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Self-Assembly of Dialkyltin(IV) Moieties and Aromatic Dicarboxylates to Complexes with a Polymeric or a Discrete Trinuclear Macrocyclic Structure in the Solid State and a Mixture of Fast Interchanging Cyclooligomeric Structures in Solution

Reyes García-Zarracino, Jesús Ramos-Quiñones, and Herbert Höpfl*

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos,
Av. Universidad 1001, C.P. 62210 Cuernavaca, Mexico

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It is well-known that the structures of trialkyltin(IV) carboxylates can be either monomeric, polymeric, or cyclooligomeric in the solid state. In contrast, all dialkyltin(IV) dicarboxylates characterized so far in the solid state have monomeric or polymeric structures, however, for some cases it has been proposed that their solution-state structure is cyclooligomeric. In order to generate more information on this subject, dimethyl- and di-*n*-butyltin(IV) complexes with phthalic and isophthalic acid have been prepared and analyzed both in solution and in the solid state. The solid-state structures of the two dialkyltin(IV) phthalates examined herein contain polymeric molecular chains, however, with supramolecular Sn···O′ interactions, which result in the generation of cyclooligomeric units. This provides evidence for the presence of discrete cyclooligomeric structures in solution, which are involved in fast dynamic exchange equilibria as evidenced by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. In the case of the two dialkyltin(IV) isophthalate complexes studied herein (R = Me, *n*-Bu), only the di-*n*-butyltin derivative is soluble and NMR spectroscopy as well as FAB$^+$ spectrometry indicates the formation of cyclic dinuclear, trinuclear, and/or tetranuclear species in solution, which may be involved also in fast dynamic exchange equilibria. In the solid state, however, discrete cyclotrinuclear units can be identified, in which the 24-membered macrocyclic cavity is almost completely planar, having six oxygen atoms directed into its interior and six Sn–*n*-butyl groups approximately perpendicular to the molecular plane. The diameter of the cyclic cavity can be described by the transannular O···O distances that vary from 7.68 to 7.84 Å, being large enough for the introduction of linear alkyl groups. This can be demonstrated by the supramolecular structure of this compound, which contains a new type of bis[2]pseudorotaxane formed between two molecules through mutual threading via two of the Sn–butyl groups. Such a supramolecular entity has been unknown so far, since the usual composition of bis[2]pseudorotaxanes is the trimolecular combination of a macrocyclic ring system with two threads.

1. Introduction

Metal-directed self-assembly of organic ligands and metal ions or organometallic substances to well-defined structures can be applied for the generation of two different types of chemical substances, both being interesting for a wide range of possible applications. The first type are compounds with discrete molecular structures and frequently a more or less huge cavity[1] and the second are materials with polymeric and microporous structures in the solid state.[2] Although this chemistry has been developed now for more than 15 years, only a relatively small number of such structures have been reported so far with main group elements.[1c,f,g,3]

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* Author to whom correspondence should be addressed. Fax: (+52) 777 329 79 97. E-mail: hhopfl@buzon.uaem.mx.

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Among the most common ligands used for the construction of compounds with polymeric and microporous structures in the solid state are dicarboxylic[4−6] and tricarboxylic acids,[7] which permit the preparation of neutral complexes with 2- or 3-fold charged metal ions, respectively, if they are reacted in a 1:1 stoichiometric ratio. However, until now little is known with respect to the synthesis of discrete oligomeric macrocyclic complexes with these ligands.[8,9]

It is well-known that the solid-state structures of trialkyltin(IV) carboxylates can be either mono-,[10] oligo-,[11] poly-,[11] or cyclooligomeric,[12,13] whereby the oligo- and polymeric structures are formed through intermolecular Sn−O−C═O→Sn bonds. Since these bonds are relatively weak, a discrete molecular structure can be expected in solution. Exceptions are neutral[14] and anionic[15] triorganotin(IV) complexes of dicarboxylic acids, in which the dicarboxylate is bound through covalent Sn−O bonds or even a bidentate coordination mode. Because of the interest in the creation of oligo- and polymeric structures with strong binding interactions between the repeating units, we became interested in the structural chemistry of diorganotin(IV) derivatives of dicarboxylic acids, and a literature search shows that the first complexes of this type have been prepared already 50 years ago.[8a−8b] Since then different diorganotin(IV) moieties, mainly dimethyl and di-*n*-butyltin(IV), have been combined with the most common dicarboxylic acids, e.g., oxalic,[16] malonic,[8d] succinic,[8d] adipic,[8d] maleic,[8c] phthalic,[17] and terephthalic acid,[17c] mostly because of their application as PVC stabilizers[18] as well as catalysts for transesterification reactions,[19] polyurethane polymerizations,[19] and RTV silicone curing reactions.[20] A series of diorganotin(IV) derivatives of dicarboxylic acids have been tested also as antitumor agents.[21] However, a conclusive characterization of diorganotin(IV) derivatives of dicarboxylic acids with respect to their structures in the liquid state is not trivial, since they are frequently insoluble due to their polymeric or oligomeric nature, and for the case that they are soluble, they are often involved in dynamic equilibria with fast ligand exchange reactions.[22] It has been also proposed that polymeric solid-state structures may be transformed to cyclooligomeric solution-state structures,[8c,d] but so far, aside from cryoscopic[17c] and osmometric[8d] molecular weight determinations, conclusive evidence has not been reported. To the best of our knowledge, until now an X-ray crystallographic characteriza-

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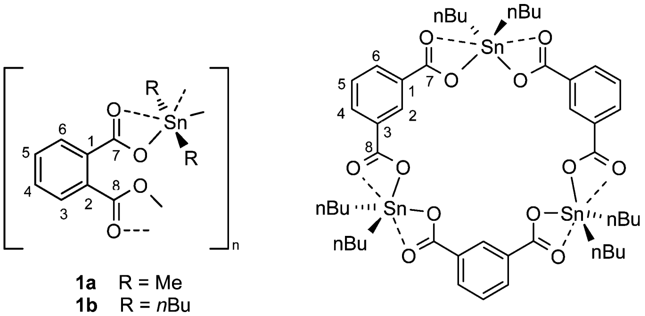
Chart 1. Molecular Structures of the Compounds Studied in This Contribution



1a R = Me
1b R = *n*Bu

2b

tion of the structure of a cyclooligomeric diorganotin(IV) dicarboxylate has not been published.[23]

In order to generate more information on this subject, we prepared dimethyl- and di-*n*-butyltin(IV) complexes with phthalic and isophthalic acid, which according to molecular models seem to be the most adequate candidates for the formation of cyclooligomeric structures. In the first part of this contribution we report on the solid-state structures of dimethyl- and di-*n*-butyltin(IV) phthalate, which both contain a cyclooligomeric unit, thus providing possibly evidence for the formation of cyclooligomeric structures in solution. In the second part, our results on the solution- and solid-state study of di-*n*-butyltin(IV) isophthalate are presented, which forms a new type of trinuclear macrocyclic compound with a so far unknown supramolecular structure containing dimolecular bis[2]pseudorotaxane units in the solid state (Chart 1).

2. Experimental Section

Instrumental. NMR studies were carried out with Varian Gemini 200, Varian Inova 400, and JEOL Eclipse 400 instruments. Standards were TMS (internal, ^{1}H, ^{13}C) and $SnMe_4$ (external, ^{119}Sn). Chemical shifts are stated in parts per million; they are positive, when the signal is shifted to higher frequencies than the standard. COSY, HETCOR, and COLOC experiments have been carried out in order to assign the ^{1}H and ^{13}C spectra completely. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. The FAB mass spectrum of **2b** was obtained on JEOL JMS-700 equipment. Elemental analyses have been carried out on Perkin-Elmer series II 2400 and Elementar Vario ELIII instruments.

