoheptanedioate (4)

To a solution of ketopimelic acid (0.5 g; 2.874 mmol) in isopropanol (30 ml) was added KOH (0.32 g; 7.356 mmol, 13% excess) and Bz_3SnCl (2.45 g; 5.747 mmol). The mixture was stirred for 3 h. The reaction gave after filtration **4** white crystalline material (1.61 g; 64%), mp: >250 °C. The sample for NMR study was crystallized from methanol. 1H NMR ($CDCl_3$, 300 K, ppm): 7.04 (12H, m, H-3), 6.91 (18H, m, H-4, 5), 4.90 (MeOH), 3.90 (MeOH), 2.36 (12H, s, H-1), 2.33 (4H, t, H-2'), 2.05 (4H, t, H-1'). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): 207.66 ($C=O$), 178.86 ($COOSn$), 139.05 (C-2), 128.8 (C-3), 128.02 (C-4), 124.6 (C-5), 50.12 (MeOH), 38.25 (C-2'), 28.46 (C-1'), 24.18 (C-1), $^1J(^{119}Sn, ^{13}C) = 310.0$ Hz. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): -13.4. Positive-ion MS: m/z 1351

$[M + SnBz_3]^+$, 1%; m/z 997 $[M + K]^+$, 4%; m/z 803 $[HOSnBz_3 + SnBz_3 + H]^+$, 8%; m/z 393 $[SnBz_3]^+$, 4%; m/z 211 $[SnBz]^+$, 100%. MS/MS of 1351: m/z 867 $[M + H - toluene]^+$. MS/MS of 997: m/z 813 $[M + K - 2 * toluene]^+$; m/z 331 $[LSn + K]^+$. MS/MS of 803: m/z 527 $[(SnBz_3)_2O + H - 3 * toluene]^+$; m/z 411 $[SnBz_3 + H_2O]^+$; m/z 393 $[SnBz_3]^+$. MS/MS of 211: m/z 121 $[HSn]^+$; m/z 91 $[Bz]^+$. Negative-ion MS: m/z 1167, 2%; m/z 565 $[M - SnBz_3]^-$, 100%; m/z 463, 11%; m/z 383 $[M - SnBz_3 - 2 * 91]^-$, 11%; m/z 211 $[L + K]^-$, 47%; m/z 193 $[L + K - H_2O]^-$, 14%; m/z 173 $[LH]^-$, 9%; m/z 155 $[LH - H_2O]^-$, 7%; m/z 137 $[LH - 2 * H_2O]^-$, 5%; m/z 129 $[LH - CO_2]^-$, 3%; m/z 111 $[LH - H_2O - CO_2]^-$, 6%. MS/MS of 565: m/z 473 $[M - SnBz_3 - toluene]^-$; m/z 383 $[M - SnBz_3 - 2 * 91]^-$; m/z 291 $[M - SnBz_3 - 2 * Bz - toluene]^-$. MS/MS of 211: m/z 193 $[L + K - H_2O]^-$. MS/MS of 173: m/z 155 $[LH - H_2O]^-$; m/z 137 $[LH - 2 * H_2O]^-$; m/z 129 $[LH - CO_2]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 155: m/z 137 $[LH - 2 * H_2O]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 137: m/z 93 $[LH - 2 * H_2O - CO_2]^-$. MS/MS of 129: m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 111: m/z 93 $[LH - 2 * H_2O - CO_2]^-$; m/z 83 $[LH - H_2O - CO - CO_2]^-$; m/z 67 $[LH - H_2O - 2 * CO_2]^-$. IR analysis (nujol mulls): 1700 ($\nu(CO)$, m), 1570 ($\nu_{as}(CO_2)$, vs), 1480 (m), 1455 (nujol), 1370 (nujol), 1205 (m), 755 (m), 695 (m), 545 (w); ($CHCl_3$ solution): 1705 ($\nu(CO)$, s), 1600 ($\nu_{as}(CO_2)$, vs), 1550 ($\nu_{as}(CO_2)$, vs), 1390 (vs), 1455 (s), 1400 ($\nu_s(CO_2)$, s), 1350 ($\nu_s(CO_2)$, s), 1030 (m), 1000 (m), 830 (m), 695 (vs) cm^{-1} . Elemental analysis found: C, 61.5%; H, 5.2%. Requires: C, 61.54%; H, 5.27%.

