Contents lists available at ScienceDirect

Journal of Organometallic Chemistry



journal homepage: www.elsevier.com/locate/jorganchem

Macrocyclic organotin(IV) carboxylates based on benzenedicarboxylic acid derivatives: Syntheses, crystal structures and antitumor activities

Dafeng Du^a, Zijiang Jiang^b, Chunling Liu^a, Adama Moussa Sakho^a, Dongsheng Zhu^{a,*}, Lin Xu^a

^a Department of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, PR China ^b Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, PR China

ARTICLE INFO

Article history: Received 21 January 2011 Received in revised form 23 March 2011 Accepted 29 March 2011

Keywords: Organotin(IV) carboxylates 1,3-Benzenedicarboxylic acid derivatives 1,4-Benzenedicarboxylic acid derivatives Crystal structure

ABSTRACT

Six new organotin carboxylates based on 1,3-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid derivatives, namely (Ph₃Sn)₂(2,5-L¹)(C₂H₅OH)₂ (1) (2,5-H₂L¹ = 2,5-dibenzoylterephthalic acid), (Ph₃Sn)₂(2,5-L²)(C₂H₅OH)₂ (2) (2,5-H₂L² = 2,5-bis(4-methylbenzoyl)terephthalic acid), (Ph₃Sn)₂(2,5-L³)(C₂H₅OH)₂ (3) (2,5-H₂L³ = 2,5-bis(4-ethylbenzoyl)terephthalic acid), [(*n*-Bu₂Sn)₄(4,6-L¹) O₂(OH)(OC₂H₅)]₂·2(C₂H₅OH) (4) (4,6-H₂L¹ = 4,6-dibenzoylisophthalic acid), [(*n*-Bu₂Sn)₄(4,6-L¹) O₂(OH)(OC₄H₉)]₂·2(C₄H₉OH) (5) and [(*n*-Bu₂Sn)₄(4,6-L²)O₂(OH)(OC₂H₅)]₂·2(C₂H₅OH) (6) (4,6-H₂L² = 4,6-bis(4-methylbenzoyl)isophthalic acid), have been synthesized. All the organotin carboxylates have been characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy and X-ray crystallog-raphy diffraction analyses. The structural analysis reveals that complexes 1–3 show similar structures, containing binuclear triorganotin skeletons. The significant intermolecular O–H···O hydrogen bonds linked the complexes 1–3 to form a novel 2D network polymer with 38-member macrocycles. In complexes 4–6, two Sn₄O₄ ladders are connected by two 1,3-benzenedicarboxylic acid derivatives to yield ladder-like octanuclear architectures and form macrocycle with 24 atoms. In addition, the antitumor activities of complexes 1–6 have been studied.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Antitumor activities

There is considerable interest in the assembly and structural analysis of organotin complexes [1–3]. So far, a large number of organotin complexes have been prepared and structurally characterized because of their biological properties as well as their unusual structural motifs [4–6]. Among them, organotin carboxylates are particularly interesting because of their potential industrial applications and topological structures [7–10]. Recently, considerable advances have been made in this area, mono-, dicarboxylic acids and tricarboxylic acids have been extensively investigated [11–20]. The diverse structural motifs found in this family of complexes are attributed to the coordinate characterization of the carboxylate ligands. It is therefore necessary to select the new carboxylate ligands with different structural features. Typically, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid and

1,3,5-benzene-tricarboxylic acid have been widely used for the design and synthesis of the organotin carboxylates [21,22]. As far as we know, no organotin carboxylates based on 1,3-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid derivatives have been reported. To further understand the coordination chemistry of 1,3-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid derivatives and to prepare novel organotin carboxylates with beautiful architecture and good antitumor activities, we start to elaborate and synthesize 1,3-benzenedicarboxylic acid and 1,4benzenedicarboxylic acid derivatives: 2,5-H₂L¹, 4,6-H₂L¹, 2,5-H₂L², 4,6-H₂L², 2,5-H₂L³ and 4,6-H₂L³, by reaction of pyromellitic dianhydride with benzene, toluene, and ethylbenzene (Scheme 1), respectively. The self-assembly of rigid aryl dicarboxylate (H₂L ligands) with triphenyltin hydroxide and di-n-butyltin oxide form a series of novel organotin carboxylates (Scheme 2). In the present paper, we report the syntheses, crystal structures and antitumor activities of six macrocyclic organotin carboxylates, (Ph₃Sn)₂(2,5- $L^{1}(C_{2}H_{5}OH)_{2}$ (1), $(Ph_{3}Sn)_{2}(2,5-L^{2})(C_{2}H_{5}OH)_{2}$ (2), $(Ph_{3}Sn)_{2}(2,5-L^{3})$ $(C_2H_5OH)_2$ (**3**), $[(n-Bu_2Sn)_4(4,6-L^1)O_2(OH)(OC_2H_5)]_2 \cdot 2(C_2H_5OH)$ (**4**), $[(n-Bu_2Sn)_4(4,6-L^1)O_2(OH)(OC_4H_9)]_2 \cdot 2(C_4H_9OH)$ (5) and $[(n-Bu_2-1)O_2(OH)(OC_4H_9)]_2 \cdot 2(C_4H_9OH)$ (5) $Sn_4(4,6-L^2)O_2(OH)(OC_2H_5)]_2 \cdot 2(C_2H_5OH)$ (6).



^{*} Corresponding author. Tel.: +86 043185098620; fax: +86 0431 85098768. *E-mail address:* zhuds206@nenu.edu.cn (D. Zhu).

⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2011.03.048



Scheme 1. The reaction scheme for the syntheses of H_2L^1 , H_2L^2 and H_2L^3 .

2. Experimental

2.1. General and instrumental

The reagents were used as supplied, while the solvents were purified according to standard procedures [23]. The melting point was obtained with Kofler micro-melting point apparatus and was uncorrected. Elemental analyses (C, H) were carried out on a Perkin–Elmer PE 2400 CHN instrument. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury operating at 300 and 75 MHz, respectively. IR spectra (KBr pellets) were recorded on an Alpha Centauri FI/IR spectrometer (400–4000 cm⁻¹ range).

2.2. X-ray crystallography

Diffraction intensities for **1–6** were collected on a Bruker CCD Area Detector image plate diffractometer by using the ω/φ scan technique with Mo-K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using multiscan techniques. The structure was solved by direct methods with SHELXS-97 [24] and refined using SHELXL-97 [25]. All non-hydrogen atoms were refined with anisotropic temperature parameters; hydrogen atoms were refined as rigid groups. Crystal data and refinement results for **1–6** are listed in Tables 1 and 3.

2.3. Antitumor studies

HeLa (cervical), HT1080 (fibrosarcoma) and U87 (glioma) were obtained from the American Tissue Culture Collection (ATCC). The cells were cultured with culture reagents and dissolved in dimethyl sulfoxide (DMSO) and stored at 4 °C. The [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide] (MTT) assay that differentiates dead from living cells was adapted [26]. The assay was carried out as follows: A total of 1×10^4 cells were seeded into a 96-well microplate and incubated for 24 h. Thereafter, the cells were treated with various concentrations of both complexes **1–6** for 24 h. The MTT (final concentration = 0.5 mg/ml) was added to each well for 4 h

of incubation at 37 °C, then 200 μ l of DMSO was added to each well. The optical density (OD) was then read at a wavelength of 570 nm. The decrease in OD measures the extent of decrease in the number of cancer cells exposed to the test compounds.

2.4. Syntheses

The details of synthetic experiments of ligands and complexes **1–6** were shown in Scheme 1 and Scheme 2.