Preparative Part. Commercial starting materials and solvents have been used. Me_2SnO has been prepared according to a method reported in the literature.[24]

Preparation of Dimethyltin(IV) Phthalate (1a). Method A. A mixture of phthalic acid (0.18 g, 1.06 mmol) and dimethyltin(IV) oxide (0.18 g, 1.06 mmol) in toluene/ethanol (5:1) is refluxed for 8 h using a Dean–Stark trap. After cooling to room temperature, the solvent mixture is removed under vacuum, obtaining **1a** as a colorless product, which is washed with hot ethanol. Compound **1a** is slightly soluble in DMSO and DME. Yield: 79%. Mp: >300 °C.

Method B. To a solution of phthalic acid(0.082 g, 0.49 mmol) and potassium hydroxide (0.055 g, 0.96 mmol) in 2 mL of water is added dimethyltin(IV) chloride (0.107 g, 0.49 mmol) in 3 mL of water, whereupon a white product precipitates, which has been identified as **1a**. Crystals suitable for X-ray crystallography were obtained, when more diluted solutions of the starting materials were combined without agitation. Yield: 62%. Mp: >300 °C.

IR (KBr) $\tilde{\nu}_{max}$: 3093 (w), 3011 (w), 2922 (w), 1722 (w), 1586 (s), 1495 (m), 1449 (w), 1389 (s), 1299 (w), 1267 (w), 1148 (w), 1084 (w), 1033 (w), 867 (w), 803 (m), 762 (m), 711 (m), 657 (w), 587 (w), 549 (w), 485 (m), 449 (w) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6, 20 °C, TMS): $\delta = 0.90$ (s, 6H, CH_3, $^{2}J_{Sn-H} = 45$ Hz), 7.45 (m, 2H, H3, H6), 7.57 (m, 2H, H4, H5) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 20 °C, TMS): $\delta = 8.3$ (br, CH_3), 128.3 (C3, C6), 129.5 (C4, C5), 135.1 (C1, C2), 172.5 (br, C=O) ppm. ^{119}Sn NMR (149 MHz, DMSO-d_6, 20 °C, $SnMe_4$): $\delta = -203$ (br) ppm.

Preparation of Di-*n*-butyltin(IV) Phthalate (1b). A mixture of phthalic acid (0.25 g, 1.50 mmol) and di-*n*-butyltin(IV) oxide (0.37 g, 1.50 mmol) in toluene/ethanol (5:1) is refluxed for 8 h using a Dean–Stark trap. After cooling to room temperature, the solvent mixture is removed under vacuum, obtaining **1b** as a colorless product, which is washed with hexane. Crystals suitable for X-ray crystallography were grown from chloroform and acetonitrile. Yield: 59%. Mp: 223–225 °C.

IR (KBr) $\tilde{\nu}_{max}$: 2959 (m), 2929 (m), 2867 (w), 1597 (s), 1494 (w), 1456 (w), 1372 (s), 1297 (w), 1262 (w), 1149 (w), 1082 (w), 862 (m), 794 (w), 760 (m), 713 (m), 685 (m), 660 (w), 593 (w), 492 (m), 456 (m) cm^{-1}.

NMR Data in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.79$ (t, 6H, Hδ), 1.29 (tq, 4H, Hγ), 1.72 (tt, 4H, Hβ), 1.91 (t, 4H, Hα), 7.52 (dd, 2H, H4, H5), 7.73 (dd, 2H, H3, H6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 13.5$ (Cδ), 25.5 (Cα, $^{1}J_{Sn-C} = 563$ Hz), 26.4 (Cγ, $^{3}J_{Sn-C} = 102$ Hz), 26.9 (Cβ, $^{2}J_{Sn-C} = 29$ Hz), 129.2 (C3, C6), 130.9 (C4, C5), 132.6 (C1, C2), 177.5 (C7, C8) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, $SnMe_4$): δ (−60 °C) = −126 (br), δ (20 °C) = −136 (br), δ (60 °C) = −135 (br, $h_{1/2} = 40$ Hz) ppm.

NMR Data in C_6D_6. ^{1}H NMR (400 MHz, C_6D_6, 20 °C, TMS): $\delta = 0.81$ (t, 6H, Hδ), 1.32 (tq, 4H, Hγ), 1.92 (m, 4H, Hβ), 2.12 (t, 4H, Hα), 6.95 (m, 2H, H4, H5), 7.90 (m, 2H, H3, H6) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C, TMS): $\delta = 14.1$ (Cδ), 26.2 (Cα, $^{1}J_{Sn-C} = 567$ Hz), 27.1 (Cγ, $^{3}J_{Sn-C} = 98$ Hz), 27.8 (Cβ, $^{2}J_{Sn-C} =$ 28 Hz), 129.9 (C3, C6), 131.1 (C4, C5), 134.1 (C1, C2), 178.3

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(C7, C8) ppm. ^{119}Sn NMR (149 MHz, C_6D_6, 20 °C, $SnMe_4$): $\delta = -139$ (br) ppm.

NMR Data in DMSO-d_6. ^{1}H NMR (200 MHz, DMSO-d_6, 20 °C, TMS): $\delta = 0.88$ (t, 6H, Hδ), 1.34 (tq, 4H, Hγ), 1.67 (m, 8H, Hα), Hβ), 7.45 (m, 2H, H4, H5), 7.52 (m, 2H, H3, H6) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 20 °C, TMS): $\delta = 13.8$ (br, Cδ), 26.1 (br, Cα), 26.9 (Cβ, Cγ), 127.8 (C3, C6), 129.3 (C4, C5), 134.9 (C1, C2), 172.3 (C7, C8) ppm. ^{119}Sn NMR (149 MHz, DMSO-d_6, 20 °C, $SnMe_4$): $\delta = -230$ (br) ppm.

Preparation of Dimethyltin(IV) Isophthalate (2a). A mixture of isophthalic acid (0.25 g, 1.50 mmol) and dimethyltin(IV) oxide (0.25 g, 1.50 mmol) in toluene/ethanol (5:1) is refluxed for 6 h using a Dean−Stark trap. After cooling to room temperature, the solvent mixture is removed under vacuum, obtaining **2a** as a colorless product, which is washed with hot ethanol. Compound **2a** is insoluble in all commonly used solvents. Yield: 51%. Mp: >300 °C.

IR (KBr) $\tilde{\nu}_{max}$: 3069 (w), 1694 (m), 1613 (s), 1562 (m), 1368 (s), 1320 (m), 1279 (w), 1160 (w), 1075 (w), 934 (w), 858 (w), 737 (s), 684 (w), 664 (w), 583 (w), 568 (w), 448 (w) cm^{-1}.

Elemental anal. Calcd for $(C_9H_{10}O_4Sn)_n$: C, 38.38; H, 3.20. Found: C, 39.47; H, 3.24.

Preparation of Di-*n*-butyltin(IV) Isophthalate (2b). A mixture of isophthalic acid (0.25 g, 1.50 mmol) and di-*n*-butyltin(IV) oxide (0.37 g, 1.50 mmol) in toluene/ethanol (5:1) is refluxed for 6 h using a Dean−Stark trap. After cooling to room temperature, the solvent mixture is removed under vacuum, obtaining **2b** as a colorless product, which is washed with hexane. Crystals suitable for X-ray crystallography were grown from benzene. Yield: 50%. Mp: 326−328 °C.

IR (KBr) $\tilde{\nu}_{max}$: 3079 (w), 2960 (m), 2928 (m), 2865 (w), 1615 (m), 1572 (m), 1489 (w), 1459 (w), 1399 (m), 1369 (s), 1271 (w), 1164 (w), 1078 (w), 848 (w), 744 (m), 687 (w), 667 (w), 552(w), 474 (w) cm^{-1}.

MS (FAB$^+$): *m/z* (%): 1590 (3), 1530.5 (12), 1190.7 (11), 1133.0 (17), 795.0 (18), 399.1 (100).

