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Coordination polymers constructed from triorganotin(IV) nodes and fumarato spacers

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ABSTRACT

Two novel coordination polymers have been constructed from triorganotin nodes, $\{R_3Sn\}$, and fumarato (fum^{2-}) spacers: $^{2}_{\infty}[(Me_3Sn)_2(fum)]$ **1** and $^{3}_{\infty}[(^nBu_3Sn)_2(fum)]$ **2**. In both compounds the fumarato ion acts as a tetradentate ligand and the tin atoms are 5-coordinate with a trigonal bipyramidal geometry, with the apical positions occupied by oxygen atoms from the fum^{2-} ligands. The crystal structure of **1** consists of infinite parquet-like layers (2-D), formed by coordination driven self-assembly. Compound **2** is a 3-D self-assembled polymer, whose architecture results by fusing two types of metallacycles, each one containing six tin atoms. The multinuclear NMR spectra of the solutions obtained by dissolving compounds **1** and **2** in $CDCl_3$ and DMSO-d_6 indicate that the polymeric structures are not preserved.

1. Introduction

Organotin(IV) halides, R_nSnX_{4-n}, are useful building-blocks in designing oligonuclear tin(IV) complexes, as well as 1-D, 2-D or 3-D polymers formed by coordination driven self-assembly. They are quite robust and good Lewis acids, the tin-carbon bond being rather stable towards air and water. Moreover, tin(IV) has a strong tendency to increase its coordination number above four, facilitating the formation of multinuclear species when appropriate ligands are employed. The corresponding organotin(IV) $\{R_nSn\}$ groups interact easily with, for example, carboxylate ions [1] or pyridyl-based ligands [2]. The richness of this chemistry is based upon the large number of organotin(IV) halides available, which result by changing the number and nature of the organic groups bound to tin. The high interest in these compounds arises from their catalytic [3] and biological properties [4]. Let us recall here several representative examples. Numerous multinuclear complexes have been obtained using polycarboxylato ligands. Dakternieks et al. described a trinuclear complex that results from the reaction of triphenyltin chloride with trimesic acid in toluene [5]. Each tin atom is coordinated by three phenyl groups and by a carboxylato oxygen atom. A similar compound was obtained starting from trimethyltin(IV) chloride [6]. The reaction between tri-*n*-butyltin chloride and *meso*-2,3-dibromosuccinic acid in the presence of sodium ethoxide affords an interesting 3-D coordination polymer in which the carboxylate groups from the spacers are coordinated into the apical positions of the five-coordinated tin atoms [7]. The anions of nicotinic, isonicotinic, and quinaldic acids have been employed as *N,O*-ligands [8]. For the nicotinato and isonicotinato ligands, 1-D coordination polymers with $\{Me_3Sn\}$ nodes have been assembled [9]. Starting from Bz_2SnCl_2 or Bz_3SnCl (Bz = benzyl) and using Schiff-base ligands derived from amino-acids, Basu Baul et al. obtained a series of oligonuclear complexes and coordination polymers and, for some of them, the cytotoxic activity was tested [10]. The 3-D coordination polymers constructed from $\{R_nSn\}$ nodes have also relevance in MOF chemistry. For example, Chandrasekhar et al. obtained a trimethyltin coordination polymer with a sqc topology, using imidazole-4,5-dicarboxylate as a spacer [11]. This compound shows selective gas adsorption, preferring CO_2/H_2 over N_2. This chemistry was further enlarged with heterometallic systems containing tin and a transition metal ion. Such compounds, with a rich structural variety, have been obtained using

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polycyanidometallo ligands: $[Fe(CN)_6]^{n-}$ (n = 3, 4), $[Cu(CN)_3]^{2-}$, $[M(CN)_2]^-$ (M = Ag, Au) [12]. In 2015, atmospheric CO_2 capture was described during the reaction of Ph_3SnCl and 1,2-bis(4-pyridyl) ethane leading to polynuclear carbonate-bridged species [13] In this paper we report on two novel 2-D and 3-D coordination polymers constructed from triorganotin moieties and fumarato bridges, which are formed by coordination driven self-assembly processes.

2. Experimental part

2.1. Syntheses

The reagents employed in this study were purchased from commercial sources and used without further purification.

Preparation of compound **1**: To a solution of Me_3SnCl (39.8 mg, 0.2 mmol) in methanol was slowly added, under stirring, a solution of fumaric acid (11.6 mg, 0.1 mmol) in methanol, deprotonated with a slight excess of aqueous NaOH solution. The turbid reaction mixture was stirred for an hour and then filtered. Good quality transparent, colorless, cubic single crystals were obtained, by slow evaporation of the solvent, in two weeks. Yield: 65% (based on tin). Anal. Calcd for $C_5H_{10}O_2Sn$ (%): C, 27.19; H, 4.56. Found (%): C, 27.06; H, 4.49. IR (KBr, pellets, cm^{-1}): 552vs, 573m, 690vs, 778vs, 978s, 1190m, 1210m, 1353vs, 1576vs, 2923m, 2996m.

