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Structural characterization of dimethyl- and di-*n*-butyltin(IV) 2,3-pyridinedicarboxylate in solution and in the solid state†

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Potassium 2,3-pyridinedicarboxylate (K_2pdc) has been reacted with dimethyl- and di-*n*-butyltin(IV) dichloride to give complexes with polymeric structures: $[Me_2Sn\text{-}\mu_2\text{-pdc}]_n$ (1) and $[nBu_2Sn\text{-}\mu_2\text{-pdc}]_n$ (2). IR, NMR (^{1}H, ^{119}Sn) spectroscopic and X-ray crystallographic studies of 1 and 2 proved the expected 1 : 1 stoichiometric composition of the complexes. In solution compounds 1 and 2 have either cyclooligomeric or polymeric structures with a coordination number of 7 for the tin atoms. In polar solvents rapid exchange reactions of coordinated solvent molecules take place at the tin centers. In the solid state, polymeric helicoidal structures are found, in which one solvent molecule is coordinated to each tin atom. For 1 the DMSO adduct was characterized and, interestingly, in the case of 2 two different solid-state structures having very similar three-dimensional structures and crystal lattice parameters, but different solvent molecules coordinated to the tin atoms (H_2O and MeOH), could be isolated. The solid-state structures of 1-DMSO, 2-H_2O and 2-MeOH differ in the number of units required for a complete turn of the helix (two for 1-DMSO, three for 2-H_2O and 2-MeOH), which may be explained by the different steric requirements of the organic substituents at the tin centers (R = Me for 1-DMSO, R = *n*Bu for 2-H_2O and 2-MeOH) and the fact that different solvent molecules are coordinated to them. In all three cases the crystal lattices contain small voids that are filled with either the backbones of the coordinated solvent molecules and/or disordered, uncoordinated solvent molecules. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: self-assembly; supramolecular chemistry; carboxylate ligands; pyridine; tin; NMR; X-ray crystallography

INTRODUCTION

Mono-, di-, tri- and tetracarboxylate anions and their derivatives are useful ligands for the construction of new interesting supramolecular entities that possess discrete or polymeric structures. Of them, systems with cavities or pores have received special attention since a series of possible applications emerged.[1–7] Although a large number of such hybrids has been prepared during the last few years, there are still only a few examples containing representative elements.[8–28]

The chemistry and structural properties of organotin(IV) carboxylates have been studied extensively; however, their potential for the construction of new supramolecular systems is almost unexplored so far.[21–28] In order to fill this void we initiated the exploration of the self-assembly processes of different benzenedicarboxylates with diorganotin(IV) moieties and made the observation that systems with either a discrete molecular or a polymeric structure can be obtained.[29,30] From the examples shown in Scheme 1 it can be seen that dimethyl- and di-*n*-butyltin phthalates have polymeric solid-state structures, while the structures of di-*n*-butyltin isophthalate and di-*n*-butyltin 2,5-pyridinedicarboxylate are trinuclear cyclic.[29,30] ^{1}H and ^{119}Sn NMR studies have shown that polymeric organotin carboxylates are often not stable in solution, since fast ligand exchange reactions occur; however, it is possible that during this process cyclooligomeric species are generated.[31] It has been also found that the tin atoms in diorganotin(IV) carboxylates can enhance their coordination

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†Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

environment through solvent coordination or intermolecular aggregation.[29,30,32–35]

In a continuation of this research project, we describe herein the preparation and structural characterization of two new diorganotin(IV) dicarboxylates **1** and **2** (Scheme 1). In contrast to phthalate, the 2,3-pyridinedicarboxylate ligand contains a donor atom capable of coordination to the tin atom. Complexes **1** and **2** could be characterized both in solution and in the solid state.