2.4.1. Syntheses of ligands

2,5- H_2L^1 (para) and 4,6- H_2L^1 (meta) were prepared by a standard method reported in the literature [27]. Typically, pyromellitic dianhydride (4.36 g, 0.02 mol), anhydrous aluminum chloride (10.67 g, 0.08 mol) and dry benzene (18.75 g, 0.24 mol) were added into a three-neck flask. The reaction mixture was stirred for 3 h in a water-bath at 65-70 °C. The mixture is then poured into ice water of containing concentrated hydrochloric acid, which is distilled in a current of steam. When the benzene has been completely removed, the crude mixtures of acids produced are left in the form of white. These are washed with water, and dissolved in boiling dilute potassium hydroxide solution. After filtration to remove a little insoluble matter, the usual mixture of meta and para are obtained with hydrochloric acid (Yield: 73.4%). Separated by crystallization from glacial acetic acid, the para could be obtained first from glacial acetic acid. The meta usually crystallized upon aqueous dilution of the filtrates [28]. The para and meta isomers are obtained in a ratio of 4:3. For para: Mp: 318-321 °C ¹H NMR (acetone- d_6 , 300 MHz): δ 7.55 (t, 4H, I = 7.5 Hz, Ar–H); 7.67 (t, 2H, I = 7.5 Hz, Ar–H); 7.87 (d, 4H, I = 7.2 Hz, Ar–H); 8.10 (s, 2H, Ar–H). ¹³C NMR (acetone- d_6 , 75 MHz): δ 194.96 (C=O); 166.13 (COO); 144.76, 142.38, 133.69, 132.21, 129.71, 129.03 (4C), 127.18 (4C), (carbon protons of aryl groups); (all peaks 2C unless otherwise noted). For meta: Mp: 278–280 °C ¹H NMR (acetone- d_6 , 300 MHz): δ 7.52 (t, 4H, J = 7.5 Hz, Ar–H); 7.64 (t, 2H, J = 7.5 Hz, Ar–H); 7.82 (d, 4H, J = 7.2 Hz, Ar–H); 8.10 (s, 1H, Ar–H); 8.78 (s, 1H, Ar–H). ¹³C NMR (acetone-*d*₆, 75 MHz): δ 195.16 (C=O); 165.82 (COO); 147.26,



Scheme 2. The reaction scheme for the syntheses of 1–6.

Table 1Crystal data and details of structure refinement parameters for 1–3.

	1	2	3
Empirical formula	C ₆₂ H ₅₄ O ₈ Sn ₂	C ₆₄ H ₅₈ O ₈ Sn ₂	C ₆₆ H ₆₂ O ₈ Sn ₂
Formula weight	1164.43	1192.48	1220.54
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2(1)/c	P 2(1)/c	P 2(1)/n
a (Å)	9.8933(7)	10.0462(8)	10.3408(7)
b (Å)	14.1532(10)	14.6232(11)	14.5643(10)
c (Å)	19.2542(13)	19.4363(15)	19.6272(13)
α (°)	90.0	90.0	90.0
β (°)	95.2630(10)	98.6660(10)	100.0610(10)
γ (°)	90.0	90.0	90.0
V (Å ³)	2684.6(3)	2822.7(4)	2910.5(3)
Ζ	2	2	2
$\mu(\text{mm}^{-1})$	0.985	0.939	0.912
Reflections collected	22553	14058	24427
Independent Reflections	5277	4954	5736
R(int)	0.0931	0.0221	0.0869
Final <i>R</i> indices $[I > 2\sigma(I)]$	0.0373, 0.0720	0.0309, 0.0795	0.0396, 0.0801
R indices (all data)	0.0724, 0.0803	0.0431, 0.0834	0.0883, 0.0917

137.17, 133.69, 132.54, 131.25 (1C), 129.58 (1C), 129.00 (4C), 127.45 (4C), (carbon protons of aryl groups); (all peaks 2C unless otherwise noted).

The preparation of 2,5-H₂L² (para) and 4,6-H₂L² (meta) is similar to that of H_2L^1 except that the dry toluene (22.11 g, 0.24 mol) was used to take place of dry benzene (Yield: 69.2%). The separation of two isomers is similar to that of 2.5-H₂L¹ and 4.6-H₂L¹. The para and meta isomers are obtained in a ratio of 4:1. For para: Mp: 332–335 °C ¹H NMR (acetone- d_6 , 300 MHz): δ 7.38 (d, 4H, I = 8.1 Hz, Ar–H); 7.76 (d, 4H, I = 8.1 Hz, Ar–H); 8.12 (s, 2H, Ar–H); 2.37 (s, 6H, $-CH_3$). ¹³C NMR (acetone- d_6 , 75 MHz): δ 194.86 (C=O); 165.53 (COO); 144.58, 142.58,134.88, 132.21, 129.89, 127.45 (4C), 125.87 (4C), (carbon protons of aryl groups); 21.11 (C, carbon protons of methyl groups of 4-methylphenyl groups); (all peaks 2C unless otherwise noted). For meta: Mp: 289–291 °C ¹H NMR (acetone- d_6 , 300 MHz): δ 7.34 (d, 4H, I = 7.8 Hz, Ar–H); 7.71 (d, 4H, J = 8.1 Hz, Ar-H); 7.47 (s, 1H, Ar-H); 8.77 (s, 1H, Ar-H); 2.34 (s, 6H, $-CH_3$). ¹³C NMR (acetone- d_6 , 75 MHz): δ 194.83 (C=O); 165.49 (COO); 146.49, 144.59, 134.75, 132.55, 130.65 (1C), 129.76 (1C), 127.20 (4C), 125.87 (4C), (carbon protons of aryl groups); 21.12 (C, carbon protons of methyl groups of 4-methylphenyl groups); (all peaks 2C unless otherwise noted).

The preparation of 2,5-H₂L³ (para) and 4,6-H₂L³ (meta) is similar to that of H_2L^1 except that the dry ethylbenzene (25.48 g, 0.24 mol) was used to take place of dry benzene (Yield: 68.8%). The separation of two isomers is similar to that of $2,5-H_2L^1$ and $4,6-H_2L^1$. The para and meta isomers are obtained in a ratio of 6:1. For para: Mp: 347–350 °C ¹H NMR (acetone- d_6 , 300 MHz): δ 7.41 (d, 4H, I = 7.8 Hz, Ar-H); 7.79 (d, 4H, I = 8.1 Hz, Ar-H); 8.07 (s, 2H, Ar-H); 2.73 (q, 4H, I = 6.9 Hz, $-CH_2-$); 1.25 (t, 6H, I = 6.9 Hz, $-CH_3$). ¹³C NMR (acetone-*d*₆, 75 MHz): δ 194.85 (C=O); 165.56(COO); 150.73, 132.95, 130.60, 130.01, 129.69, 128.51 (4C), (carbon protons of aryl groups); 125.26 (4C); 27.28 (C-α, carbon protons of ethyl groups of 4-ethylphenyl groups); 15.62 (C- β , carbon protons of ethyl groups of 4-ethylphenyl groups) (all peaks 2C unless otherwise noted). For meta: Mp: 308–311 °C ¹H NMR (acetone- d_6 , 300 MHz): δ 7.35 (d, 4H, J = 8.1 Hz, Ar-H; 7.74 (d, 4H, J = 8.1 Hz, Ar-H); 8.07 (s, 1H, Ar-H); 8.78 (s, 1H, Ar-H); 2.71 (q, 4H, J = 7.2 Hz, -CH₂-); 1.25 (t, 6H, J = 7.2 Hz, $-CH_3$). ¹³C NMR (acetone- d_6 , 75 MHz): δ 194.82 (C= 0); 165.45 (COO); 149.56, 146.93, 134.98, 132.94, 130.62 (1C), 129.00 (1C), 127.23 (4C), 125.85 (4C), (carbon protons of aryl groups); 27.36 (C- α , carbon protons of ethyl groups of 4-ethylphenyl groups); 15.51 (C-β, carbon protons of ethyl groups of 4-ethylphenyl groups); (all peaks 2C unless otherwise noted).