NMR Data in C_6D_6. ^{1}H NMR (400 MHz, C_6D_6, 20 °C, TMS): $\delta = 0.79$ (t, 6H, Hδ), 1.33 (m, 4H, Hγ), 1.82 (m, 8H, Hα, Hβ), 7.00 (dt, 1H, H5), 8.44 (dd, 2H, H4, H6), 9.48 (t, 1H, H2) ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C, TMS): $\delta = 13.9$ (Cδ), 26.4 (Cα, $^1J_{Sn-C} = 608$ Hz), 27.0 (Cγ, $^3J_{Sn-C} = 96$ Hz), 27.5 (Cβ, $^2J_{Sn-C} = 34$ Hz), 129.1 (C5), 131.5 (C1, C3), 133.3 (C2), 135.8 (C4, C6) 176.3 (C7, C8) ppm. ^{119}Sn NMR (149 MHz, C_6D_6, 20 °C, $SnMe_4$) $\delta = -161$ (s, $h_{1/2} = 33$ Hz) ppm.

NMR Data in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 6H, Hδ), 1.41 (tq, 4H, Hγ), 1.72 (m, 4H, Hβ), 1.81 (m, 4H, Hα), 7.61 (t, 1H, H5), 8.35 (dd, 2H, H4, H6), 9.07 (t, 1H, H2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 13.7$ (Cδ), 26.0 (Cα), 26.6, 26.9 (Cβ, Cγ), 128.6 (C5), 130.4 (C1, C3), 132.6 (C2), 135.4 (C4, C6), 176.3 (C7, C8) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 20 °C, $SnMe_4$): $\delta = -160$ (s, $h_{1/2} = 14$ Hz) ppm.

NMR Data in $CD_3C(O)CD_3$. ^{1}H NMR (400 MHz, $CD_3C(O)CD_3$, 20 °C, TMS): $\delta = 0.85$ (t, 6H, Hδ), 1.41 (tq, 4H, Hγ), 1.72 (m, 4H, Hβ), 1.84 (m, 4H, Hα), 7.71 (t, 1H, H5), 8.37 (dd, 2H, H4, H6), 8.98 (br, s, 1H, H2) ppm. ^{119}Sn NMR (149 MHz, $CD_3C(O)CD_3$, 20 °C, $SnMe_4$): $\delta = -172$ (br, $h_{1/2} = 70$ Hz) ppm.

NMR Data in C_5D_5N at −40 °C. ^{1}H NMR (400 MHz, C_5D_5N, 20 °C, TMS): $\delta = 0.51$ (t, 6H, Hδ), 1.10 (m, 4H, Hγ), 1.73 (m, 4H, Hβ), 1.89 (m, 4H, Hα), 7.69 (t, 1H, H5), 8.70 (d, 2H, H4, H6), 9.80 (br, s, 1H, H2) ppm.

NMR Data in C_5D_5N at 20 °C. ^{1}H NMR (400 MHz, C_5D_5N, TMS): $\delta = 0.62$ (t, 6H, Hδ), 1.20 (tq, 4H, Hγ), 1.77 (m, 4H, Hβ), 1.95 (m, 4H, Hα), 7.66 (t, 1H, H5), 8.67 (d, 2H, H4, H6), 9.77 (br, s, 1H, H2) ppm.

NMR Data in C_5D_5N at 110 °C. ^{1}H NMR (400 MHz, C_5D_5N, TMS): $\delta = 0.81$ (t, 6H, Hδ), 1.39 (tq, 4H, Hγ), 1.89 (tt, 4H, Hβ), 2.03 (t, 4H, Hα), 7.61 (t, 1H, H5), 8.58 (d, 2H, H4, H6), 9.47 (br, s, 1H, H2) ppm. ^{119}Sn NMR (149 MHz, C_5D_3N, $SnMe_4$): $\delta = -238$ (br, $h_{1/2} = 210$ Hz) ppm.

Elemental anal. Calcd for $C_{48}H_{66}O_{12}Sn_3$ (%): C, 48.40; H, 5.58. Found: C, 48.38; H, 5.64.

X-ray Crystallography. X-ray diffraction studies were carried out on a BRUKER-AXS APEX diffractometer with a CCD area detector ($\lambda_{MoK\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at $T = 100$ or 293 K via ω-rotation ($\Delta/\omega = 0.3°$) at 10 s per frame (SMART[25]). The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT[26]). Structure solution, refinement, and data output were carried out with the SHELXTL-NT program package.[27] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. DFIX, DANG, and AFIX 65 instructions have been applied for the slightly disordered *n*-Bu groups and the benzene molecules in **1b** and **2b**, respectively. The molecular structures were created by the CRYSTALS software package.[28,29]

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-194420, 199126, 199127. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

3. Results and Discussion

3.1. Characterization of Dimethyl- and Di-*n*-butyltin(IV) Phthalate. 3.1.1. Preparation and Spectroscopic Characterization.

Compounds **1a** and **1b** have been prepared as reported by reaction of phthalic acid with an equimolar quantity of the corresponding dialkyltin(IV) oxide (R = Me for **1a**, R = *n*-Bu for **1b**) in a 5:1 solvent mixture of toluene and ethanol.[8d,30] While the dimethyltin(IV) complex is only slightly soluble in DMSO and DME, the di-*n*-butyltin(IV) derivative can be dissolved in polar and unpolar solvents, e.g., in benzene, chloroform, ethyl acetate, acetone, ethanol, and acetonitrile.

Both compounds have been previously studied by elemental analysis and IR spectroscopy,[8,17] furthermore by Mössbauer spectroscopy in the case of **1a**[17a] and NMR in the case of **1b**.[8d, 17c] On the basis of these data anisobidentate coordination modes of the carboxylate groups to the tin center have been proposed, resulting in a highly distorted 6-coordinate octahedral geometry with the two Sn−alkyl groups in trans orientation. The anisobidentate coordination mode

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Table 1. ^{1}H (400 MHz) and ^{119}Sn (149 MHz) NMR Spectroscopic Data (ppm) for Phthalic Acid and Compounds **1a** and **1b**, Including Solvents of Different Coordinative Strength

	H3/H6	H4/H5	Hα	Hβ	Hγ	Hδ	^{119}Sn
phthalic acid[a]	7.70 (d)	7.60 (d)					
1a[a]	7.57 (m)	7.45 (m)	0.90[b] (br)				−203 (br)
1b[a]	7.52 (m)	7.45 (m)	1.67 (m)	1.67 (m)	1.34 (tq)	0.88 (t)	−230 (br)
1b							
$CDCl_3$	7.73 (dd)	7.52 (dd)	1.91 (t)	1.72 (tt)	1.29 (tq)	0.79 (t)	−136 (br)
C_6D_6	7.90 (m)	6.95 (m)	2.12 (t)	1.92 (m)	1.32 (h)	0.81 (t)	−139 (br)

[a] Data in DMSO-d_6. [b] $^{2}J_{Sn-H} = 45$ Hz.

Table 2. ^{13}C (100 MHz) NMR Spectroscopic Data (ppm) for Phthalic Acid and Compounds **1a** and **1b**

	C1/C2	C3/C6	C4/C5	C=O	Cα	Cβ	Cγ	Cδ
phthalic Acid[a]	132.7	130.6	128.2	168.5				
1a[a]	135.1	128.3	129.5	172.5	8.3			
1b[a]	134.9	127.8	129.3	172.3	26.1	26.9	26.9	13.8
1b								
$CDCl_3$	132.6	129.2	130.9	177.5	25.5[b]	26.9[c]	26.4[d]	13.5
C_6D_6	134.1	129.9	131.1	178.3	26.2[e]	27.8[f]	27.1[g]	14.1

[a] Data in DMSO-d_6. [b] $^{1}J_{Sn-C} = 563$ Hz. [c] $^{2}J_{Sn-C} = 29$ Hz. [d] $^{3}J_{Sn-C} = 102$ Hz. [e] $^{1}J_{Sn-C} = 567$ Hz. [f] $^{2}J_{Sn-C} = 28$ Hz. [g] $^{3}J_{Sn-C} = 98$ Hz.