Preparation of compound **2**: Compound **2** was obtained following the same procedure as for compound **1**. To a solution of Bu_3SnCl (48.8 mg, 0.15 mmol) in methanol was slowly added, under stirring, a solution of fumaric acid (11.6 mg, 0.1 mmol) in methanol, deprotonated with a slight excess of aqueous NaOH solution. The obtained reaction mixture was stirred for an hour and then filtered. Colorless, transparent, single crystals were obtained, by slowly evaporation of the solvent, in almost one week. Yield: 55% (based on tin). Anal. Calcd for $C_{12}H_{27}ClSn$ (%): C, 44.28; H, 8.36. Found (%): C, 44.16; H, 8.49. IR (KBr, pellets, cm^{-1}): 506m, 556s, 607m, 746w, 795w, 876w, 981m, 1076w, 1183m, 1290m, 1378s, 1416w, 1578vs, 1725m, 2855m, 2871m, 2923s, 2957vs.

2.2. Physical measurements and elemental analysis

IR spectra were recorded on a FTIR Bruker Tensor V-37

Table 1
Crystal data and structure refinement parameters for compounds **1** and **2**.

	1	2
Formula	$C_5H_{10}O_2Sn$	$C_{84}H_{168}O_{12}Sn_6$
Formula weight/g mol^{-1}	220.82	2082.31
T/K	293	293
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Trigonal
Space group	C 2/c	P 32
Unit cell		
a/Å	13.0015(12)	25.820(4)
b/Å	9.5157(7)	25.820(4)
c/Å	13.1929(12)	13.421(3)
α/deg	90	90
β/deg	110.834(7)	90
γ/deg	90	120
V/$Å^3$	1525.5(2)	7749(3)
Z	8	3
Calculated density/g cm^{-3}	1.923	1.328
Absorption coefficient/cm^{-1}	3.272	1.475
F(000)	848	3156
Crystal size/mm × mm × mm	0.55 × 0.4 x 0.4	0.5 × 0.35 x 0.2
θ range/deg	2.719 to 26.998	1.770 to 26.995
Limiting indices	$-16 < h < 16$, $-12 < k < 12$, $-16 < l < 13$	$-32 < h < 32$, $-32 < k < 32$, $-17 < l < 17$
Collected reflections	4367	99212
Symmetry independent reflections	1654	22524
R_{int}	0.0389	0.0705
Data/restraints/parameters	1654/0/73	22524/45/612
GOF on F^2	1.156	1.033
Final R indices	R1 = 0.0238 wR2 = 0.0616	R1 = 0.0918 wR2 = 0.2563
Largest diff peak and hole/e $Å^{-3}$	0.963 and −0.576	4.643 and −1.475