2.4.2. Synthesis of $(Ph_3Sn)_2(2,5-L^1)(C_2H_5OH)_2$ **1**

A mixture of triphenyltin hydroxide (0.73 g, 2 mmol) and 2,5- H_2L^1 (0.37 g, 1 mmol) was heated under reflux in benzene (30 ml) for 10 h in a Dean-Stark apparatus for azeotropic removal of the water formed in the reaction. After cooling to room temperature, the reaction mixture was filtered and evaporated to afford the products at room temperature. The products were then recrystallized from ethanol to give colorless crystals. Yield: 72.6%: Mp: 100–102 °C. Anal. Calcd for C₆₂H₅₄O₈Sn₂: C, 63.95; H, 4.67. Found: C, 63.82; H, 4.81%. IR (cm⁻¹): v (C–H) 2962, 2909; v_{as} (COO) 1652, 1608; v_s (COO) 1436, 1385; v (Sn–O) 457. ¹H NMR (CDCl₃, ppm): δ 6.91–7.71 (m, 40H, Ar–H); 8.12 (s, 2H, Ar–H); 3.63 (q, 4H, J = 7.2 Hz, $-CH_2$, hydrogen protons of ethyl groups); 1.14 (t, 6H, J = 6.9 Hz, $-CH_3$, hydrogen protons of ethyl groups). ¹³C NMR (CDCl₃, ppm): δ 194.56 (C=0); 171.45 (COO); 149.68, 147.32, 144.16, 138.65, 136.49, 134.76, 132.18, 130.56, 129.48, 128.69, 126.56 (carbon protons of aryl groups); 57.69 (C-α, carbon protons of ethanol); 18.47 (C- β , carbon protons of ethanol).

2.4.3. Synthesis of $(Ph_3Sn)_2(2,5-L^2)(C_2H_5OH)_2$ 2

The preparation of **2** is similar to that of **1** except that the 2,5- H_2L^2 (0.40 g, 1 mmol) was used to take place of 2,5- H_2L^1 . Yield: 76%; Mp: 102–105 °C. Anal. Calcd for C₆₄ $H_{58}O_8Sn_2$: C, 64.46; H, 4.90. Found: C, 64.12; H, 4.68%. IR (cm⁻¹): v (C–H) 2926, 2782; v_{as} (COO) 1654, 1604; v_s (COO) 1428, 1382; v (Sn–O) 450. ¹H NMR (CDCl₃, ppm): δ 7.01–7.55 (m, 38H, Ar–H); 8.09 (s, 2H, Ar–H); 2.32 (s, 6H Ar–CH₃); 3.47 (q, 4H, J = 7.2 Hz, –CH₂–, hydrogen protons of ethyl groups); 1.23 (t, 6H, J = 7.2 Hz, –CH₃, hydrogen protons of ethyl groups). ¹³C NMR (CDCl₃, ppm): δ 195.97 (C=O); 171.86 (COO); 144.17, 143.28, 137.71, 137.11, 136.79, 134.76, 130.53, 130.00, 129.62, 129.20, 128.77 (carbon protons of aryl groups); 57.64 (C- α , carbon protons of ethanol); 21.13 (C, carbon protons of methyl groups of 4-methylphenyl groups), 18.62 (C- β , carbon protons of ethanol).

2.4.4. Synthesis of $(Ph_3Sn)_2(2,5-L^3)(C_2H_5OH)_2$ 3

The preparation of **3** is similar to that of **1** except that the 2,5-H₂L³ (0.43 g, 1 mmol) was used to take place of 2,5-H₂L¹. Yield: 68.2%; Mp: 108–111 °C. Anal. Calcd for C₆₆H₆₂O₈Sn₂: C, 64.94; H, 5.12. Found: C, 64.82; H, 5.31%. IR (cm⁻¹): v (C–H) 2971, 2926; v_{as} (COO) 1646, 1603; v_s (COO) 1428, 1388; v (Sn–O) 451. ¹H NMR (CDCl₃, ppm): δ 6.84–7.56 (m, 38H, Ar–H); 8.08 (s, 2H, Ar–H); 1.25 (t, 6H, *J* = 6.9 Hz, Ar–C–CH₃); 2.64 (q, 4H, *J* = 7.5 Hz, Ar–CH₂–); 3.71 (q, 4H, *J* = 7.5 Hz, –CH₂–, hydrogen protons of ethyl groups); 1.18 (t, 6H, *J* = 7.5 Hz, –CH₃, hydrogen protons of ethyl groups). ¹³C NMR (CDCl₃, ppm): δ 196.10 (C=O); 170.31 (COO); 150.33, 147.47, 143.37, 137.45, 136.80, 134.94, 133.16, 130.21, 129.21, 128.79, 125.11 (carbon protons of aryl groups); 58.81 (C- α , carbon protons of ethyl groups); 18.80 (C- β , carbon protons of ethanol); 15.85 (C- β , carbon protons of ethyl groups).

2.4.5. Synthesis of $[(n-Bu_2Sn)_4(4,6-L^1)O_2(OH)(OC_2H_5)]_2 \cdot 2(C_2H_5OH)$ **4**

A mixture of di-*n*-butyltin oxide (0.99 g, 4 mmol) and 4,6-H₂L¹ (0.37 g, 1 mmol) was heated under reflux in benzene (30 ml) for 10 h in a Dean–Stark apparatus for azeotropic removal of the water formed in the reaction. After cooling to room temperature, the reaction mixture was filtered and evaporated to afford the products at room temperature. The products were then recrystallized from ethanol to give colorless crystals. Yield: 75.7%; Mp: 292–295 °C. Anal. Calcd for C₁₁₆H₁₉₂O₂₂Sn₈: C, 48.24; H, 6.70. Found: C, 48.27; H, 6.74%. IR (cm⁻¹): v (C–H) 2957, 2925, 2862; v_{as} (COO) 1635, 1605; v_s (COO) 1397, 1340; v (Sn–O) 494; v (Sn–O–Sn) 608. ¹H NMR (CDCl₃, ppm): δ 6.91–7.77 (m, 20H, Ar–H); 8.01 (s, 2H, Ar–H); 8.73 (s, 2H, Ar–H); 1.19–1.56 (m, 96H, SnCH₂CH₂CH₂–); 0.86 (t, 48H, *J* = 7.2 Hz,

–CH₃). ¹³C NMR (CDCl₃, ppm): δ 197.21 (C=O); 170.72 (COO); 144.51, 137.71, 134.54, 133.81, 133.15, 129.82, 128.70, 125.74 (carbon protons of aryl groups); 27.43 (αCH₂), 25.04 (βCH₂), 23.75 (γCH₂), 13.95 (CH₃) (carbon protons of butyl groups).

2.4.6. Synthesis of $[(n-Bu_2Sn)_4(4,6-L^1)O_2(OH)(OC_4H_9)]_2 \cdot 2(C_4H_9OH)$ **5**

The preparation of **5** is similar to that of **4** except that the *n*-butanol was used to take place of alcohol. Yield: 61.4%; Mp: 298-300 °C. Anal. Calcd for $C_{124}H_{208}O_{22}Sn_8$: C, 49.63; H, 6.99.



Fig. 1. Perspective views of the molecular structure of complexes 1-3.

Found: C, 49.67; H, 6.95%. IR (cm⁻¹): v (C–H) 2953, 2916, 2878; v_{as} (COO) 1641, 1612; v_s (COO) 1391, 1332; v (Sn–O) 483; v (Sn–O–Sn) 601. ¹H NMR (CDCl₃, ppm): δ 6.87–7.71 (m, 20H, Ar–H); 8.03 (s, 2H, Ar–H); 8.76 (s, 2H, Ar–H); 1.17–1.55 (m, 96H, SnCH₂CH₂CH₂–); 0.83 (t, 48H, J = 7.2 Hz, –CH₃). ¹³C NMR (CDCl₃, ppm): δ 197.12 (C= O); 170.86 (COO); 144.34, 137.85, 135.82, 133.76, 132.29, 130.07, 128.95, 125.81 (carbon protons of aryl groups); 27.31 (α CH₂), 25.09 (β CH₂), 23.76 (γ CH₂), 13.91 (CH₃) (carbon protons of butyl groups).