EXPERIMENTAL

Instruments

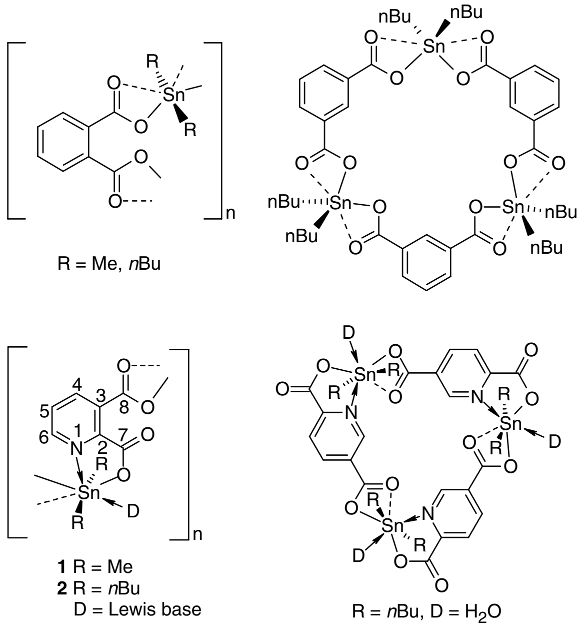
NMR studies were carried out with Varian Gemini 200 and Varian Inova 400 instruments. Standards were TMS (internal, ^{1}H) and $SnMe_4$ (external, ^{119}Sn). Chemical shifts are stated in parts per million; they are positive when the signal is shifted to higher frequencies than the standard. IR spectra were recorded on a Bruker Vector 22 FT spectrophotometer.

Preparation

Commercial starting materials and solvents were used.

*Catena[dimethyl-μ_2-(2,3-pyridinedicarboxylato-O,O′,N)tin] (**1**)*

2,3-Pyridinedicarboxylic acid (0.056 g, 0.339 mmol) and potassium hydroxide (0.039 g, 0.678 mmol) were dissolved in 2 ml of H_2O to prepare the corresponding potassium salt. Then, a solution of dimethyltin(IV) dichloride (0.075 g, 0.339 mmol) in 3 ml of H_2O was added, giving immediately a colorless solid that was filtered and washed with small quantities of ethanol. Crystals suitable for X-ray crystallography were obtained after recrystallization from DMSO. Yield 55%; m.p. 289–291 °C.



Scheme 1. Diorganotin(IV) dicarboxylates derived from benzenedicarboxylic acid derivatives can have polymeric or cyclooligomeric structures.[29,30] Compounds **1** and **2** are the objects of study in the present contribution.

IR (KBr) $\tilde{\nu}_{max}$: 3440 (br, m), 3386 (br, m), 3086 (m), 1651 (s), 1583 (s), 1470 (w), 1414 (s), 1356 (s), 1270 (w), 1231 (w), 1161 (w), 1106 (m), 882 (w), 842 (m), 801 (m), 732 (w), 702 (w), 671 (w), 583 (w), 553 (w), 455 (w) cm^{-1}.

^{1}H NMR (200 MHz, DMSO-d_6) $\delta = 0.83$ (br, s, 6H, CH_3, $^{2}J_{Sn-H} = 111$ Hz), 7.80 (br, dd, 1H, H5), 8.17 (br, d, 1H, H4), 9.04 (br, d, 1H, H6) ppm.

^{119}Sn NMR (149 MHz, DMSO-d_6) $\delta = -451$ (s) ppm.

*Catena[di-n-butyl-μ_2-(2,3-pyridinedicarboxylato-O,O′,N)tin] (**2**)*

2,3-Pyridinedicarboxylic acid (0.021 g, 0.125 mmol) and potassium hydroxide (0.014 g, 0.250 mmol) were dissolved in 2 ml of a 1 : 1 mixture of MeOH and H_2O to prepare the corresponding potassium salt. Then, a solution of di-*n*-butyltin(IV) dichloride (0.037 g, 0.125 mmol) in 3 ml MeOH was added, giving immediately a colorless solid that was filtered and washed with small quantities of ethanol. Crystals suitable for X-ray crystallography were obtained upon slow diffusion of a solution of potassium 2,3-pyridinedicarboxylate in EtOH/H_2O or MeOH/H_2O into a solution of di-*n*-butyltin(IV) dichloride dissolved in the corresponding alcohol. The crystal lattice parameters of the crystals grown from each solvent mixture are similar; however, the solid-state structures differ in the solvent coordinated to the tin atoms (**2**-H_2O and **2**-MeOH). Yield 84%; m.p. 245–247 °C.

IR (KBr) $\tilde{\nu}_{max}$: 3089 (w), 2962 (m), 2927 (m), 2864 (m), 1651 (s), 1609 (s), 1585 (m), 1461 (m), 1390 (s), 1353 (s), 1272 (m), 1226 (m), 1149 (w), 1101 (m), 1029 (w), 968 (w), 878 (m), 846 (m), 782 (w), 735 (w), 703 (m), 673 (m), 615 (w), 561 (w), 464 (m) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 0.74$ (br, 6H, CH_3), 1.20 (br, 8H, β-CH_2, γ-CH_2), 1.58 (br, 4H, α-CH_2), 7.89 (br, s, 1H, H5), 8.06 (br, s, 1H, H4), 8.98 (br, s, 1H, H6) ppm.