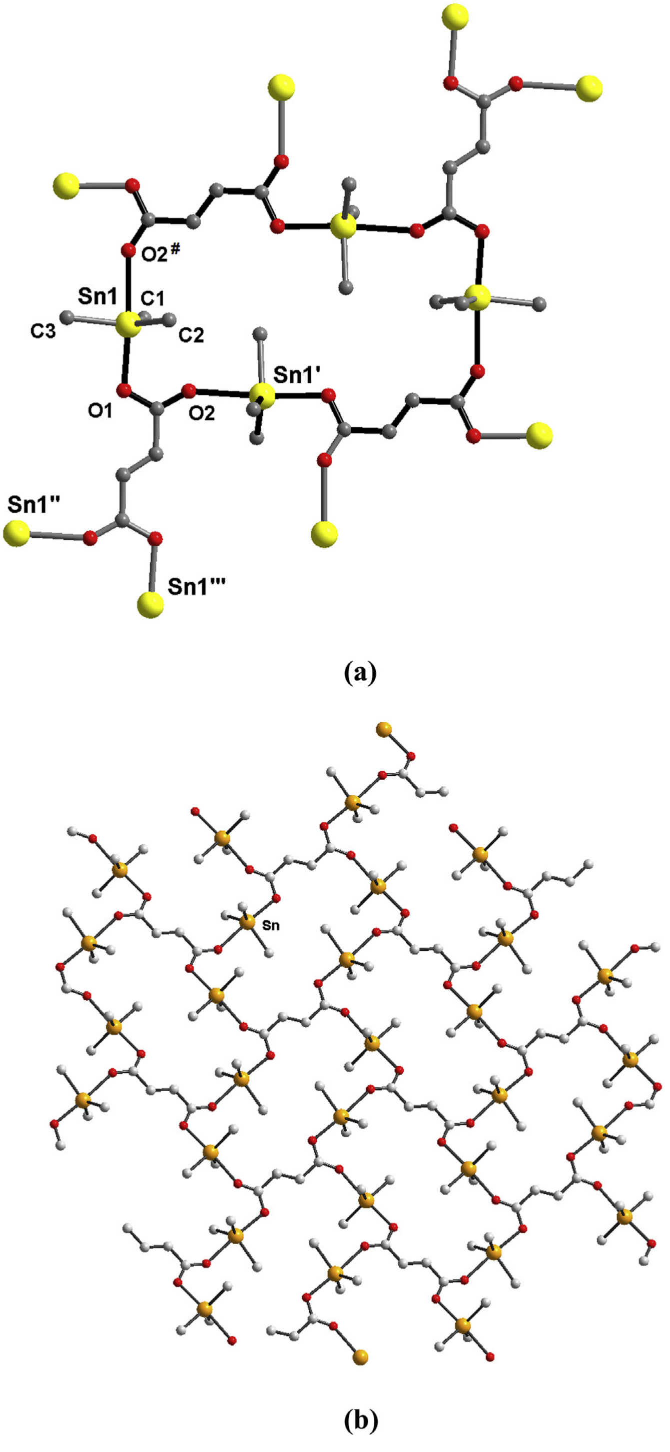

Fig. 1. (a) Repeating motif (bonds drawn in black) within the 2-D coordination polymer **1** (' = 1.5−*x*, −0.5 + *y*, 0.5−*z*;" = −0.5 + *x*, 0.5−*y*, −0.5 + *z*;''' = 1−*x*, −*y*, −*z*); (b) Perspective view of one layer.

spectrophotometer (KBr pellets) in the range of 4000–400 cm^{-1}. Elemental analyses (C, H, N) were performed on a EuroEA Elemental Analyzer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at room temperature on a Bruker Avance III 400 and 600 instruments, while ^{119}Sn NMR spectra were recorded on a Bruker Avance III 400 instrument. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent ($CDCl_3$, 7.26 ppm; DMSO-d_6, 2.50 ppm) [14]. The ^{13}C{^{1}H} chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent ($CDCl_3$, 77.16 ppm; DMSO-d_6: 39.52 ppm) [14]. The ^{119}Sn chemical shifts are quoted in δ units (ppm) relative to $SnMe_4$ as the external standard. The NMR spectra were processed using the *MestReNova* software [15].

$^{2}_{\infty}[(Me_3Sn)_2(fum)]$ **1**: ^{1}H NMR (DMSO-d_6, 600.13 MHz) δ[ppm]: 0.40 (s, 18H, $SnCH_3$, $^{2}J_{SnH}$ 69.0 Hz), 6.28 (s, 2H, $CH{=}CH$). ^{13}C NMR (DMSO-d_6, 150.90 MHz) δ[ppm]: 0.48 (s, $SnCH_3$, $^{1}J_{SnC}$ 522.4 Hz), 135.33 (s, $CH{=}CH$), 169.13 (s, COO). ^{119}Sn (DMSO-d_6, 149.21 MHz) δ [ppm]: −16.4 (s, br).

$^{3}_{\infty}[(^{n}Bu_3Sn)_2(fum)]$ **2**: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ[ppm]: 0.90 (t, 18H, $SnCH_2CH_2CH_2CH_3$, $^{3}J_{HH} = 7.3$ Hz), 1.28 (t, 12H, $SnCH_2CH_2CH_2CH_3$, $^{3}J_{HH} = 8.0$ Hz, $^{2}J_{SnH} = 51.9$ Hz), 1.36 (tq, 12H, $SnCH_2CH_2CH_2CH_3$, $^{3}J_{HH} = 7.4$ Hz), 1.61 (tt, 12H, $SnCH_2CH_2CH_2CH_3$, $^{3}J_{HH} = 7.7$ Hz, $^{3}J_{SnH} = 63.8$ Hz), 6.77 (s, 2H, $CH{=}CH$). ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ[ppm]: 13.80 (s, C_δ), 16.69(s, C_α, $^{1}J_{117/119SnC}$ 339.7/355.8 Hz), 27.17 (s, C_γ, $^{3}J_{SnC}$ 65.1 Hz), 27.91 (s, C_β, $^{2}J_{SnC}$ 20.8 Hz), 134.84 (s, $CH{=}CH$), 170.72 (s, COO). ^{119}Sn ($CDCl_3$, 149.21 MHz) δ [ppm]: 121.4 (s).

^{1}H NMR (DMSO-d_6, 400.13 MHz) δ[ppm]: 0.84 (t, 18H, $SnCH_2CH_2CH_2CH_3$, $^{3}J_{HH} = 7.3$ Hz), 1.05 (m, 12H, $SnCH_2CH_2CH_2CH_3$, $^{2}J_{SnH} = 62.6$ Hz), 1.28 (tq, 12H, $SnCH_2CH_2CH_2CH_3$, $^{3}J_{HH} = 7.4$ Hz), 1.55 (tt, 12H, $SnCH_2CH_2CH_2CH_3$, $^{3}J_{HH} = 7.7$ Hz, $^{3}J_{SnH} = 62.1$ Hz), 6.31 (s, 2H, $CH{=}CH$). ^{119}Sn (DMSO-d_6, 149.21 MHz) δ[ppm]: −26.4 (s, br).