2.4.7. Synthesis of $[(n-Bu_2Sn)_2(4,6-L^2)O_2(OH)(OC_2H_5)]_2 \cdot 2(C_2H_5OH)$ **6**

The preparation of **6** is similar to that of **4** except that the 4,6- H_2L^2 (0.402 g, 1 mmol) was used to take place of 4,6- H_2L^1 . Yield: 69.1%; Mp: 296–298 °C. Anal. Calcd for $C_{120}H_{200}O_{22}Sn_8$: C, 48.95; H, 6.85. Found: C, 48.67; H, 6.78%. IR (cm⁻¹): v (C–H) 2956, 2924, 2862; v_{as} (COO) 1634, 1605; v_s (COO) 1398, 1341; v (Sn–O) 493; v (Sn–O–Sn) 611. ¹H NMR (CDCl₃, ppm): δ 6.91–7.65 (m, 16H, Ar–H); 8.01 (s, 2H, Ar–H); 8.72 (s, 2H, Ar–H); 2.38 (s, 12H, Ar–CH₃); 1.16–1.62 (m, 96H, SnCH₂CH₂CH₂–); 0.88 (t, 48H, *J* = 6.9 Hz, –CH₃). ¹³C NMR (CDCl₃, ppm): δ 197.00 (C=O); 170.79 (COO); 144.65, 143.78, 135.54, 133.99, 133.79, 129.96, 129.39, 125.77 (carbon protons of aryl groups); 27.44 (α CH₂), 25.06 (β CH₂), 23.74 (γ CH₂), 13.94 (CH₃) (carbon protons of butyl groups); 21.99, (C, carbon protons of methyl groups of 4-methylphenyl groups).

3. Results and discussion

3.1. IR spectra

For the organotin carboxylates **1–6**, the stretching frequencies of interests are those associated with the COO, Sn-O and Sn-O-Sn groups. The bands at 3100–3550 cm⁻¹ which appear in the free ligands H_2L^1 , H_2L^2 and H_2L^3 as the v(O-H) stretching vibrations, are not observed in complexes 1-6, thus indicating metal-ligand bond formation through these sites. The two different absorption bands in the ranges of 1603-1654 cm⁻¹ and 1332-1436 cm⁻¹ correspond to the v_{as} (COO) and v_s (COO) modes of the coordinated carbonyl groups, respectively. Deacon has proposed that $\Delta v [v_{as} (COO) - v_s]$ (COO)] values >200 cm⁻¹ are associated with unidentated coordination [29]. The Δv values of the complexes **1–3** and **4–6** are about 215-226 and 236-280 cm⁻¹, which indicate that the carboxylate ligands L^1 , L^2 and L^3 coordinate to the Sn atoms in the manner of monodentates. The Δv values of the complexes **1–6** are close to 200 cm⁻¹, which indicates that Sn…O interactions exist between tin atoms and non-bonded oxygen atoms of carboxyl groups. The Δv values of the complexes **1–3** are smaller than those of **4–6**, which indicates that Sn…O interactions in **1–3** are stronger than those of **4–6**. This was confirmed by X-ray structural analysis. A band in the 450–494 $\rm cm^{-1}$ region is assigned to the stretching frequency associated with the Sn-O bond. A strong band in 601–611 cm⁻¹ for complexes **4**–**6** is assigned to ν (Sn–O–Sn), indicating a Sn-O-Sn bridged structure [30].

3.2. NMR spectra

In the ¹H NMR spectra of the H_2L^1 , H_2L^2 and H_2L^3 ligands, the signal of the two hydrogen protons on central aromatic rings in the 4,6- H_2L ligand has one more than that of the corresponding 2,5- H_2L ligand. The COOH group resonance appears at 11–12 ppm [31]. However, this resonance disappears when the carboxylate group participated in coordination to the Sn atom in complexes **1–6**. The same chemical shifts of the two hydrogen protons on central aromatic rings of complexes **1–3** exhibit signals at 8.08–8.12 ppm as single peak, and the different chemical shifts of the two hydrogen protons on central aromatic rings of complexes **4–6** at 8.01–8.03 and 8.72–8.76 ppm as single peak and the chemical



Fig. 2. The 2D supramolecular structures with 38-member macrocycles formed through intermolecular $O-H\cdots O$ hydrogen-bond interactions in complexes 1-3.

shifts of the hydrogen protons on the other phenyl groups of complexes 1-6 at 6.84–7.77 ppm as multiplets.

The ¹³C NMR spectra of the complexes **1–6** show a significant downfield shift of all carboxylate carbon resonances compared with the free ligands H_2L^1 , H_2L^2 and H_2L^3 . The shift is a consequence of electron density transfer from the ligand to the Sn atom. The carbon protons of central aromatic rings present three and four kinds of chemical environment in complexes **1–3** and complexes **4–6**, respectively. The single resonances at 194.56–197.21 and 170.72–171.86 are attributed to the C=O and COO groups in complexes **1–6**. These data are consistent with the structures of **1–6**.

3.3. Crystal structures

3.3.1. Crystal structures of 1-3

The molecular and 2D supramolecular structures of 1-3 are shown in Figs. 1 and 2, respectively, selected bond lengths and angles for 1-3 are given in Table 2. From the structures we can see that the complexes 1-3 show similar structures, containing binuclear triorganotin skeletons. In the complexes 1–3, each of the two tin atoms has a coordination number of five. The geometry at Sn1 is a distorted trigonal bipyramid with the ethanolic oxygen (O1 for 1; O1 for 2; O3 for 3) and the carboxylate O atom (O2 for 1; O3 for 2; O2 for 3) in the axial sites. Three phenyl carbon atoms (C3, C9 and C15 for 1; C15, C21 and C27 for 2; C3, C9 and C15 for 3) occupy the equatorial plane. The axial O-Sn1-O angles of 1-3 are not 180° but 174.81(9)° for O2-Sn1-O1 of 1, 174.16(9) for O3-Sn1-O1 of 2, and 171.88(11)° for O2–Sn1–O3 of 3, which prove the distortion of the geometry. The Sn1–O (ethanolic oxygen atom) bond lengths of 1–3 are 2.447(3), 2.473(2), and 2.515(3) Å, which are slightly longer than the Sn–O covalent bond length (2.13 Å) but considerably shorter than the sum of the van der Waals radii of the two atoms (3.68 Å) [32]. It indicates that the ethanolic oxygen atom and tin atom form a stable

Table 2

Selected bond lengths (Å) and angles (°) for 1–3.