^{119}Sn NMR (149 MHz, DMSO-d_6) $\delta = -409$ (s) ppm.

X-ray crystallography

X-ray diffraction studies were performed on a Bruker-AXS APEX diffractometer with a CCD area detector ($\lambda_{MoK\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at $T = 100$ K (**2**-H_2O and **2**-MeOH) and $T = 293$ K (**1**-DMSO) via ω- and Φ-rotation at 10 s (**1**-DMSO, **2**-MeOH) and 30 s (**2**-H_2O) per frame (SMART[36]). The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT[37]). Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.[38] Part of the organic substituents of the nBu_2Sn moieties in the structures of **2**-H_2O and **2**-MeOH were disordered, so that some restraints (DFIX) had to be introduced in order to obtain reasonable structural data. Furthermore, in the crystal lattice of **1**-DMSO disordered solvent molecules were present, which were also restrained as far as necessary. The crystal of compound **1**-DMSO decomposed during the data collection, so that a correction for decay was applied. Only smears of electron density could be detected in the channels present in the crystal lattice of **2**-H_2O. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model (with exception of the hydrogen atoms in the disordered, uncoordinated solvent molecules in **1**-DMSO, which were not calculated). The O–H hydrogen atoms in **2**-H_2O and **2**-MeOH were localized by difference Fourier maps, but their O–H distances and U_{iso} factors were fixed to 0.84 Å and 1.5 times the U_{equiv} value of the neighboring oxygen atom. The molecular structures were illustrated by the CRYSTALS software package.[39,40]

RESULTS AND DISCUSSION

The dimethyl- and di-*n*-butyltin(IV) complexes $[Me_2Sn\text{-}\mu_2\text{-pdc}]_n$ (**1**) and $[nBu_2Sn\text{-}\mu_2\text{-pdc}]_n$ (**2**) were prepared from the dipotassium salt of 2,3-pyridinedicarboxylic acid (H_2pdc) and the corresponding diorganotin(IV) dichloride. Compounds **1** and **2** are slightly soluble in polar organic solvents like dimethyl sulfoxide and 1,2-dimethoxyethane (DME), and could be therefore characterized apart from IR spectroscopy by liquid NMR spectroscopy (^{1}H and ^{119}Sn) and X-ray crystallography. The analogous compounds with 2,6-pyridinedicarboxylic acid are dimeric with a central Sn_2O_2 core,[41,42] but with Ph_2Sn a polymeric chain is formed through intermolecular O → Sn coordinative bonds between one of the carbonyl groups of the coordinated ligand and the tin atoms of a neighboring molecule.[43] For di-*n*-butyltin 2,5-pyridinedicarboxylate a cyclotrimeric structure has been reported (Scheme 1).[30]

Spectroscopic characterization

The IR spectra of **1** and **2** reveal strong absorptions at $\tilde{\nu} = 1651$, 1583, 1414 and 1356 cm^{-1} for **1**, and 1651, 1609, 1390 and 1353 cm^{-1} for **2**, corresponding to the symmetric and antisymmetric carboxylate stretches, which are typical for mono- and/or anisobidentate coordination modes to the diorganotin(IV) groups.[44]

The ^{1}H NMR spectra for **1** and **2** indicate the formation of 1 : 1 complexes between the pyridinedicarboxylate and the diorganotin(IV) moieties and that both carboxylate groups are coordinated to tin atoms. Two of the three signals of the central, disubstituted pyridine rings are shifted to lower fields in the ^{1}H NMR spectra of **1** and **2**, $\Delta\delta = 0.16/0.25$ ppm for H5 and $\Delta\delta = 0.28/0.22$ ppm for H6 (Table 1). Owing to the fact that the chemical shift is relatively high for the H6 hydrogen atom, it can be proposed that the pyridine nitrogen atom is coordinated to the tin atom.

Table 1. Selected chemical ^{1}H (400 MHz) and ^{119}Sn (149 MHz) NMR chemical shifts of 2,3-pyridinedicarboxylic acid, $[Me_2Sn\text{-}\mu_2\text{-pdc}]_n$ (**1**) and $[nBu_2Sn\text{-}\mu_2\text{-pdc}]_n$ (**2**) in DMSO-d_6

	H4	H5	H6	Hα	^{119}Sn
2,3-Pyridinedi-carboxylic acid	8.27 (d)	7.64 (d)	8.76 (d)	—	—
1	8.17 (d, br)	7.80 (d, br)	9.04 (d, br)	0.83[a] (br)	−451 (s)
2	8.06 (s, br)	7.89 (s, br)	8.98 (s, br)	1.58 (s, br)	−409 (s)

[a] $^2J(\text{Sn, C}) = 111$ Hz.