2.3. X-ray data collection and crystal structure refinement

X-ray diffraction measurements were performed on a STOE IPDS II diffractometer, operating with Mo-Kα ($\lambda = 0.71073$ Å) X-ray tube with graphite monochromator. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. The crystal structure of compound **2** was refined as a two component inversion twin. Geometrical restraints were used for the refinement of the *n*-butyl chains. Two tin atoms, Sn4 and Sn5, were found to be disordered over two positions, with s. o. f. of 82/18 and, respectively, 75/25. A summary of the crystallographic data and the structure refinement for crystals **1** and **2** is given in Table 1.

3. Results and discussion

The reactions between Me_3SnCl and, respectively, $^{n}Bu_3SnCl$ with fumaric acid, deprotonated with aqueous NaOH solution, were carried out in methanol, in open athmosphere, and afforded two novel, air-stable, coordination polymers: $^{2}_{\infty}[(Me_3Sn)_2(fum)]$ **1** and $^{3}_{\infty}[(^{n}Bu_3Sn)_2(fum)]$ **2**. Both compounds are constructed from triorganotin nodes and fumarato spacers.

3.1. Description of the crystal structures

The crystal structure of **1** consists of infinite parquet-like layers, the tin atoms being crystallographically equivalent. The fumarato

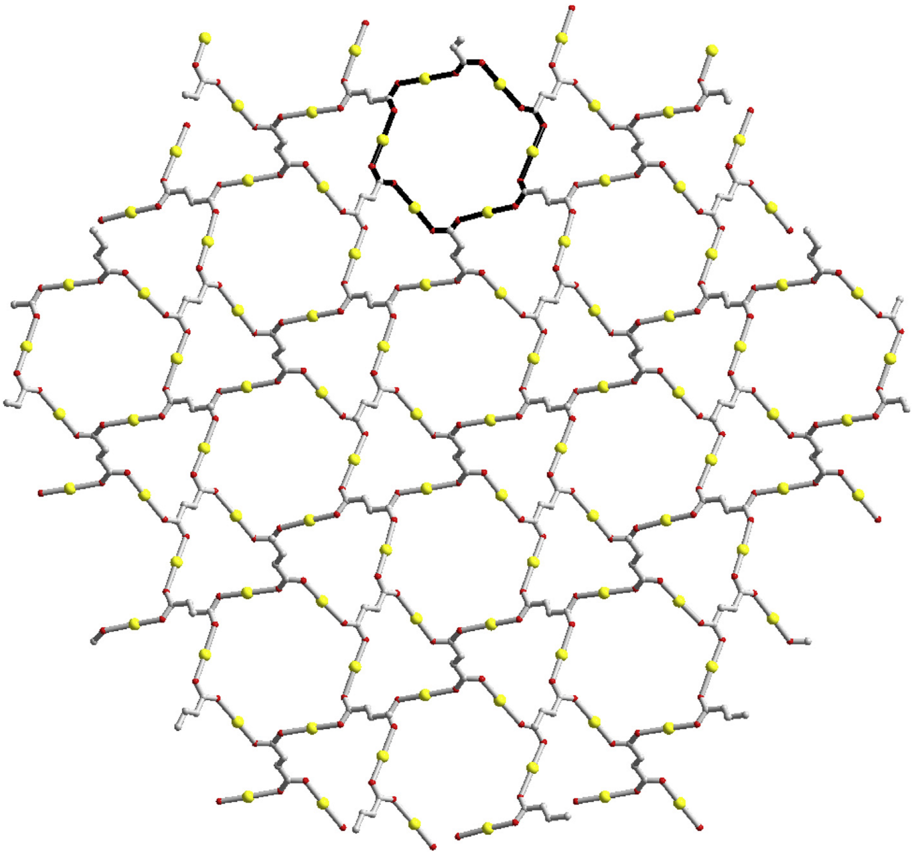

Fig. 2. View along the crystallographic *c* axis of the 3-D network in crystal **2** (the ^{n}Bu groups attached to the tin atoms are removed for clarity).

ion connects four tin atoms, each carboxylato group showing the *syn-anti* bridging mode. The repeating motif is illustrated in Fig. 1a, and a view of the 2-D coordination polymer is shown in Fig. 1b. Each tin atom has a coordination number of five and a trigonal bipyramidal geometry: the equatorial plane is made by three carbon atoms (Sn1−C1 = 2.120(4), Sn1−C2 = 2.109(3), Sn1−C3 = 2.118(3) Å), the apical positions being occupied by the oxygen atoms arising from two carboxylato groups (Sn1−O1 = 2.185(2), Sn1−O2# = 2.443(2) Å; # = 1.5−*x*, 0.5 + *y*, 0.5−*z*). The distances between the tin atoms bridged by the *syn-anti* carboxylato group are Sn1···Sn1' = 5.042 Å (' = 1.5−*x*, −0.5 + *y*, 0.5−*z*), while the distances to the other two tin atoms connected by the same fumarato ligand are: Sn1···Sn1" = 7.769 Å (" = −0.5 + *x*, 0.5−*y*, −0.5 + *z*) and Sn···Sn1‴ = 9.321 Å,‴ = 1−*x*, −*y*, −*z*).