Complex 1			
Bond lengths			
Sn(1)-O(1)	2.447(3)	Sn(1)-C(9)	2.121(4)
Sn(1)-O(2)	2.158(2)	Sn(1)-C(3)	2.118(4)
Sn(1)-C(15)	2.131(4)		
Bond angles			
C(3) - Sn(1) - C(9)	122.7(2)	C(15) - Sn(1) - O(2)	89.25(13)
C(3) - Sn(1) - C(15)	122.21(15)	C(3) - Sn(1) - O(1)	84.55(13)
C(9) - Sn(1) - C(15)	112.6(2)	C(9) - Sn(1) - O(1)	82.92(13)
C(3) - Sn(1) - O(2)	95.00(12)	C(15)-Sn(1)-O(1)	86.64(13)
C(9)-Sn(1)-O(2)	101.60(13)	O(2)-Sn(1)-O(1)	174.81(9)
Complex 2			
Bond lengths			
Sn(1) - O(1)	2.473(2)	Sn(1) - C(21)	2.129(4)
Sn(1) - O(3)	2.148(2)	Sn(1) - C(15)	2.124(4)
Sn(1) - C(27)	2.117(3)		
Bond angles			
C(27) - Sn(1) - C(15)	121.35(13)	C(21) - Sn(1) - O(3)	101.04(11)
C(27) - Sn(1) - C(21)	122.27(14)	C(27) - Sn(1) - O(1)	84.05(10)
C(15) - Sn(1) - C(21)	114.07(14)	C(15)-Sn(1)-O(1)	86.75(11)
C(27) - Sn(1) - O(3)	95.35(10)	C(21) - Sn(1) - O(1)	84.12(11)
C(15)-Sn(1)-O(3)	88.62(11)	O(3)-Sn(1)-O(1)	174.16(9)
Complex 3			
Bond lengths			
Sn(1) - O(2)	2.135(3)	Sn(1) - C(9)	2.114(5)
Sn(1) - O(3)	2.515(3)	Sn(1)-C(3)	2.114(4)
Sn(1) - C(15)	2.106(4)		
Bond angles			
C(15) - Sn(1) - C(9)	119.6(2)	C(3) - Sn(1) - O(2)	101.97(15)
C(15) - Sn(1) - C(3)	121.8(2)	C(15)-Sn(1)-O(3)	83.49(14)
C(9) - Sn(1) - C(3)	115.6(2)	C(9) - Sn(1) - O(3)	84.40(14)
C(15) - Sn(1) - O(2)	96.64(14)	C(3) - Sn(1) - O(3)	84.72(14)
C(9)-Sn(1)-O(2)	88.51(14)	O(2)-Sn(1)-O(3)	171.88(11)

intermolecular coordinative bond. The Sn1–O (oxygen atom of carboxylate ligand) (O2 for 1; O3 for 2; O2 for 3) bond lengths of 1–3 are 2.158(2), 2.148 (2) and 2.135(3) Å, respectively, which prove that the carboxylate O atom is coordinated to the tin atom by a strong chemical bond. However, the Sn1…O (oxygen atom of carboxylate ligand) (O3 for 1; O2 for 2; O1 for 3) distances (3.122 Å for 1; 3.061 Å for 2; 3.097 Å for 3) are considerably shorter than the sum of the van der Waals radii of the Sn and O atom (3.68 Å), therefore the oxygen atom is involved in intramolecular interactions with tin [32]. If the weak Sn(1)…O interaction is taken into consideration, the geometry of tin atoms is best described as distorted octahedron. In addition, the distance between Sn1 and Sn1A in 1–3 decrease in the order of 3 (11.487 Å) > 2 (11.437 Å) > 1 (11.431 Å), and this phenomenon is attributed to the volume of group (ethylbenzoyl > methylbenzoyl > benzoyl) on central aromatic ring.

Besides, for complexes **1–3**, intermolecular hydrogen-bond interactions between the ethanol and the oxygen atom of carbonyl in an adjacent molecule $[O(1)-H\cdots O(4A) = 2.829$ Å for **1**, $O(1)-H\cdots O(4A) = 2.820$ Å for **2**, and $O(3)-H\cdots O(4A) = 2.884$ Å for **3**] result in the formation of a two dimensional network. It is noteworthy that the 38-member of complex **1–3** is formed via the two intermolecular O–H···O interactions. As can be seen from Fig. 2, the infinite macrocycles constitute 2D supramolecular structures.

3.3.2. Crystal structures of 4-6

Selected bond distances and angles for 4-6 are listed in Tables 4-6, and the structures of 4-6 are shown in Figs. 3-5. respectively. Each of the three structures consists of two novel Sn_4O_4 ladders connected by two carboxylate ligands. These structures of the ladder parts are very similar to the complex $[(iPrOCS_2)]$ Me₂Sn(OEt)OSnMe₂]₂ which features a centrosymmetric core arranged as a ladder [33]. In the Sn₄O₄ ladders, the four tin atoms are almost coplanar, with the largest deviation being 0.0181 Å for 4, 0.0659 Å for 5 and 0.0589 Å for 6. According to their different coordination environments, the four tin atoms can be divided into two types: the endocyclic tin (Sn1 and Sn4 for 4; Sn2 and Sn3 for 5; Sn2 and Sn3 for 6) and the exocyclic tin (Sn2 and Sn3 for 4; Sn1 and Sn4 for 5; Sn1 and Sn4 for 6). The endocyclic and exocyclic tin atoms are connected by the μ_3 -oxygen atoms (O1 and O2 for **4**; O2 and O3 for **5**; O8 and O9 for **6**) and the μ_2 -oxygen atoms (O3 and ethanolic oxygen O4 for **4**; O4 and butanolic oxygen O1 for **5**; O10 and ethanolic oxygen O7 for 6). All of the tin atoms of 4-6 are fivecoordinated by two n-Bu groups and three O atoms, resulting in

Table 3	
Crystal data and details of structure refinement parameters for 4-6	j.

	4	5	6
Empirical formula	C116H192O22Sn8	C ₁₂₄ H ₂₀₈ O ₂₂ Sn ₈	C ₁₂₀ H ₂₀₀ O ₂₂ Sn ₈
Formula weight	2888.22	3000.42	2944.32
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	P2(1)/n
a (Å)	29.5685(12)	30.0543(17)	13.4647(8)
b (Å)	21.4564(9)	21.3451(12)	19.5797(12)
c (Å)	24.6164(10)	25.1368(14)	25.9828(16)
β (°)	119.5920(10)	120.2260(10)	100.5710(10)
V (Å ³)	13580.4(10)	13933.2(14)	6733.7(7)
Z	4	4	2
Dc (Mg/m ³)	1.413	1.430	1.452
μ (mm ⁻¹)	1.504	1.468	1.518
F(000)	5856	6112	2992
θ Range (°)	1.58, 26.04	1.77, 26.03	1.59, 26.04
Reflections collected	37303	38258	36938
Independent reflections	13262	13506	13257
R(int)	0.0681	0.0337	0.0394
Completeness to θ_{max}	98.8%	98.4%	99.9%
Goodness-of-fit (F ²)	0.937	1.025	1.024
Final <i>R</i> indices $[I > 2\sigma(I)]$	0.0488, 0.1145	0.0360, 0.0973	0.0522, 0.1214

D. Du et al. / Journal of Organometallic Chemistry 696 (2011) 2549-2558

ladie 4	
Selected bond lengths (Å) and angles (°)	for 4 .

....