5.10. Bis(tricyclohexyltin)-4-oxoheptanedioate (5)

Bis(tricyclohexyltin)-4-oxoheptanedioate was prepared by reaction of 4-ketopimelic acid (0.5 g; 2.874 mmol) by *c*-Hex₃SnCl (1.386 g; 5.747 mmol) and KOH (0.482 g; 11.08 mmol, 19% excess) in refluxing isopropanol. After 2 h the mixture was cooled and filtered then the solvent was evaporated. Pure **5** was obtained (1.21 g; 46%), mp: 110–114 °C. ¹H NMR ($CDCl_3$, 300 K, ppm): 2.73 (4H, t, H-2'), 2.57 (4H, t, H-1'), 1.86 (24H, m, C-2), 1.64 (36H, m, C-1, C-4), 1.30 (24H, m, C-3). ¹³C{¹H} NMR ($CDCl_3$, 300 K, ppm): 207.99 (C=O), 177.91 (COOSn), 38.69 (C-2'), 28.96 (C-1'), 33.89 (C-1), ¹J(¹¹⁹Sn, ¹³C) = 325.1 Hz; 31.23 (C-2), ²J(¹¹⁹Sn, ¹³C) = 14.1 Hz; 29.10 (C-3), ³J(¹¹⁹Sn, ¹³C) = 64.8 Hz; 27.09 (C-4). ¹¹⁹Sn NMR ($CDCl_3$, 300 K, ppm): 13.5. Positive-ion MS: m/z 1279 $[M + Sn - c - Hex_3]^+$, 6%; m/z 949 $[M + K]^+$, 2%; m/z 933 $[M + Na]^+$, 3%; m/z 911 $[M + H]^+$, 5%; m/z 769 $[CH_3OSn - c - Hex_3 + Snc - Hex_3]^+$, 5%; m/z 755 $[HOSnc - Hex_3 + Snc - Hex_3]^+$, 100%; m/z 369 $[Snc - Hex_3]^+$, 15%; m/z 287 $[HSnc - Hex_2]^+$, 12%; m/z 205 $[H_2Snc - Hex]^+$, 10%. MS/MS of 1279: m/z 369 $[Snc - Hex_3]^+$. MS/MS of 949: m/z 331 $[LSn + K]^+$. MS/MS of 933: m/z 565 $[Snc - Hex_3 + LH + Na]^+$; m/z 315 $[LSn + Na]^+$. MS/MS of 911: m/z 827 $[M + H - c$

hexane]⁺; m/z 369 $[Snc - Hex_3]^+$; m/z 287 $[HSnc - Hex_2]^+$. MS/MS of 755: m/z 369 $[Snc - Hex_3]^+$; m/z 305 $[HSnc - Hex_2 + H_2O]^+$; m/z 287 $[HSnc - Hex_2]^+$. MS/MS of 369: m/z 305 $[HSnc - Hex_2 + H_2O]^+$; m/z 287 $[HSnc - Hex_2]^+$; m/z 223 $[H_2Snc - Hex + H_2O]^+$; m/z 205 $[H_2Snc - Hex]^+$. MS/MS of 287: m/z 305 $[HSnc - Hex_2 + H_2O]^+$; m/z 223 $[H_2Snc - Hex + H_2O]^+$; m/z 205 $[H_2Snc - Hex]^+$. MS/MS of 205: m/z 223 $[H_2Snc - Hex + H_2O]^+$; m/z 121 $[SnH]^+$; m/z 81 $[cyclohexadiene + H]^+$. Negative-ion MS: m/z 1451 $[2 * M - Snc - Hex_3]^-$, 4%; m/z 541 $[M - Snc - Hex_3]^-$, 100%; m/z 173 $[M + H - 2 * Snc - Hex_3]^-$, 28%. MS/MS of 1451: m/z 541 $[M - Snc - Hex_3]^-$. MS/MS of 989: m/z 541 $[M - Snc - Hex_3]^-$. MS/MS of 945: m/z 541 $[M - Snc - Hex_3]^-$. MS/MS of 541: m/z 457 $[M - Snc - Hex_3 - cyclohexane]^-$; m/z 375 $[M - Snc - Hex_3 - cyclohexane - cyclohexene]^-$; m/z 173 $[LH]^-$; m/z 155 $[LH - H_2O]^-$. MS/MS of 173: m/z 155 $[LH - H_2O]^-$; m/z 137 $[LH - 2 * H_2O]^-$; m/z 129 $[LH - CO_2]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. IR analysis (nujol mulls): 1720 ($\nu(CO)$, s), 1635 ($\nu_{as}(CO_2)$, vs), 1450 (nujol), 1375 (nujol), 1260 (m), 1170 (m), 990 (m); ($CHCl_3$ solution): 1720 ($\nu(CO)$, s), 1640 ($\nu_{as}(CO_2)$, vs), 1450 (vs), 1350 ($\nu_s(CO_2)$, s), 1270 (s), 1170 (s), 1100 (m), 990 (s), 880 (m), 840 (m); (KBr disc): 1725 ($\nu(CO)$, s), 1645 ($\nu_{as}(CO_2)$, vs), 1575 ($\nu_{as}(CO_2)$, m), 1450 (s), 1405 ($\nu_s(CO_2)$, w), 1350 ($\nu_s(CO_2)$, m), 1310 (s), 1260 (s), 1090 (s), 990 (s), 880 (m), 840 (m), 800 (m) cm^{-1} . Elemental analysis found: C, 56.8%; H, 8.2%. Calculated: C, 56.85%; H, 8.21%.