of the ligand can be proved by the $\Delta\tilde{\nu}$ differences between the symmetric and antisymmetric carboxylate stretches of 197 cm^{-1} for **1a** and 225 cm^{-1} for **1b**, respectively.[14b]

^{1}H, ^{13}C, and ^{119}Sn spectroscopic data have not been reported so far for compound **1a** and have been summarized in Tables 1 and 2 together with the chemical shift displacements of phthalic acid. The already reported NMR signal shift assignments of complex **1b** have been corroborated undoubtedly by two-dimensional COSY, HETCOR, and COLOC experiments and are included in the same tables for comparison. The ^{1}H and ^{13}C NMR spectra of **1a** and **1b** show signals corresponding either to a species with a highly symmetric structure or to a fast dynamic exchange equilibrium between two or more species with local asymmetry. The fact that no signals were detected that are characteristic for the end groups in a polymeric chain permits one to conclude that in solution either oligomeric fragments with a rather high molecular mass or oligomers with a cyclic structure are present.[8d] In the ^{1}H and ^{13}C NMR spectra the most relevant chemical shift differences between the ligand and the corresponding diorganotin(IV) complexes are observed for the carbon atoms of the carboxylate groups with a low-field shift upon coordination of $\Delta\delta = 3.8-4.0$ ppm and $\Delta\delta = 9.0-9.8$ ppm, depending on whether the spectrum was recorded in a coordinating (DMSO-d_6) or a noncoordinating solvent ($CDCl_3$). The ^{119}Sn NMR shifts recorded for **1b** in the noncoordinating solvents $CDCl_3$, $\delta = -136$ ppm, and C_6D_6, $\delta = -139$ ppm, are comparable to the ones reported for di-*n*-butyltin(IV) dicarboxylates with discrete molecular structures in solution, δ (^{119}Sn) ranging from −111 to −195 ppm.[22,31] The fact that this range is typical for a five-coordinate di-*n*-butyltin(IV) center confirms the asymmetric chelate arrangement of the carboxylate groups to the tin atoms with Sn−O bonds of various strengths (anisobidentate coordination mode), so that the strength of this type of bonding can be considered as intermediate between four- and six-coordinate (4 + 2 coordination).[22] In the presence of coordinating solvent molecules such as DMSO the ^{119}Sn NMR signals are high-field shifted, $\delta = -203$ ppm for **1a** and $\delta = -230$ ppm for **1b**, thus indicating an increase of the coordination number of the metal center, however, apparently with a low activation barrier for exchange. The signals in the ^{1}H decoupled ^{119}Sn NMR spectra (149 MHz) of **1a** and **1b** are broad and have the form of overlapping singlets. In order to interpret this phenomenon, the spectra of the more soluble complex **1b** have been recorded also at higher and lower temperatures. Although the shift displacements of the ^{1}H and ^{119}Sn NMR spectra recorded in $CDCl_3$ at 60 °C remained practically unchanged in comparison to the ones recorded at 20 °C, $\delta(^{119}\mathrm{Sn}) = -136$ ppm at 20 °C and −135 ppm at 60 °C, the signal shapes narrowed in both cases. In the case of the ^{119}Sn NMR spectrum the signal shape changed from a broad signal of overlapping singlets to one sharp singlet ($h_{1/2} = 40$ Hz), and in the case of the ^{1}H NMR spectrum the resolution of the signals was enhanced at higher temperatures. Consequently, at −60 °C the resolution of the ^{1}H NMR spectrum is reduced to such a grade that coupling is not observed anymore. At the same time the signals in the ^{13}C NMR spectrum are broadened, especially the ones for the Sn−Cα and aromatic carbon atoms. Accordingly, the overlapping singlets constituting the ^{119}Sn NMR signal are more separated ($\delta = -124.4$ to −127.9 ppm) and, additionally, a shift displacement of about 10 ppm to lower fields occurred, which is unusual for a dynamic exchange reaction. In contrast, in the spectra recorded in benzene-d_6 at $T = 20$ and 70 °C both signal shape and shift displacements remained unchanged. Thus, the NMR data give evidence for (i) an oligomeric nature of compound **1b** in solution, (ii) the occurrence of a fast dynamic ligand and/or solvent exchange equilibrium in $CDCl_3$, and probably (iii) a change of the coordination number at the tin atoms in $CDCl_3$, when the temperature is lowered.

In the literature two independent studies based on cryoscopic and osmometric molecular weight determinations have proposed the transformation of the polymeric solid-state structure of **1b** into a mixture of cyclooligomeric molecules with an average of 2.7−4.6 *n*-Bu_2Sn(phthalate) units per cycle in solution.[8d,17c] In order to obtain more structural details on this subject, an X-ray crystallographic study has been realized for compounds **1a** and **1b**.

3.1.2. X-ray Crystallographic Study of 1a and 1b. Due to the low solubility of dimethyltin(IV) phthalate, crystals suitable for X-ray crystallography could be obtained only when an aqueous solution of dimethyltin(IV) dichloride was combined with phthalic acid in the presence of potassium hydroxide (1:1:2). The IR spectrum of the crystals obtained through this in situ preparative method is identical to the one for the complex formed between dimethyltin(IV) oxide and phthalic acid. Crystals of di-*n*-butyltin(IV) phthalate with identical unit cells can be grown by slow evaporation of solutions of chloroform or acetonitrile. The most relevant

Table 3. Crystallographic Data[a] for Compounds **1a**, **1b**, and **2b**

	1a	**1b**[e]	**2b**
	Crystal Data		
formula	$C_{10}H_{10}O_4Sn$	$C_{32}H_{44}O_8Sn_2$	$C_{48}H_{66}O_{12}Sn_3\cdot 2C_6H_6$
cryst size (mm^3)	0.06 × 0.09 × 0.19	0.33 × 0.21 × 0.07	0.11 × 0.41 × 0.48
MW	312.87	794.05	1347.29
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
	Cell Parameters		
a (Å)	9.4966(17)	11.7166(6)	13.5232(16)
b (Å)	10.4578(19)	9.8931(5)	26.670(3)
c (Å)	11.316(2)	29.4262(16)	17.996(2)
α (deg)	90	90	90
β (deg)	96.766(3)	94.2430(10)	103.078(2)
γ (deg)	90	90	90
V (Å^3)	1116.0(4)	3401.5 (3)	6322.1(13)
Z	4	4	4
μ (mm^{-1})	2.280	1.514	1.231
ρ_{calcd} (g cm^{-3})	1.862	1.551	1.416
	Data Collection		
θ limits (deg)	$2 < \theta < 25$	$2 < \theta < 25$	$2 < \theta < 25$
hkl limits	−11, 11; −12, 12; −13, 13	−13, 13; 0, 11; 0, 34	−16, 15; −31, 31; −21, 21
no. of collected reflns	10363	39331	45917
no. of indep reflns (R_{int})	1974 (0.042)	8584 (0.032)	11130 (0.11)
no. of obsd reflns[b]	1834	5726	4009
no. of params	136	384	653
	Refinement		
R[c]	0.033	0.038	0.058
R_w[d]	0.072[f]	0.079[g]	0.155[h]
GOF	1.212	1.188	0.799
$\Delta\rho_{min}$ (e Å^{-3})	−1.04	−0.50	−0.41
$\Delta\rho_{max}$ (e Å^{-3})	0.46	2.08	1.25

[a] Data collection on a Bruker Apex CCD diffractometer, $T = 293$ K, Mo Kα; monochromator: graphite. [b] $F_o > 4\sigma(F_o)$. [c] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. [d] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [e] Data collection at $T = 100$ K. [f] $w^{-1} = \sigma^2 F_o^2 + (0.0250P)^2 + 1.03P$; $P = (F_o^2 + 2F_c^2)/3$. [g] $w^{-1} = \sigma^2 F_o^2 + (0.0657P)^2 + 0.00P$; $P = (F_o^2 + 2F_c^2)/3$. [h] $w^{-1} = \sigma^2 F_o^2 + (0.0657P)^2 + 0.00P$; $P = (F_o^2 + 2F_c^2)/3$.

crystallographic data for **1a** and **1b** have been summarized in Table 3. Selected bond lengths, bond angles, and torsion angles are outlined in Table 4.