beleeted bolid lengths (A) and angles () i		
Sn(1)-O(2)	2.043(3)	Sn(3)–O(3)	2.047(3)
Sn(1)-C(34)	2.125(7)	Sn(3) - C(26)	2.087(7)
Sn(1)-C(30)	2.130(6)	Sn(3)–O(2)	2.107(3)
Sn(1) - O(1)	2.136(3)	Sn(3)–C(22)	2.133(6)
Sn(1)-O(3)	2.168(4)	Sn(3)-O(5)	2.263(4)
Sn(2)-O(1)	1.997(3)	Sn(4) - O(1)	2.046(3)
Sn(2)-C(55)	2.113(8)	Sn(4)–O(2)	2.099(3)
Sn(2) - C(48)	2.120(7)	Sn(4)–C(38)	2.114(7)
Sn(2)-O(7A)	2.162(4)	Sn(4) - C(42)	2.122(7)
Sn(2)-O(4)	2.197(4)	Sn(4)-O(4)	2.192(4)
O(2)-Sn(1)-C(34)	114.3(2)	O(3)-Sn(3)-C(26)	108.7(2)
O(2) - Sn(1) - C(30)	115.9(2)	O(3)-Sn(3)-O(2)	74.35(13)
C(34)-Sn(1)-C(30)	129.7(2)	C(26)-Sn(3)-O(2)	99.6(2)
O(2)-Sn(1)-O(1)	74.48(13)	O(3)-Sn(3)-C(22)	109.10(19)
C(34)-Sn(1)-O(1)	96.0(2)	C(26)-Sn(3)-C(22)	140.9(2)
C(30)-Sn(1)-O(1)	96.5(2)	O(2)-Sn(3)-C(22)	99.52(19)
O(2)-Sn(1)-O(3)	73.12(13)	O(3)-Sn(3)-O(5)	82.40(13)
C(34)-Sn(1)-O(3)	97.1(2)	C(26)-Sn(3)-O(5)	86.6(2)
C(30)-Sn(1)-O(3)	97.6(2)	O(2)-Sn(3)-O(5)	156.72(13)
O(1)-Sn(1)-O(3)	147.60(13)	C(22)-Sn(3)-O(5)	89.02(19)
O(1) - Sn(2) - C(55)	113.0(3)	O(1) - Sn(4) - O(2)	75.24(13)
O(1) - Sn(2) - C(48)	115.6(3)	O(1) - Sn(4) - C(38)	117.2(2)
C(55)-Sn(2)-C(48)	130.8(3)	O(2)-Sn(4)-C(38)	99.4(2)
O(1)-Sn(2)-O(7A)	80.39(13)	O(1) - Sn(4) - C(42)	117.2(2)
C(55)-Sn(2)-O(7A)	98.8(2)	O(2) - Sn(4) - C(42)	98.1(2)
C(48)-Sn(2)-O(7A)	96.0(2)	C(38) - Sn(4) - C(42)	125.4(3)
O(1)-Sn(2)-O(4)	72.20(14)	O(1)-Sn(4)-O(4)	71.43(14)
C(55)-Sn(2)-O(4)	93.2(3)	O(2)-Sn(4)-O(4)	146.67(14)
C(48) - Sn(2) - O(4)	94.6(2)	C(38) - Sn(4) - O(4)	95.9(2)
O(7A)-Sn(2)-O(4)	152.55(14)	C(42)-Sn(4)-O(4)	96.9(2)

Symmetry transformations used to generate equivalent atoms: A -x, -y, -z.

 $n-Bu_2SnO_3$ trigonal bipyramidal coordination environments with the two n-Bu groups and one O atom in equatorial positions and the other two O atoms in axial positions. The axial O-Sn-O angles range from 146.67(14) to 158.59(15) for **4–6**, and thus deviate

Table 5

Selected bond lengths (Å	 and angl 	es (°) for 5
--------------------------	------------------------------	--------------

Sn(1)-O(2)	2.007(2)	Sn(3)-O(3)	2.049(2)
Sn(1)-C(25)	2.115(6)	Sn(3)-C(33)	2.127(4)
Sn(1)-C(29)	2.134(5)	Sn(3)-C(21)	2.131(4)
Sn(1)-O(7)	2.174(2)	Sn(3)-O(2)	2.137(2)
Sn(1)-O(1)	2.207(3)	Sn(3)-O(4)	2.162(2)
Sn(2)-O(2)	2.043(2)	Sn(4)-O(4)	2.059(2)
Sn(2)-O(3)	2.102(2)	Sn(4)-O(3)	2.110(2)
Sn(2)-C(45)	2.126(4)	Sn(4)-C(49)	2.120(4)
Sn(2)-C(41)	2.132(4)	Sn(4)-C(53)	2.120(4)
Sn(2)-O(1)	2.185(3)	Sn(4)-O(6A)	2.285(2)
O(2)-Sn(1)-C(25)	113.9(2)	O(3)-Sn(3)-C(33)	113.11(14)
O(2)-Sn(1)-C(29)	114.4(2)	O(3)-Sn(3)-C(21)	116.84(14)
C(25)-Sn(1)-C(29)	131.6(3)	C(33)-Sn(3)-C(21)	130.03(17)
O(2)-Sn(1)-O(7)	80.04(9)	O(3)-Sn(3)-O(2)	74.48(9)
C(25)-Sn(1)-O(7)	94.1(2)	C(33)-Sn(3)-O(2)	97.59(13)
C(29)-Sn(1)-O(7)	97.06(18)	C(21)-Sn(3)-O(2)	94.38(13)
O(2) - Sn(1) - O(1)	72.53(9)	O(3)-Sn(3)-O(4)	73.37(9)
C(25)-Sn(1)-O(1)	96.36(19)	C(33)-Sn(3)-O(4)	96.85(13)
C(29)-Sn(1)-O(1)	94.80(17)	C(21)-Sn(3)-O(4)	98.10(13)
O(7) - Sn(1) - O(1)	152.56(10)	O(2)-Sn(3)-O(4)	147.77(9)
O(2)-Sn(2)-O(3)	75.36(9)	O(4) - Sn(4) - O(3)	74.26(9)
O(2)-Sn(2)-C(45)	119.35(15)	O(4) - Sn(4) - C(49)	110.38(13)
O(3) - Sn(2) - C(45)	97.25(13)	O(3) - Sn(4) - C(49)	102.51(13)
O(2)-Sn(2)-C(41)	114.22(15)	O(4)-Sn(4)-C(53)	109.05(13)
O(3)-Sn(2)-C(41)	100.96(15)	O(3)-Sn(4)-C(53)	101.19(13)
C(45)-Sn(2)-C(41)	126.15(18)	C(49) - Sn(4) - C(53)	138.11(15)
O(2)-Sn(2)-O(1)	72.34(10)	O(4)-Sn(4)-O(6A)	81.78(9)
O(3)-Sn(2)-O(1)	147.27(10)	O(3)-Sn(4)-O(6A)	155.96(9)
C(45)-Sn(2)-O(1)	93.94(14)	C(49)-Sn(4)-O(6A)	83.86(13)
C(41) - Sn(2) - O(1)	96.92(15)	C(53) - Sn(4) - O(6A)	88.27(12)

Symmetry transformations used to generate equivalent atoms: A -x + 1, -y + 2, -z + 1.

Table 6

Selected bond lengths (Å) and angles (°) for 6 .						
Sn(1)-O(10)	2.037(4)	Sn(3)-O(8)	2.034(4)			
Sn(1)-C(47)	2.106(7)	Sn(3)–C(43)	2.116(10)			
Sn(1)-C(51)	2.112(7)	Sn(3)–O(9)	2.124(4)			
Sn(1)-O(9)	2.114(4)	Sn(3)-C(57)	2.129(9)			
Sn(1)-O(4A)	2.254(4)	Sn(3)–O(7)	2.176(4)			
Sn(2)-O(9)	2.029(4)	Sn(4)–O(8)	2.016(4)			
Sn(2)-C(39)	2.111(8)	Sn(4)–C(27)	2.110(9)			
Sn(2)-C(35)	2.115(8)	Sn(4)-C(31)	2.134(7)			
Sn(2)-O(8)	2.134(4)	Sn(4)-O(1)	2.168(4)			
Sn(2)-O(10)	2.192(4)	Sn(4)-O(7)	2.204(4)			
O(10)-Sn(1)-C(47)	11.7(2)	O(8)-Sn(3)-C(43)	114.2(3)			
O(10)-Sn(1)-C(51)	114.0(2)	O(8)-Sn(3)-O(9)	75.06(15)			
C(47) - Sn(1) - C(51)	134.2(3)	C(43)-Sn(3)-O(9)	99.1(3)			
O(10)-Sn(1)-O(9)	74.51(15)	O(8)-Sn(3)-C(57)	117.7(3)			
C(47)-Sn(1)-O(9)	98.3(2)	C(43)-Sn(3)-C(57)	128.0(4)			
C(51)-Sn(1)-O(9)	97.5(2)	O(9)-Sn(3)-C(57)	96.4(2)			
O(10)-Sn(1)-O(4A)	84.16(15)	O(8)-Sn(3)-O(7)	72.43(15)			
C(47)-Sn(1)-O(4A)	91.1(2)	C(43) - Sn(3) - O(7)	96.8(3)			
C(51)-Sn(1)-O(4A)	89.3(2)	O(9)-Sn(3)-O(7)	147.35(16)			
O(9)-Sn(1)-O(4A)	158.59(15)	C(57)-Sn(3)-O(7)	96.0(2)			
O(9) - Sn(2) - C(39)	116.4(3)	O(8) - Sn(4) - C(27)	120.6(3)			
O(9) - Sn(2) - C(35)	118.2(3)	O(8) - Sn(4) - C(31)	114.2(2)			
C(39)-Sn(2)-C(35)	125.4(3)	C(27)-Sn(4)-C(31)	125.0(3)			
O(9)-Sn(2)-O(8)	74.96(15)	O(8)-Sn(4)-O(1)	79.88(15)			
C(39)-Sn(2)-O(8)	98.5(3)	C(27) - Sn(4) - O(1)	96.1(3)			
C(35)-Sn(2)-O(8)	97.0(2)	C(31) - Sn(4) - O(1)	98.5(2)			
O(9)-Sn(2)-O(10)	73.01(15)	O(8)-Sn(4)-O(7)	72.18(15)			
C(39)-Sn(2)-O(10)	94.6(2)	C(27)-Sn(4)-O(7)	95.3(3)			
C(35)-Sn(2)-O(10)	99.0(3)	C(31)-Sn(4)-O(7)	95.9(2)			
O(8) - Sn(2) - O(10)	147.94(15)	O(1) - Sn(4) - O(7)	151.86(15)			