5.11. Bis(triphenyltin)-4-oxoheptanedioate (6)

Bis(triphenyltin)-4-oxoheptanedioate was obtained by the reaction of ketopimelic acid (1 g; 5.747 mmol) with KOH (0.8 g; 16.66 mmol; 14.5% excess) and Ph₃SnCl (3.54 g; 11.494 mmol). This mixture was refluxed in isopropanol (50 ml) for 3 h. The cooled mixture was filtered. The solvent was removed in vacuo and **6** was isolated as a white solid (2.32 g; 46%), mp: 189–191 °C. ¹H NMR ($DMSO-d_6$, 300 K, ppm): 7.56 (12H, d, H-2), 7.12 (18H, m, H-3, 4), 2.16(4H, t, H-2'), 1.93 (4H, t, H-1'). ¹³C{¹H} NMR ($DMSO-d_6$, 300 K, ppm): 209.52 (C=O), 175.43 (COOSn), 145.35 (C-1); 136.5 (C-2), ²J(¹¹⁹Sn, ¹³C) = 45.8; 128.35 (C-4), 127.9 (C-3), ³J(¹¹⁹Sn, ¹³C) = 70.8; 38.41 (C-2'), 30.94 (C-1'). ¹¹⁹Sn{¹H} NMR ($DMSO-d_6$, 300 K, ppm): -272.9. Positive-ion MS: m/z 1225 $[M + SnPh_3]^+$, 8%; m/z 913 $[M + K]^+$, 9%; m/z 733 $[CH_3OSnPh_3 + SnPh_3]^+$, 27%; m/z 719 $[HOSnPh_3 + SnPh_3 + H]^+$, 100%; m/z 638, 15%; m/z 406 $[SnPh_3 + CH_3ONa]^+$, 12%; m/z 351 $[SnPh_3]^+$, 87%. MS/MS of 1225: m/z 797 $[M + H - benzene]^+$; m/z 719 $[M + H - 2 * benzene]^+$. MS/MS of 733: m/z 407 $[HSnPh_3 + CH_3ONa + H]^+$; m/z 351 $[SnPh_3]^+$. MS/MS of 719: m/z 659 $[HOSnPh_3 + SnPh_3 + H - benzene + H_2O]^+$; m/z 581 $[HOSnPh_3 + SnPh_3 + H - 2 * benzene + H_2O]^+$; m/z 407 $[HSnPh_3 + CH_3ONa + H]^+$; m/z 351 $[SnPh_3]^+$.

Negative-ion MS: m/z 1083, 4%; m/z 523 $[M - SnPh_3]^-$, 100%; m/z 351 $[SnPh_3]^-$, 42%; m/z 211 $[L + K]^-$, 93%; m/z 193 $[L + K - H_2O]^-$, 52%; m/z 173 $[LH]^-$, 37%; m/z 155 $[LH - H_2O]^-$, 56%; m/z 137 $[LH - 2 * H_2O]^-$, 72%; m/z 129 $[LH - CO_2]^-$, 11%; m/z 111 $[LH - H_2O - CO_2]^-$, 44%. MS/MS of 523: m/z 445 $[M - SnPh_3 - benzene]^-$; m/z 155 $[LH - H_2O]^-$. MS/MS of 439: m/z 351 $[SnPh_3]^-$. MS/MS of 211: m/z 193 $[L + K - H_2O]^-$. MS/MS of 173: m/z 155 $[LH - H_2O]^-$; m/z 137 $[LH - 2 * H_2O]^-$; m/z 129 $[LH - CO_2]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 155: m/z 137 $[LH - 2 * H_2O]^-$; m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 137: m/z 93 $[LH - 2 * H_2O - CO_2]^-$. MS/MS of 129: m/z 111 $[LH - H_2O - CO_2]^-$. MS/MS of 111: m/z 93 $[LH - 2 * H_2O - CO_2]^-$; m/z 83 $[LH - H_2O - CO - CO_2]^-$; m/z 67 $[LH - H_2O - 2 * CO_2]^-$. IR analysis (nujol mulls): 1720–1700 ($\nu(CO)$, s), 1540 ($\nu_{as}(CO_2)$, vs), 1460 (nujol), 1430, 1375 (nujol), 1080 (w), 730 (m), 700 (m), 450 (w) cm^{-1} . Elemental analysis found: C, 59.2%; H, 4.3%. Calculated: C, 59.22%; H, 4.39%.

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