The solid-state structures of both compounds contain infinite polymeric chains with the difference that the asymmetric unit of **1a** is formed by a fragment consisting of one dialkyltin(IV) moiety and one ligand molecule (Figure 1), while the asymmetric unit of **1b** contains a fragment with two metal centers and two dicarboxylates (Figure 2). At first sight, in both cases the metal centers are hexacoordinated and the coordination environment can be considered either as skew-trapezoidal bipyramidal[32] or as bicapped tetrahedral,[23b] the tetrahedron being formed by the covalent Sn−C and Sn−O bonds. The bond angles describing the tetrahedron vary from 82.31(12)° to 150.6(2)° for **1a** and 81.5(1)° to 152.5(2)° for **1b**, of which the O_{cov}−Sn−O_{cov} and C−Sn−C bond angles are the ones with the largest deviations from the ideal tetrahedral bond angle (Table 4). Interestingly, the two C−Sn−C bond angles for Sn1 and Sn2 in the asymmetric unit of **1b** are significantly different from each other, 143.8(2)° and 152.5(2)°, indicating that there may be intermolecular contacts in the crystal lattice (vide infra). Nevertheless, both values are within the range observed for other diorganotin(IV) dicarboxylates, where values between 130.6° and 151.1° have been measured.[23] The trapezoidal basis of the coordination polyhedron around the tin atoms is formed by the four oxygen atoms and can be best described by the O_{cov}−Sn−O_{cov} and O_{coord}−Sn−O_{coord} bond angles, with values of 81.5(1)−82.3(1)° and 165.6(1)−169.0(1)°, respectively. Due to the anisobidentate coordination mode of the carboxylate groups to the tin atoms, two groups of different Sn−O bond lengths are found, one group corresponding to Sn−O bonds of covalent character, 2.126(3)−2.141(3) Å for **1a** and 2.093(2)−2.143(3) Å for **1b**, and the other group corresponding to Sn−O bonds of coordinative

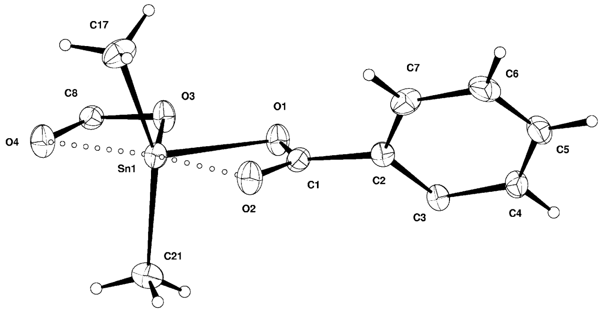

Figure 1. Repeating fragment in the polymeric solid state structure of **1a** (asymmetric unit).

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compounds **1a** and **1b**

		compound **1b**	
	compound **1a**	Sn1	Sn2
	Bond Lengths (Å)		
Sn−O_{cov}	2.126(3)	2.125(2)	2.093(2)
	2.141(3)	2.143(3)	2.110(2)
Sn−C	2.093(5)	2.111(4)	2.121(4)
	2.099(5)	2.121(4)	2.131(4)
C−O_{cov}	1.290(5)	1.282(4)	1.301(4)
	1.291(5)	1.288(4)	1.293(4)
C−O_{coord}	1.227(5)	1.241(4)	1.233(4)
	1.237(5)	1.240(4)	1.237(4)
C_{COO}−C_{Ph}	1.480(6)	1.496(5)	1.491(5)
	1.491(6)	1.500(5)	1.496(5)
Sn···O_{coord}	2.493(3)	2.562(3)	2.515(3)
	2.585(3)	2.595(3)	2.617(3)
Sn···$O'_{intermol}$	2.915(3)	2.950(3)	
	Bond Angles (deg)		
O_{cov}−Sn−O_{cov}	82.31(12)	81.5(1)	82.3(1)
O_{cov}−Sn−O_{coord} (cis)	54.33(11)	54.4(1)	54.5(1)
	55.97(11)	55.0(1)	55.8(1)
O_{cov}−Sn−C	100.64(18)	97.9(1)	101.9(1)
	100.76(17)	97.8(1)	103.1(1)
	100.95(17)	105.2(1)	103.7(1)
	101.70(18)	100.2(1)	105.2(1)
O_{coord}−Sn−O_{coord}	167.34(11)	169.0(1)	165.6(1)
O_{coord}−Sn−$O'_{intermol}$	67.42(11)	65.5(1)	
Sn−O−Sn′	112.58(11)	114.5(1)	
Sn−O_{cov}−C	99.1(3)	100.9(2)	100.6(2)
	102.3(3)	102.6(1)	103.3(2)
Sn−O_{coord}−C	82.4(3)	81.7(2)	80.8(1)
	84.2(3)	82.6(2)	83.3(2)
C−Sn−C	150.6(2)	152.5(2)	143.8(2)
	Torsion Angles (deg)		
O_{cov}−C−C−C (syn)	−61.2(6)	97.5(4)	114.4(5)
	−27.9(6)	23.6(5)	−32.7(5)

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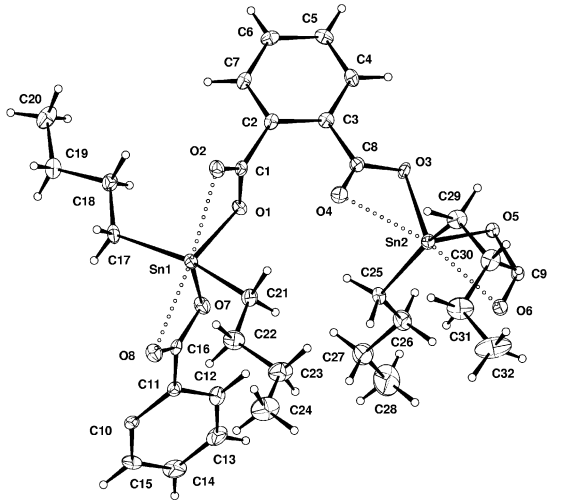

Figure 2. Repeating fragment in the polymeric solid state structure of **1b** (asymmetric unit).

character, 2.493(3)−2.585(3) Å for **1a** and 2.515(3)−2.617(3) Å for **1b**. In related dialkyltin(IV) dicarboxylates bond lengths of 2.07−2.15 and 2.45−2.71 Å, respectively, have been measured.[23]

All carboxylate groups in the molecular structures of **1a** and **1b** adopt a nonsymmetrical conformational arrangement, in which they are twisted out of the molecular plane of the central phthalate aromatic ring, $O_{cov}-C-C-C(syn) = -27.9(6)°/-61.2(6)°$ for **1a** and 23.6(5)°/−32.7(5)°/97.5(4)°/114.4(5)° for **1b**.