Symmetry transformations used to generate equivalent atoms: A - x + 1, -y + 1, -z.

considerably from 180°, which indicate that the structures are distorted trigonal bipyramidal. The distortions are partly due to the rigid framework of the ladders. Moreover, each carboxylate group coordinates to an exocyclic Sn atom exclusively in the monodentate mode to generate a macrocycle containing two ladders (Fig. 3).

The formation of **4–6** represents an example of ladder-type carboxylates in which the insertion of μ_2 -OR (R = CH₃CH₂— or CH₃CH₂CH₂CH₂—) group occurs. Crystal structure of **4–6** features a μ_2 -coordination of –OR. This result can be interpreted in terms of donor strength competition, in which the –OR groups show higher donor capacity than the carboxylates group of the HL [34,35].

The Sn2 \cdots O8A for **4**, Sn1 \cdots O8 for **5** and Sn4 \cdots O2 for **6** distance is 3.143, 3.192 and 3.092 Å, which is less than the sum of van der Waals radii (3.68 Å) [32]. Thus, if this weak interaction is considered sufficiently, the geometry around Sn atom is best described as skew-trapezoidal bipyramidal geometry.

The O6 for **4**, O5A for **5** and O3A for **6** of the carboxylate have weak interactions with Sn: the bond lengths of Sn3…O6 (3.522 Å) for **4**, Sn4…O5A (3.567 Å) for **5** and Sn1…O3A (3.451 Å) for **6**. Intermolecular Sn…O interactions exist between Sn (Sn3 for **4**, Sn4 for **5** and Sn1 for **6**) and O (ethanolic oxygen O11B for **4**, ethanolic oxygen O11B for **5** and carbonylic oxygen O5B for **6**) at 3.017, 2.903 and 3.393 Å, in which the ethanolic oxygen shows stronger coordination than carbonylic oxygen. The influence of the intermolecular O atoms is so strong that it causes the expansion of the C–Sn–C angle [C26–Sn3–C22 140.9(2)° for **4**, C49–Sn4–C53 138.11(15)° for **5** and C47–Sn1–C51 134.2(3)° for **6**]. If these oxygen atoms can be considered as bonding, each tin atom (Sn3 for **4**, Sn4 for **5** and Sn1 for **6**) is seven-coordinated.

In the interesting structures of complex **4** and **5**, the ethanolic oxygen forms weak $Sn\cdots O$ interactions and $O-H\cdots O$ (2.818 Å for **4** and 2.783 Å for **5**) hydrogen bonds, which construct the 2D supramolecular network structure with each other's adjacent macrocycle containing two ladders to afford a novel macrocycle (II) (Fig. 4).



Fig. 3. The molecular structures of complexes 4-6 with thermal ellipsoids at 15% probability level. Solvent molecules have been omitted for clarity.

It is noteworthy that the self-assembly occurs through an extensive set of intermolecular Sn…O interactions in **6** and helps the molecules form a 1D infinite chains with another type of a novel macrocycle (II) having larger cavity (Fig. 5). The novel macrocyclic



Fig. 4. The supramolecular structure of **4** and **5**, showing the 2D supramolecular network structure by intermolecular Sn \cdots O interactions and O–H \cdots O hydrogen bonds. Parts of the *n*-butyl groups have been omitted for clarity.

(II) voids of complex **6** allow for two ethanol molecules, but the obvious interactions $[(n-Bu_2Sn)_2(4,6-L^2)O_2(OH)(OC_2H_5)]_2$ moiety and the ethanol molecules have not been found. For clarity, the ethanolic guest molecule is space-filling.

3.3.3. Antitumor activity

Table 7 shows antitumor effects against three cancer cell lines in different concentrations (0.3, 1, 3, 10, and 30 mg/ml) of complexes **1–6**. From the data of Table 7, we can see that the growth inhibition of all cells to 10 mg/ml solutions of complexes **1–6** are partly the best. In addition, 0.3 mg/ml of **2** and **4** do not show antitumor effects against HT1080, the same with 0.3 mg/ml of **4** and **6** to HeLa. In comparison with complexes **1** and **2**, **3** is the best antitumor agent for HeLa (**3** > **1** > **2**), and so is **1** for HT1080 (**1** > **3** > **2**) and U87 (**1** > **2** > **3**). Compared with complexes **4** and **6**, **5** is the best antitumor agent for HeLa (**5** > **6** > **4**), and so is **4** for HT1080 (**4** > **6** > **5**) and U87 (**4** > **6** > **5**). The relative effectiveness of the anti-cancer activities shows that the different complexes act against the same



Fig. 5. The supramolecular structure of the complex **6**, showing the inclusion of solvent molecules within the macrocycle void, macrocyclic network and 1D chain of rings connected by intermolecular Sn…O interactions. Parts of the *n*-butyl groups have been omitted for clarity.

 Table 7

 The in vitro antitumor activities of 1–6 against HeLa, HT1080 and U87 cells.

Drug labeling Dose (µg/n	nl) Anticance	Anticancer activity (%)						
	HeLa		HT10	080		U87		
Complex	1 2	3	1	2	3	1	2	3
0.3	11.7 14.	5 24.3	6.3	-2.1	8.9	52.3	40.0	28.2
1	33.2 26.4	4 50.4	25.0	19.0	15.3	67.1	55.9	40.0
3	43.4 38.	1 56.9	56.6	42.0	54.6	72.4	67.6	43.1
10	44.4 44.	5 57.6	66.0	65.8	65.5	74.7	73.6	43.7
30	43.9 43.9	56.8	66.0	65.2	62.5	72.8	73.3	44.2
Complex	4 5	6	4	5	6	4	5	6
0.3	-2.3 9.	1 -1.4	-3.1	1.6	0.7	50.9	9.8	6.5
1	6.5 47.	5 -0.2	10.2	4.1	-0.4	64.2	31.3	9.5
3	30.8 52.	2 7.3	14.0	2.7	3.6	69.4	40.5	53.8
10	42.6 56.	34.2	61.7	17.8	28.8	73.6	42.9	70.2
30	42.1 55.	9 43.8	61.0	22.0	45.3	71.0	43.4	71.2

cell with different effects, while the same complex acts against the different cells also with different effects. The results indicate that complexes act against cells selectively and the substituent groups of the ligands have an effect on antitumor activity.