Compound **2** is a 3-D coordination polymer, with a quite interesting architecture. A view along the crystallographic *c* axis is shown in Fig. 2. We notice first the 24-membered hexagonal rings (**A**), with a chair-like conformation, which result by connecting six {^{n}Bu$_3$Sn} nodes by six *syn-anti* carboxylato groups (Fig. 3a and b). The other carboxylato group from the fumarato ligand is involved in the formation of a similar hexagonal ring. Each hexagonal ring is thus connected to six other similar rings, their arrangement generating 36-membered rings (**B**), which also show a chair-like conformation. Each **A** ring is surrounded by six **B** rings, while a **B** ring is surrounded by four **A** rings and four **B** rings (Fig. 3c). A perspective view or the 3-D skafold in compound **2** is shown in Fig. 4. The distances between the tin atoms within a hexagonal ring (**A**) vary between 5.444 and 5.530 Å. The six crystallographically non-equivalent tin atoms are pentacoordinated (trigonal-bipyramidal geometry). The basal plane is formed by three carbon atoms and the apical positions are occupied by carboxylato oxygen atoms. Similar to compound **1**, one of the Sn−O bonds is shorter than the other. For example, in the case of Sn1, the two Sn−O bond lengths are Sn1−O1 = 2.207(16) Å and Sn1−O12 = 2.375(14) Å. Selected bond distances and angles for compounds **1** and **2** are collected in Tables 2 and 3.

3.2. Solution NMR spectra

The coordination polymers usually decompose when solved in polar solvents. In order to investigate the solution behavior of organotin(IV) compounds and to distinguish between molecular structures or oligomeric associations, *i.e.* the coordination geometry at the metal center, the multinuclear NMR studies are generally appropriate. Despite their polymeric structure in solid state, good quality multinuclear NMR spectra could be recorded for both compounds **1** and **2**, which displayed enough solubility in the coordinating DMSO-d$_6$ solvent. While compound **1** was insoluble in CDCl$_3$ and only slightly soluble in DMSO-d$_6$, compound **2** showed enhanced solubility in both solvents, as expected due to the presence of the longer alkyl substituents. Selected data from the room temperature NMR spectra is summarized in Table 4; for comparison, values recorded for the triorganotin(IV) chlorides that were used as starting materials are also included.

Regardless the solvent used, for both compounds **1** and **2** the ^{1}H and ^{13}C NMR spectra acquired at room temperature showed only one set of characteristic resonances for the organic groups bonded to tin and one set of signals for the fumarate fragment, in a 2:1 ratio between R$_3$Sn and fumarate moieties (by integration of the corresponding resonance signals), indicating that a highly symmetrical species is present in solution. Only one resonance was observed in the room temperature ^{119}Sn NMR spectra, consistent with the presence of a dinuclear organotin(IV) species with equivalent tin atoms per "(R$_3$Sn)$_2$(fum)" unit in solution of **1** (in DMSO-d$_6$) and **2** (in both CDCl$_3$ and DMSO-d$_6$). However, while in the coordinating