The analysis of the supramolecular structure in the crystal lattice of **1a** reveals that neighboring polymeric chains are aligned in upside-down orientations, being connected between each other by weak intermolecular Sn···O′ interactions and the formation of Sn_2O_2 units (Figure 3). In such a way two-dimensional layers are formed, which are not interconnected between each other, neither through coordinative bonds nor through hydrogen bridges. In the case of **1b** the two-dimensional network is reduced to the formation of polymeric double chains, because only every second tin atom is participating in intermolecular Sn···O′ interactions, thus also explaining the large difference mentioned above between the two individual C−Sn−C bond angles in the asymmetric unit of this complex. The intermolecular Sn···O′ distances are significantly shorter than the sum of the van der Waals radii of tin and oxygen (3.68 Å), 2.92 Å for **1a** and 2.95 Å for **1b**. The Sn_2O_2 units are highly distorted as evidenced by the difference in the O···Sn···O′ bond angles, 67.4(1)° for **1a** and 65.5(1)° for **1b**, and Sn···O···Sn′ bond angles, 112.6(1)° for **1a** and 114.5(1)° for **1b**. Considering the Sn···O′ interactions, the coordination environment of all tin atoms in the case of **1a** and half of the tin atoms in **1b** can be described also as distorted bipyramidal-pentagonal. Such a coordination environment seems to be quite common, since in at least 5 of the 17 reported crystal structures of diorganotin(IV) dicarboxylates similar intermolecular Sn···O′ interactions are present, with distances between 2.93 and 3.44 Å.[23] The enhancement of the coordination number in the solid state through intermolecular Sn···O′ interactions is in accordance with the observation of solvent coordination in solution. However, solid-state structures with a solvent molecule coordinated to a dialkyltin(IV) dicarboxylate seem to be rare.[33]

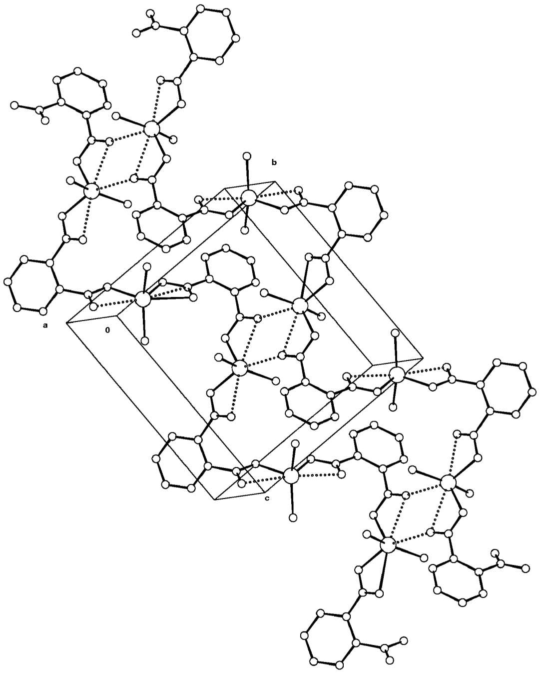

Figure 3. Section of the two-dimensional supramolecular network in the crystal lattice of **1a**, showing the intermolecular Sn···O′ interactions and Sn_2O_2 units.

Interestingly, in both supramolecular structures a cyclooligomeric structural unit consisting of four phthalate and six dialkyltin(IV) moieties with a total of four (**1a**) and two (**1b**) Sn_2O_2 cyclic units can be identified (Figure 3). The fact that the tin atoms can be coordinated finally to three carboxylate groups at a time may help to explain the fast ligand exchange process proposed by Wengrovius and Holecek in solution.[8d,22] Furthermore, the preorganization of the complex in macrocyclic units in the solid state gives an explication for the observation of cyclooligomeric structures in solution.

3.2. Characterization of Dimethyl- and Di-*n*-butyltin(IV) Isophthalate. 3.2.1. Preparation and Spectroscopic Characterization.

Compounds **2a** and **2b** have been prepared analogously to compounds **1a** and **1b** by reaction of isophthalic acid with an equimolar quantity of the corresponding diorganotin(IV) oxide (R = Me for **2a** and R = *n*-Bu for **2b**). While the resulting colorless complex **2a** cannot be dissolved in all commonly used organic solvents, complex **2b** is soluble in a series of organic solvents, e.g., in benzene, chloroform, acetone, pyridine, and acetonitrile.

The coordination of both carboxylate groups to metal centers can be deduced from the IR spectra of **2a** and **2b**, since absorptions characteristic only for the ligand are absent, $\tilde{\nu}(O-H) = 2671$ and 2556 cm^{-1}, $\delta(O-H) = 924$ and 937 cm^{-1}.[34] The IR spectra reveal furthermore strong absorptions

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Table 5. ^1H (400 MHz) and ^{119}Sn (149 MHz) NMR Spectroscopic Data (ppm) for Isophthalic Acid and Compound **2b** in Solvents of Different Coordinative Strength

solvent	H2	H4/H6	H5	^{119}Sn NMR ($h_{1/2}$ (Hz))
isophthalic acid[a]	8.55 (d)	8.22 (d)	7.68 (t)	
benzene-d_6	9.48 (t)	8.44 (dd)	7.00 (dt)	−161 (33)
chloroform-*d*	9.07 (t)	8.35 (dd)	7.61 (t)	−160 (14)
acetone-d_6	8.98 (br, s)	8.37 (dd)	7.71 (t)	−172 (70)
pyridine-d_5 (−40 °C)	9.90 (br, s)	8.70[b]	7.67 (t)	*c*
pyridine-d_5 (20 °C)	9.77 (br, s)	8.67 (d)	7.66 (t)	*c*
pyridine-d_5 (110 °C)	9.47 (br, s)	8.58 (d)	7.61 (t)	−238 (210)

[a] Data in DMSO-d_6. [b] Signal is covered by one of the signals of pyridine-d_5. [c] No signal detected.

Table 6. ^{13}C (100 MHz) NMR Spectroscopic Data (ppm) for Isophthalic Acid and Compound **2b** in Solvents of Different Coordinative Strength

solvent	C1/C3	C2	C4/C6	C5	C7/C8
isophthalic acid[a]	131.3	130.0	133.3	129.0	166.6
benzene-d_6	131.5	133.3	135.8	129.1	176.3
chloroform-*d*	130.4	132.6	135.4	128.6	175.9

[a] Data in DMSO-d_6.

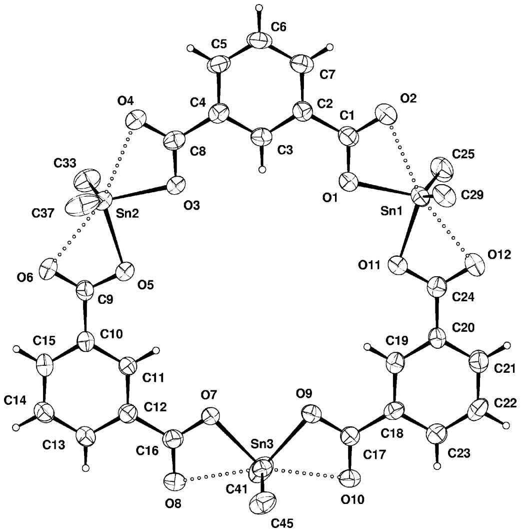


Figure 4. Molecular structure of compound **2b**. For clarity the somewhat disordered *β*, *γ*, and *δ* carbon atoms of the Sn−butyl groups have been omitted.

at $\tilde{\nu} = 1613$, 1562, and 1368 cm^{-1} for **2a** and $\tilde{\nu} = 1615$, 1573, 1399, and 1372 cm^{-1} for **2b**, corresponding to the symmetric and antisymmetric carboxylate stretches, whereby the mean $\Delta\tilde{\nu}$ differences of 245 and 246 cm^{-1}, respectively, are typical for an anisobidentate coordination mode to the diorganotin(IV) group.[14b]

As in the case of **1a** and **1b** the ^1H and ^{13}C NMR spectra of **2b** (Tables 5 and 6) indicate a highly symmetric structure or a dynamic exchange equilibrium between several cyclooligomeric molecules, since only one set of signals for both the dicarboxylate and the *n*-Bu_2Sn moiety is detected and no signals that are characteristic for the end groups in a polymeric chain are observed. In contrast to **1a** and **1b**, both carboxyl groups of the isophthalate ligand can be in the same plane as the central aromatic ring, so that the spectroscopic data properly give no straightforward evidence for a fast ligand exchange process in this case.

In benzene-d_6 the H2 hydrogen atom located between the two carboxyl groups is shifted to lower fields by $\Delta\delta = 0.93$ ppm in comparison to the uncomplexed ligand, whereas the H5 hydrogen atom localized at the meta position is high-field shifted by $\Delta\delta = 0.68$ ppm. Surprisingly, the H4/H6 hydrogen atoms are less affected upon complexation ($\Delta\delta = 0.23$ ppm). As expected, the most significant chemical shift in the ^{13}C NMR spectrum (Table 6) corresponds to the central carbon atoms of the carboxylate groups ($\Delta\delta = 9.7$ ppm). In the ^{119}Sn NMR spectrum recorded in benzene-d_6 only one sharp signal at $\delta = -161$ ppm can be seen. Although this signal is high-field shifted in comparison to **1b** ($\delta = -139$ ppm), it is still typical for an anisobidentate coordination mode of diorganotin(IV) dicarboxylates,[8d,22] thus confirming the results from the IR spectrum.