From the derived IC50 values (Table 8), **3** seems to be the most efficient antitumor agent for HeLa and its antitumor activity is higher than that of the clinically used *cis*-platin (IC = 3.50) [36]. **1**, **2** and **4** seem to be the most efficient antitumor agents for U87 and their antitumor activities are higher than that of the clinically used *cis*-platin (IC = 2.60 ± 1.00) [37]. *Cis*-platin cannot kill the HT1080 cancer cell [38], but the complexes **1**–**6** have an effect on HT1080, so we can arrive at a conclusion that **1** is best for HT1080, while antitumor effects of the complexes **2** and **3** are similar, which indicates that the ligand substituting group has little impact on HT1080.

Table 8

Concentration of complexes 1-6 to obtain 50% inhibition of HeLa, HT1080 and U87 proliferate activity.

Drug labeling	IC50				
	HeLa	HT1080	U87		
Complex 1	25.720	5.003	0.057		
Complex 2	31.743	6.395	0.598		
Complex 3	2.679	6.132	74.043		
Complex 4	29.765	10.692	0.092		
Complex 5	4.894	279.033	28.959		
Complex 6	29.696	33.377	5.323		
Cisplatin	3.50		2.60 ± 1.00		

It should be pointed out that we tested the effect of ligands (H_2L^{1-3}) alone against each cell line, however, those ligands exhibited almost no inhibition of cellular proliferation (IC50 > 300 mg/ml). In addition, fat-solubility of di-*n*-butyltin oxide and triphenyltin hydroxide are poor and they are not easily hydrolyzed into active ion (*n*-Bu₂Sn²⁺ and Ph₃Sn⁺), while organic acid ligand enhances the fat-solubility of organotin carboxylates [39–41].

Acknowledgments

We acknowledged the Postdoctoral Science foundation of China (No. 2005038561).

Appendix A. Supplementary data

CCDC 717707, 717708, 717709, 717703, 717706 and 717704 contain the supplementary crystallographic data for complexes **1–6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.03.048.

References

- V. Chandrasekhar, V. Baskar, J.J. Vittal, J. Am. Chem. Soc. 125 (2003) 2392–2393.
- [2] V. Chandrasekhar, V. Baskar, K. Gopal, J.J. Vittal, Organometallics 24 (2005) 4926–4932.
- 3] H.D. Yin, G. Li, Z.J. Gao, H.L. Xu, J. Organomet. Chem. 691 (2006) 1235-1241.
- [4] R.R. Holmes, Acc. Chem. Res. 22 (1989) 190-197.
- [5] M. Hanif, M. Hussain, S. Ali, M.H. Bhatti, M.S. Ahmed, B. Mirza, H.S. Evans, Polyhedron 29 (2010) 613-619.
- [6] S.K. Hadjikakou, N. Hadjiliadis, Coord. Chem. Rev. 253 (2009) 235-249.
- [7] C.L. Ma, J.K. Li, R.F. Zhang, J. Organomet. Chem. 691 (2006) 1713-1721.
- [8] C.L. Ma, Q. Jiang, R.F. Zhang, D.Q. Wang, Dalton Trans. (2003) 2975–2978.
- [9] R.F. Zhang, Q.F. Wang, M.Q. Yang, Y.R. Wang, C.L. Ma, Polyhedron 27 (2008) 3123-3131
- [10] T.S.B. Band, K.S. Singh, A. Linden, X.Q. Song, G. Eng, Polyhedron 25 (2006) 3441–3448.
- [11] R. Garcla-Zarracino, H. Hopfl, Angew. Chem. Int. Ed. 43 (2004) 1507-1511.
- [12] G. Prabusankar, R. Murugavel, Organometallics 23 (2004) 5644–5647.
- [13] D. Dakternieks, A. Duthie, D.R. Smyth, C.P. Stapleton, E.R.T. Tiekink, Organometallics 22 (2003) 4599–4603.
- [14] G.L. Zheng, J.F. Ma, Z.M. Su, L.K. Yan, J. Yang, Y.Y. Li, J.F. Liu, Angew. Chem. Int. Ed. 43 (2004) 2409–2411.

- [15] D. Dakternieks, A. Duthie, B. Zobel, K. Jurkschat, M. Schürmann, E.R.T. Tiekink, Organometallics 21 (2002) 647–652.
- [16] D. Kovala-Demertzi, N. Kourkoumelis, A. Koutsodimou, A. Moukarika, E. Horn, E.R.T. Tiekink, J. Organomet. Chem. 620 (2001) 194–201.
- [17] R. García-Zarracino, H. Höpfl, Angew. Chem. 116 (2004) 1533-1537.
- [18] R. García-Zarracino, H. Höpfl, J. Am. Chem. Soc. 127 (2005) 3120-3130.
- [19] R. García-Zarracino, J. Ramos-Quiñones, H. Höpfl, Inorg. Chem. 42 (2003) 3835-3845.
- [20] T.P. Lockhart, Organometallics 7 (1988) 1438-1443.
- [21] V. Chandrasekhar, S. Nagendran, V. Baskar, Coord. Chem. Rev. 235 (2002) 1-52.
- [22] V. Chandrasekhar, K. Gopal, P. Thilagar, Acc. Chem. Res. 40 (2007) 420-434.
- [23] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, second ed. Pergamon, Oxford, 1980.
- [24] G.M. Sheldrick, SHELXS-97, A Program for Automatic Solution of Crystal Structure. University of Geottingen, Germany, 1997.
- [25] G.M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement. University of Geottingen, Germany, 1997.
- [26] A. Varvaresou, K. Iakovou, Anticancer. Res. 25 (2005) 2253-2258.
- [27] M. Ueda, M. Ohkura, Y. Imai, J. Polym. Sci. Polym. Chem. Ed. 12 (1974) 719-727.
- [28] W.H. Mills, M. Mills, J. Chem. Soc. 101 (1912) 2198-2200.

- [29] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227-250.
- [30] D. Kovala-Demertzi, V.N. Dokorou, J.P. Jasinski, A. Opolski, J. Wiecek, M. Zervou, M.A. Demertzis, J. Organomet. Chem. 690 (2005) 1800–1806.
- [31] J. Holecek, A. Lycka, Inorg. Chim. Acta 118 (1986) 15-16.
- [32] W.L. Kang, X.Y. Wu, J.B. Huang, J. Organomet. Chem. 694 (2009) 2402–2408.
 [33] M.J. Cox, M.I. Mohamed-Ibrahim, E.R.T. Tiekink, Main Group Met. Chem. 20
- (1997) 207–212. [34] V. Dokorou, M.A. Demertzis, J.P. Jasinski, D. Kovala-Demertzi, J. Organomet.
- Chem. 689 (2004) 317–325. [35] D. Kovala-Demertzi, V. Dokorou, R. Kruszynski, J. Wiecek, T.J. Bartczak,
- M.A. Demertzis, Z. Anorg. Allg. Chem. 631 (2005) 241–2484. [36] G.N. Kaluderović, V.M. Dinović, Z.D. Juranić, T.P. Stanojković, T.J. Sabo, J. Inorg.
- Biochem. 99 (2005) 488–496.
- [37] T. Servidei, A. Riccardi, M. Sanguinetti, C. Dominici, R. Riccardi, J. Cell. Physiol. 208 (2006) 220–228.
- [38] B. Law, L. Quinti, Y. Choi, R. Weissleder, T. Ching-Hsuan, Mol. Cancer Ther. 5 (2006) 1944–1949.
- [39] M. Ashfaq, M.I. Khan, M.K. Baloch, A. Malik, J. Organomet. Chem. 689 (2004) 238-245.
- [40] M.I. Khan, M.K. Baloch, M. Ashfaq, J. Organomet. Chem. 689 (2004) 3370-3378.
- [41] K.C. Molloy, K. Quill, I.W. Nowell, J. Chem. Soc. Dalton Trans. (1987) 101-106.