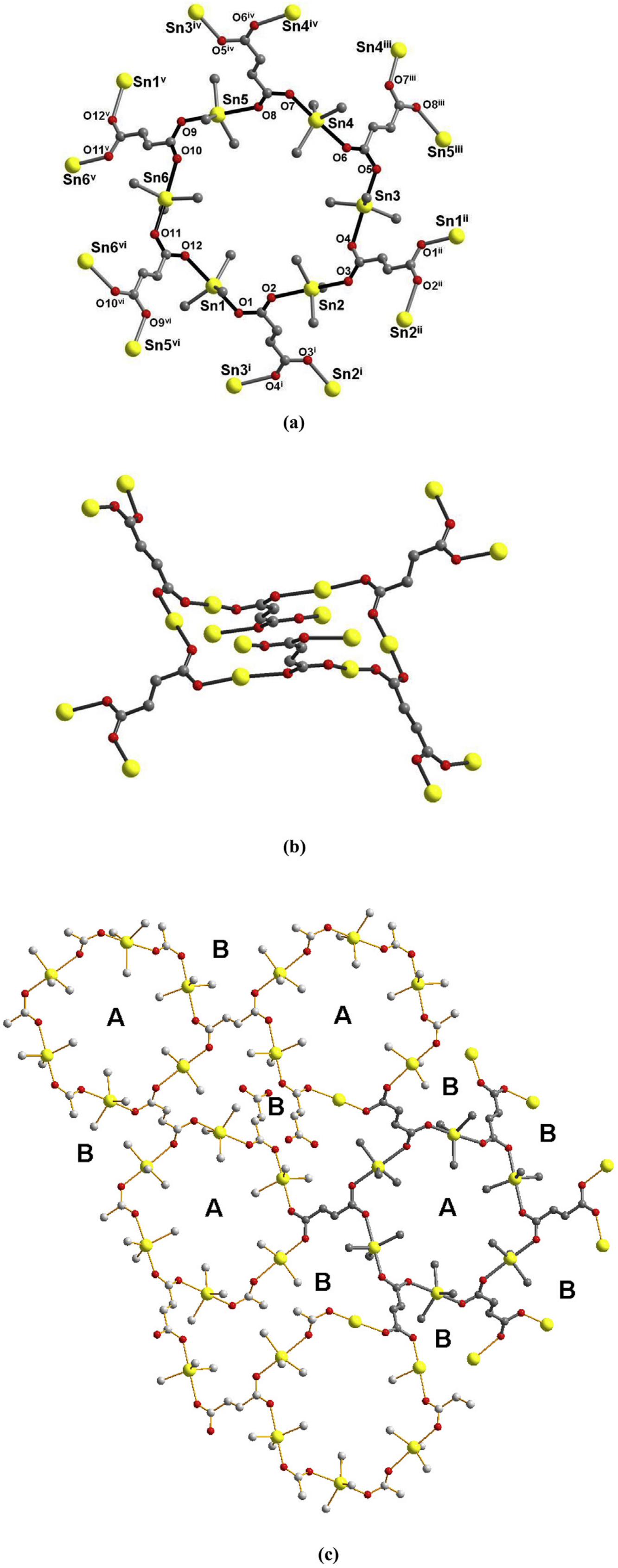

Fig. 3. (a) Hexagonal ring **A**, top view (only one carbon atom from each ^{n}Bu group is represented) (^{i} = −*y*, −1+*x*−*y*, −0.33333 + *z*; ^{ii} = 1−*x* + *y*, −*x*, 0.33333 + *z*; ^{iii} = 1−*y*, *x*−*y*, −0.33333 + *z*; ^{iv} = 1−*x* + *y*, 1−*x*, 0.33333 + *z*; ^{v} = −*y*, *x*−*y*, −0.33333 + *z*; ^{vi} = −*x* + *y*, −*x*, 0.33333 + *z*); (b) Side view of the ring **A** (the ^{n}Bu groups are removed for clarity); (c) Connectivity between the two types of rings, **A** and **B**, in compound **2**.

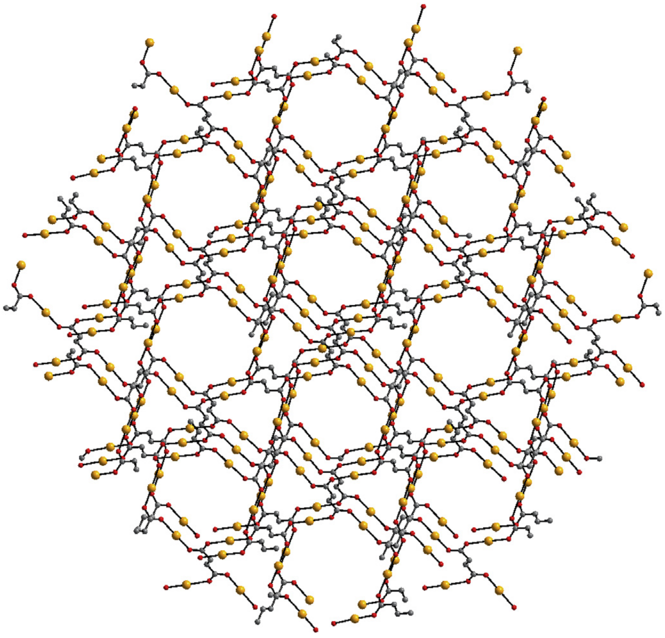

Fig. 4. Visualization of the three-dimensional network structure of compound **2** in the crystal.

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

Bond lengths	Angles
Sn(1)–C(1) = 2.120(4)	C(1) - Sn(1)–C(2) = 125.38(17)
Sn(1)–C(2) = 2.109(3)	C(1)–Sn(1) - C(3) = 117.28(16)
Sn(1)–C(3) = 2.118(3)	C(1)–Sn(1) - O(1) = 96.01(13)
Sn(1)–O(1) = 2.185(2)	C(1)–Sn(1) - O(2)#2 = 84.52(13)
Sn(1)–O(2)# = 2.443(2)	C(2)–Sn(1) - C(3) = 114.94(15)
#: 1.5-*x*, 0.5 + *y*, 0.5-*z*	C(2)–Sn(1) - O(1) = 96.62(11)
	C(2)–Sn(1) - O(2)#2 = 86.15(11)
	C(3)–Sn(1) - O(1) = 92.56(10)
	C(3)–Sn(1) - O(2)#2 = 83.80(10)
	O(1)–Sn(1) - O(2)#2 = 176.13(7)
	#: 1.5-*x*, 0.5 + *y*, 0.5-*z*

Table 3
Selected bond lengths (Å) and angles (°) of compound **2**.