Interestingly, in the ^1H but not the ^{13}C NMR spectra, the chemical shifts change significantly, when the solvent for the NMR experiment is changed from benzene-d_6 to chloroform-*d*, acetone-d_6, and pyridine-d_5 (Table 5). Thereby, the shift displacements in the weakly coordinating agents chloroform-*d* and acetone-d_6 are almost identical to one another, but change significantly in pyridine-d_5, probably because of its anisotropic ring current and its stronger coordinating capacity. Furthermore, the signal of the H2 hydrogen atom is slightly broadened in the presence of coordinating solvents, so that a fast exchange reaction of solvent molecules at the exo side of the tin centers can be proposed. This observation is supported by the high-field shifted, broad signals at $\delta = -172$ and -238 ppm in the ^{119}Sn NMR spectra recorded in acetone-d_6 ($T = 20$ °C) and pyridine-d_5 ($T = 110$ °C), respectively, and the fact that at room temperature no signal could be detected in pyridine-d_5. It should be also noticed that the ^1H NMR shift displacements in this solvent change significantly between −40 and 110 °C, especially for the H2 hydrogen atom, $\Delta\delta = 0.43$ ppm. In contrast, in $CDCl_3$ the corresponding changes in the temperature interval of −60 to 20 °C are almost insignificant (<0.1 ppm for H2).

FAB^+ mass spectrometry of **2b** in nitrobenzyl alcohol interestingly shows peaks for dimeric, trimeric, and tetrameric species. The peaks of the trinuclear and tetranuclear ions are both accompanied by peaks of higher intensity corresponding to $[M - Bu]^+$, indicating the facile loss of one of the Sn−butyl substituents. Although this seems to confirm that there exist several cyclooligomeric structures in a dynamic exchange equilibrium between each other in solution, it should be taken into account that in contrast to **1b** a well-resolved ^1H NMR spectrum and a ^{119}Sn NMR spectrum with only one signal ($h_{1/2} = 14$ Hz) are observed in $CDCl_3$, without any significant change in a temperature interval of 80 °C (−60 to 20 °C). It should be also noticed that the ^1H NMR shift displacements are unaffected by a change of concentration (1 mg ↔ 90 mg) in the same solvent. Although molecular models indicate that an almost identical chemical environment can be expected for tri- and tetrameric molecules, a cylic dinuclear complex would be nonplanar due to the presence of angular strain in a planar system, so that different shifts would be expected for such a compound in

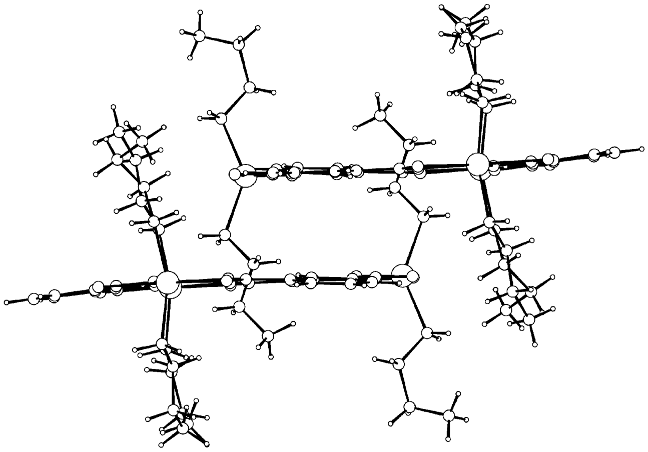


Figure 5. Dimeric bis[2]pseudorotaxane type unit in the supramolecular structure of **2b**. For clarity only one of the Sn−butyl groups per macrocyclic ring is shown.

Table 7. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compound **2b**

	Sn1	Sn2	Sn3
	Bond Lengths (Å)		
Sn−O_{cov}	2.095(5)	2.128(5)	2.121(5)
	2.097(5)	2.137(5)	2.120(5)
Sn−C	2.101(10)	2.117(9)	2.124(10)
	2.107(9)	2.172(10)	2.068(8)
C−O_{cov}	1.302(9)	1.280(8)	1.283(9)
	1.282(9)	1.287(9)	1.278(9)
C−O_{coord}	1.250(9)	1.214(9)	1.233(9)
	1.252(9)	1.248(9)	1.244(9)
C_{COO}−C_{Ph}	1.492(11)	1.504(10)	1.459(11)
	1.479(11)	1.492(11)	1.482(11)
Sn···O_{coord}	2.568(6)	2.523(6)	2.515(6)
	2.522(6)	2.525(6)	2.530(6)
Sn···$O'_{intermol}$	- -	2.920(6)	2.847(6)
	Bond Angles (deg)		
O_{cov}−Sn−O_{cov}	84.1(2)	85.1(2)	85.4(2)
O_{cov}−Sn−O_{coord} (cis)	55.7(2)	55.5(2)	55.3(2)
	55.9(2)	55.7(2)	55.3(2)
O_{cov}−Sn−C	105.1(3)	99.7(3)	99.6(3)
	105.2(3)	100.6(3)	100.8(3)
	105.7(3)	101.9(3)	101.5(3)
	106.4(3)	102.4(4)	101.7(3)
O_{coord}−Sn−O_{coord}	164.1(2)	163.7(2)	164.0(2)
O_{coord}−Sn−$O'_{intermol}$		64.5(2)	65.7(2)
Sn−O−Sn′		116.0(2)	113.8(2)
Sn−O_{cov}−C	102.1(5)	99.0(5)	100.8(5)
	101.3(5)	100.2(6)	101.3(5)
Sn−O_{coord}−C	81.6(5)	82.3(5)	83.7(5)
	82.4(5)	83.3(6)	83.0(6)
C−Sn−C	137.5(4)	149.4(4)	150.2(4)
O−C−O	120.6(9)	123.0(8)	120.2(9)
	120.3(9)	120.8(9)	120.3(8)
	Torsion Angles (deg)		
O_{cov}−C−C−C (syn)	3.6(13)	0.9(12)	0.9(13)
	1.8(13)	2.5(13)	0.9(12)

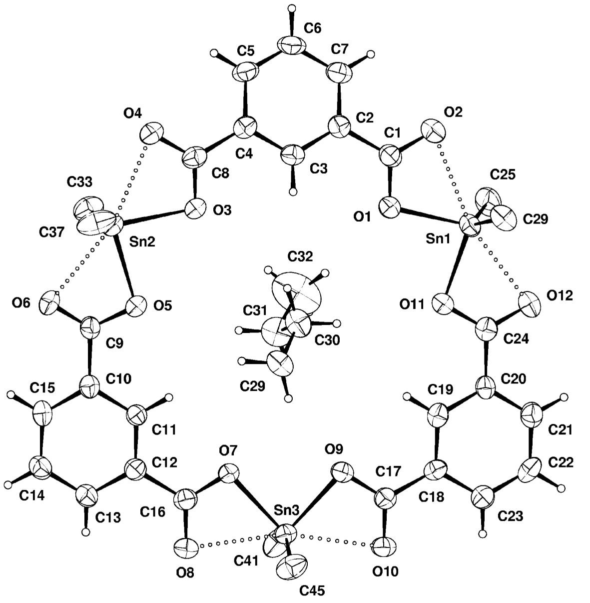
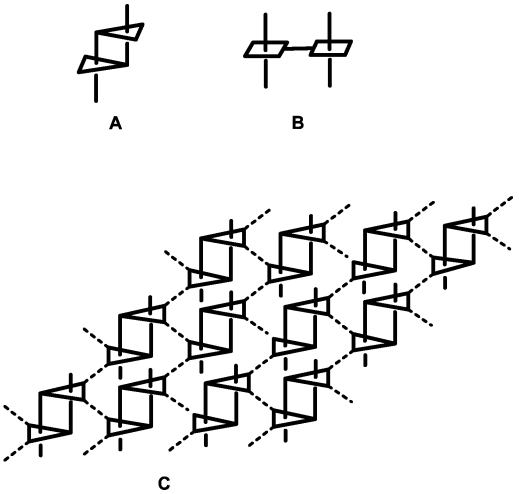


Figure 6. Fragment of the dimolecular unit present in the crystal lattice of compound **2b**, showing the thread of a Sn1−butyl group through the macrocyclic cavity of **2b**. For clarity the *β*, *γ*, and *δ* carbon atoms of the Sn−butyl groups have been omitted.