Bond lenghts	Angles
Sn(1)–C(1) = 2.17(5)	C(1)–Sn(1) - C(5) = 119.5(17)
Sn(1)–C(5) = 2.14(3)	C(1)–Sn(1) - C(9) = 116.7(17)
Sn(1)–C(9) = 2.19(4)	C(1)–Sn(1) - O(1) = 96.6(16)
Sn(1)–O(1) = 2.201(16)	C(1)–Sn(1) - O(12) = 82.2(16)
Sn(1)–O(12) = 2.364(14)	C(5)–Sn(1) - C(9) = 121.7(17)
Sn(2)–C(15) = 2.16(2)	C(5)–Sn(1) - O(1) = 88.3(9)
Sn(2)–C(19) = 2.148(18)	C(5)–Sn(1) - O(12) = 87.3(10)
Sn(2)–C(23) = 2.136(18)	C(9)–Sn(1) - O(1) = 100.1(13)
Sn(2)–O(2) = 2.359(14)	C(9)–Sn(1) - O(12) = 85.5(13)
Sn(2)–O(3) = 2.197(13)	O(1)–Sn(1) - O(12) = 174.2(7)
Sn(3)–C(29) = 2.16(2)	C(15)–Sn(2) - C(19) = 120.0(9)
Sn(3)–C(33) = 2.13(5)	C(15)–Sn(2) - C(23) = 123.8(8)
Sn(3)–C(37) = 2.13(2)	C(15)–Sn(2) - O(2) = 90.8(8)
Sn(3)–O(4) = 2.357(14)	C(15)–Sn(2) - O(3) = 95.8(8)
Sn(3)–O(5) = 2.197(15)	C(19)–Sn(2) - C(23) = 116.0(9)
Sn(4)–C(43) = 2.08(2)	C(19)–Sn(2) - O(2) = 90.8(7)
Sn(4)–C(47) = 2.20(5)	C(19)–Sn(2) - O(3) = 85.6(7)
Sn(4)–C(51) = 2.07(5)	C(23)–Sn(2) - O(2) = 83.1(6)
Sn(4)–O(6) = 2.424(15)	C(23)–Sn(2) - O(3) = 93.6(7)
Sn(4)–O(7) = 2.210(13)	O(2)–Sn(2) - O(3) = 173.4(6)
Sn(5)–C(57) = 2.20(6)	C(29)–Sn(3) - C(33) = 118.8(12)
Sn(5)–C(61) = 2.15(3)	C(29)–Sn(3) - C(37) = 120.2(9)
Sn(5)–C(65) = 2.18(5)	C(29)–Sn(3) - O(4) = 84.8(7)
Sn(5)–O(8) = 2.353(14)	C(29)–Sn(3) - O(5) = 94.5(8)
Sn(5)–O(9) = 2.19(2)	C(33)–Sn(3) - C(37) = 120.3(13)
Sn(6)–C(71) = 2.10(5)	C(33)–Sn(3) - O(4) = 87.4(14)
Sn(6)–C(75) = 2.23(3)	C(33)–Sn(3) - O(5) = 89.1(14)
Sn(6)–C(79) = 2.17(5)	C(37)–Sn(3) - O(4) = 89.8(7)
Sn(6)–O(10) = 2.407(16)	C(37)–Sn(3) - O(5) = 94.3(8)
Sn(6)–O(11) = 2.178(14)	O(4)–Sn(3) - O(5) = 175.6(7)
	C(43)–Sn(4) - C(47) = 126.1(16)
	C(43)–Sn(4) - C(51) = 120.5(14)
	C(43)–Sn(4) - O(6) = 90.6(8)
	C(43)–Sn(4) - O(7) = 89.3(8)
	C(47)–Sn(4) - C(51) = 113.3(17)
	C(47)–Sn(4) - O(6) = 91.2(15)
	C(47)–Sn(4) - O(7) = 86.8(15)
	C(51)–Sn(4) - O(6) = 86.8(16)
	C(51)–Sn(4) - O(7) = 95.4(17)
	O(6)–Sn(4) - O(7) = 177.5(6)
	C(57)–Sn(5) - C(61) = 121.9(18)
	C(57)–Sn(5) - C(65) = 126.1(18)
	C(57)–Sn(5) - O(8) = 81.9(14)
	C(57)–Sn(5) - O(9) = 92.1(15)
	C(61)–Sn(5) - C(65) = 112.0(17)
	C(61)–Sn(5) - O(8) = 94.8(9)
	C(61)–Sn(5) - O(9) = 84.7(8)
	C(65)–Sn(5) - O(8) = 92.5(13)
	C(65)–Sn(5) - O(9) = 94.4(14)
	O(8)–Sn(5) - O(9) = 172.7(8)
	C(71)–Sn(6) - C(75) = 115.1(17)
	C(71)–Sn(6) - C(79) = 124(2)
	C(71)–Sn(6) - O(10) = 82.8(15)
	C(71)–Sn(6) - O(11) = 92.8(15)
	C(75)–Sn(6) - C(79) = 119.9(17)
	C(75)–Sn(6) - O(10) = 86.6(9)
	C(75)–Sn(6) - O(11) = 87.8(8)
	C(79)–Sn(6) - O(10) = 92.9(15)
	C(79)–Sn(6) - O(11) = 96.5(15)
	O(10)–Sn(6) - O(11) = 170.6(8)

solvent DMSO-d_6, the ^{119}Sn signal is broad for both compounds, in the case of **2** the signal appears very sharp in $CDCl_3$.