Chart 2. Schematic Representations for Two Different Types of Bis[2]pseudorotaxanes **A** and **B**, Whereby Type B Is Found in the Crystal Structure of **2b**[a]



[a] C is a schematic representation of the two-dimensional polymeric network in the supramolecular structure of **2b**.

both the IR and NMR spectra. If existing, the dynamic exchange equilibrium can be displaced in the direction of the trinuclear species through fractional crystallization as it has been shown by an X-ray crystallographic study of **2b**.

3.2.2. X-ray Crystallographic Study of 2b. Crystals of **2b** that were suitable for an X-ray crystallographic study were grown from benzene. The molecular structure of **2b** is shown in Figure 4; for clarity the somewhat disordered *β*, *γ*, and *δ* carbon atoms of the Sn−butyl groups have been omitted. The most relevant crystallographic data for **2b** have been summarized in Table 3. Selected bond lengths, bond angles, and torsion angles are outlined in Table 7.

The trinuclear tin complex is characterized by a 24-membered $C_{15}O_6Sn_3$ macrocyclic ring system with all six oxygen atoms directed into the interior of the cavity and the six *n*-butyl groups attached to the tin centers approximately perpendicular to the molecular plane. The tilts of the mean planes of the carboxylate groups with respect to the mean planes of the aromatic rings of the ligand are close to 0°, 3.6−6.7°, so that D_{3h} point group symmetry can be assumed in solution. The coordination environments of the three metallic centers are analogous to the ones observed for **1a** and **1b**, being skew-trapezoidal bipyramidal or bicapped tetrahedral with an anisobidentate coordination mode of the carboxylate groups, Sn−O_{cov} = 2.095(5)−2.137(5) Å and

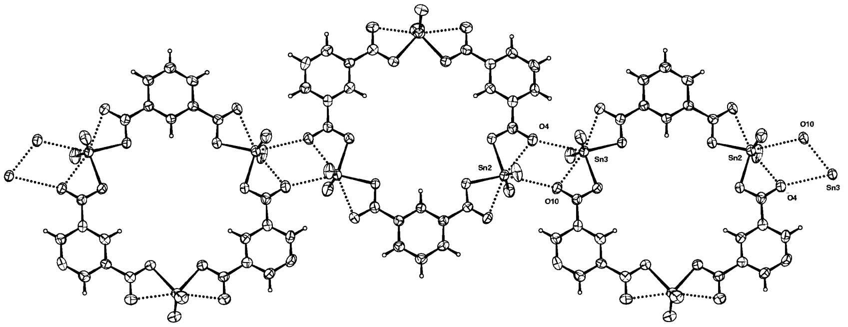


Figure 7. Polymeric zigzag chains along axis *b* formed through Sn⋯O′ intermolecular interactions between the macrocyclic trinuclear complexes present in the crystal lattice of **2b**. For clarity the Sn−butyl groups have been omitted.

$Sn-O_{coord} = 2.515(6)-2.568(6)$ Å. However, the C−Sn−C bond angles of 163.7(2)−164.1(2)° are significantly larger than in **1a** and **1b**, 143.8(2)−152.5(2)°.

The cavity in this planar macrocyclic derivative can be evaluated by the Sn⋯Sn and transannular O⋯O distances, which are 9.00−9.07 and 7.68−7.84 Å, respectively. Similar cavities have been found within the polymeric crystal structures of microporous metal−organic frameworks formed between 1,3,5-benzenetricarboxylic acid and Co(II) centers.[35] In other related polymeric systems so far only dimeric,[36] hexameric,[37] and chainlike[38] motifs have been reported.

The macrocyclic cavity of **2b** is large enough for the introduction of linear alkyl groups as can be seen from Figure 5 showing the noncovalently bound dimolecular unit present in the crystal lattice. This species is highly interesting from a supramolecular point of view, since it can be considered as a new type of bis[2]pseudorotaxane formed only between two molecules **A**, while the common case is the trimolecular combination of a macrocyclic system with two threads **B** (Chart 2).[39] The distance between the centroids of the aromatic rings present in the supramolecular dimer is 3.75 Å, so that a $\pi-\pi$ interaction can be excluded.[40] The top view of one-half of the bis[2]pseudorotaxane in Figure 6 (for clarity the β, γ, and δ carbon atoms of the macrocycle have been omitted and only the threading butyl group of the second molecule is shown) might indicate intermolecular C−H⋯O interactions; however, there are only distances very close to the sum of the van der Waals radii of oxygen and hydrogen (2.90 Å). The shortest distance was measured between oxygen O1 and one of the hydrogen atoms of the C32 methyl group, C32−H⋯O1 = 2.78 Å. The rest of the C−H⋯O distances lie in the interval between 2.80 and 4.18 Å.

In the crystal lattice the trinuclear macrocyclic rings are linked to polymeric zigzag chains along axis *b* via the formation of Sn_2O_2 units through weak intermolecular Sn⋯O′ contacts, Sn2⋯O10′ = 2.92 Å and Sn3⋯O4′ = 2.85 Å (Figure 7). Therefore, the coordination environment of two of the three tin atoms in each trinuclear complex can be considered also as distorted bipyramidal-pentagonal, thus confirming the results obtained from NMR spectroscopy (weak coordination of coordinating solvent molecules at the exo side of the tin atoms). The infinite zigzag chains are interlocked between each other by alternate threading of Sn1−butyl groups of one chain through the macrocyclic cavities of two neighboring chains. In such a way a so far unknown stepped two-dimensional polymeric network of type **C** (Chart 2) is formed.

4. Conclusions

In conclusion, this contribution has shown that the combination of a dialkyltin(IV) moiety with an aromatic dicarboxylate like phthalate or isophthalate results in the formation of complexes with either a polymeric or a discrete trinuclear macrocyclic molecular structure in the solid state. In the solution state, probably in both cases several cyclooligomeric structures are present, which are transformed between each other by fast ligand exchange reactions. Apparently, the activation energy barriers for an enhancement of the coordination number of tin atoms embedded in a skew-trapezoidal bipyramidal environment are quite low, since these reactions are even fast at low temperatures. This viewpoint is supported by the fact that, in the supramolecular structures of the dialkyltin(IV) dicarboxylates described herein, intermolecular Sn⋯O′ interactions have been detected, which lead to cyclooligomeric structural units in the case of the dialkyltin(IV) phthalates.

In the case of the so far unexplored planar trinuclear macrocyclic system described for di-*n*-butyltin(IV) isophthalate, a diameter large enough for the inclusion of small organic molecules is present, whose potential for the formation of new types of bis[2]pseudorotaxanes and two-dimensional supramolecular structures has been recognized. Be-

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cause of the insolubility of dimethyltin(IV) isopthalate, it cannot be concluded with certainty whether the solid state structure contains similar trinuclear macrocyclic units or a different type of cyclooligomeric or polymeric structure.

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Supporting Information Available: Complete tables of crystallographic data and colored figures showing a fragment of the dimolecular unit present in the crystal lattice of **2b**, space-filling model of **2b**, and polymeric zigzag chains of the macrocyclic trinuclear complexes. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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