The values of certain NMR parameters can be correlated with the coordination geometry at the metal center in the organotin(IV) derivatives [16,17]. Thus, the values of the $^2J(^{119}Sn C^1H)$ and $^1J(^{119}Sn^{13}C)$ coupling constants observed for the DMSO-d_6 solutions of **1** and **2** fall in the region for a five-coordinate triorganotin(IV) compound. Moreover, for DMSO-d_6 solutions of **1** and **2** the calculated C–Sn–C angles based on the reported relationships with $^2J(^{117/119}Sn C^1H)$ and $^1J(^{117/119}Sn^{13}C)$ coupling constants are close to 120° (see Table 4), which is consistent with a trigonal bipyramidal coordination geometry around the tin atom. The high symmetry of the "$(R_3Sn)_2$(fum)" unit as observed from the NMR spectra in DMSO-d_6 solution, together with the calculated bond angles, lead us to propose the presence of a discrete dinuclear species of the type "$DMSO \rightarrow R_3Sn–O(O)CCH=CHC(O)O–SnR_3 \leftarrow DMSO$" with organic groups R in equatorial positions (*cf* the magnitude of observed ^2J $(^{117/119}Sn C^1H)$ and ^1J $(^{117/119}Sn^{13}C)$ coupling constants and calculated C–Sn–C angles for R_3SnCl, R = Me, Bu). These dinuclear species are formed by dissociation of the infinite polymeric structures of **1** and **2** into smaller discrete species.

In contrast, the NMR data for **2** in $CDCl_3$ indicates tetracoordinate metal centers, preserving however a discrete dinuclear organotin(IV) species, "$Bu_3Sn–O(O)CCH=CHC(O)O–SnBu_3$", required for charge balance. The assumption was based on the values of the NMR chemical shifts, together with the calculated C–Sn–C angles of about 110°, correlated with the observed $^1J(^{117/119}Sn^{13}C)$ coupling constants, which are similar to those observed for Bu_3SnCl in $CDCl_3$ as result of the non-coordinating nature of the chlorinated solvent. The change in the coordination geometry around tin in $CDCl_3$ *vs* DMSO-d_6 is also consistent with the increase of the ^{119}Sn chemical shift from δ −26.4 ppm in **2**/DMSO-d_6 (5-coordinate tin atom) to δ 121.4 ppm in **2**/$CDCl_3$ (4-coordinate tin

Table 4
NMR parameters [δ (ppm); *J* (Hz)] and correlations between ^{119}SnC^{1}H and ^{119}Sn^{13}C coupling constants and C–Sn–C bond angles (θ_{CSnC}, °) for compounds **1** and **2** and the corresponding triorganotin(IV) chlorides.

Compound	Solvent	^{1}H		^{13}C		$\delta(^{119}Sn)$
			θ_{CSnC}	$^{1}J(^{119}Sn^{13}C)$	θ_{CSnC}	
$^{2}_{\infty}[(Me_3Sn)_4(fum)]$ (**1**)	DMSO-d$_6$	69.0[a]	119[b]	522.4[a]	122.6[c]	−16.4
Me_3SnCl	DMSO-d$_6$	69.9	119.8[b]	516.2	122.0[c]	−3.6
	$CDCl_3$	57.6	110.8[b]	374.6	109.6[c]	173.3
$^{3}_{\infty}[(^{n}Bu_3Sn)_4(fum)]$ (**2**)	DMSO-d$_6$	62.6[a]	–	ca. 470[a]	121.7[d]	−26.4
	$CDCl_3$	51.9[a]	–	355.8	110.3[d]	121.4
Bu_3SnCl	DMSO-d$_6$	59.7	–	464.3	121.2[d]	3.0
	$CDCl_3$	48.6	–	336.8	108.4[d]	156.8

[a] Unresolved satellites corresponding to ^{117}Sn and ^{119}Sn nuclei; therefore, the values given in the table can be assumed $^{2}J(^{117/119}SnC^{1}H)$ and $^{1}J(^{117/119}Sn^{13}C)$, respectively.
[b] $\theta = 0.0161|^{2}J|^{2} - 1.32|^{2}J| + 133.4$, for $^{2}J(^{119}SnC^{1}H)$ [18].
[c] $|^{1}J| = 11.4\,\theta - 875$, for $^{1}J(^{119}Sn^{13}C)$ [19].
[d] $|^{1}J| = 9.99\,\theta - 746$, for $^{1}J(^{119}Sn^{13}C)$ [20].

atom) [cf $\delta(^{119}Sn)$ 3.0 ppm for Bu_3SnCl/DMSO-d$_6$ *vs* 156.8 ppm for $Bu_3SnCl/CDCl_3$ solutions). These data indicate the dissociation of the polymeric structure when the polymer **2** is dissolved in the non-coordinating solvent $CDCl_3$.

4. Conclusions

We have shown that the nature of triorganotin(IV) fragments influence the dimensionality of the obtained coordination polymers in solid state. NMR studies in solution revealed different coordination geometries achieved around the tin centers of these bis(triorganotin) fumarates, depending on the coordinating or non-coordinating nature of the used deuterated solvent. The NMR data suggest that the polymeric nature of compounds **1** and **2** is not preserved in solution.

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