The coordination number of the tin atoms in compounds **1** and **2** can be derived from the ^{119}Sn NMR data. According to the spectra measured in DMSO-d_6, $\delta = -451$ ppm for **1** and $\delta = -409$ ppm for **2**, one solvent molecule forms part of the coordination sphere of the tin atoms, thus having a coordination number of 7. For the related monomeric hepta-coordinated $[R_2Sn(2\text{-picolinate})_2(DMSO)]$ complexes, values of $\delta = -444$ ppm (R = Me) and $\delta = -465$ ppm have been reported.[32] Generally, there is a shift difference between dimethyl- and di-*n*-butyltin species due to the different electronic properties of the substituents and the chemical shift difference between Me_2SnCl_2 ($\delta = 141$ ppm) and nBu_2SnCl_2 ($\delta = 122$ ppm) can be taken as reference in order to evaluate the influence of the methyl and *n*-butyl groups on the ^{119}Sn NMR shift displacements.[45] The fact that the shift difference between **1** and **2** is more than 20 ppm, namely $\Delta\delta = 42$ ppm, may indicate that the Lewis acidity of the dimethyltin(IV) derivative **1** is somewhat higher. When comparing the ^{119}Sn NMR shifts (in DMSO-d_6) of **1** and **2** with those reported for the corresponding diorganotin(IV) phthalates ($\delta = -203$ for the Me_2Sn derivative and $\delta = -230$ for the nBu_2Sn derivative),[29] a difference of approximately 200 ppm is derived. Considering that coordinative solvents like DMSO also bind to the tin atoms in these compounds, this difference indicates that the formation of the N → Sn bond contributes to a significant enhancement of the electron density at the tin atoms.

X-ray crystallographic characterization

The solid-state compositions of compounds **1** and **2** have been established by X-ray crystallographic studies of crystals grown from DMSO (**1**-DMSO), EtOH/H_2O (**2**-H_2O) and MeOH/H_2O (**2**-MeOH). In all three cases solvent molecules are coordinated to the tin atoms, thus confirming that the Lewis acidity of the pyridinedicarboxylate derivatives is significantly higher when compared to their benzenedicarboxylate analogs.[29] Similar observations have been made for a series of related diorganotin derivatives of 2-picolinic acid.[32] The most relevant crystallographic data for **1**-DMSO, **2**-H_2O and **2**-MeOH have been summarized in Table 2

Table 2. Crystallographic data for **1**-DMSO, **2**-H_2O and **2**-MeOH

	1-DMSO[a]	**2**-H_2O[b]	**2**-MeOH[c]
Crystal data			
Formula	$C_{11}H_{15}NO_5SSn$, DMSO	$C_{15}H_{23}NO_5Sn$	$C_{16}H_{25}NO_5Sn$
Crystal size (mm^3)	0.06 × 0.12 × 0.17	0.12 × 0.20 × 0.32	0.09 × 0.14 × 0.18
MW ($g\ mol^{-1}$)	470.12	416.03	430.06
Space group	*Pbca*	*R*-3	*R*-3
Cell parameters			
a (Å)	14.6893(19)	20.0669(18)	20.1208(16)
b (Å)	13.8818(19)	20.0669(18)	20.1208(16)
c (Å)	18.173(2)	22.499(3)	22.625(3)
V ($Å^3$)	3705.6(8)	7846.0(14)	7932.4(13)
Z	8	18	18
μ (mm^{-1})	1.630	1.486	1.473
ρ_{calcd} ($g\ cm^{-3}$)	1.685	1.585	1.620
Data collection			
θ limits (deg)	$2.2 < \theta < 25.0$	$1.5 < \theta < 23.0$	$1.5 < \theta < 25.0$
No. collected refl.	16 846	10 822	12 944
No. independent refl. (R_{int})	3219 (0.135)	2440 (0.055)	3114 (0.047)
No. observed refl.[d]	1814	2195	2756
No. parameters	223	207	214
Refinement			
R[e]	0.057	0.074	0.041
R_w[f]	0.155	0.144	0.095
GOF	1.02	1.24	1.12
$\Delta\rho_{max}$ ($e\ Å^{-3}$)	1.08	1.74	0.75

[a] CCDC no. 239227. [b] CCDC no. 239228. [c] CCDC no. 244741. [d] $F_o > 4\sigma(F_o)$. [e] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. [f] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

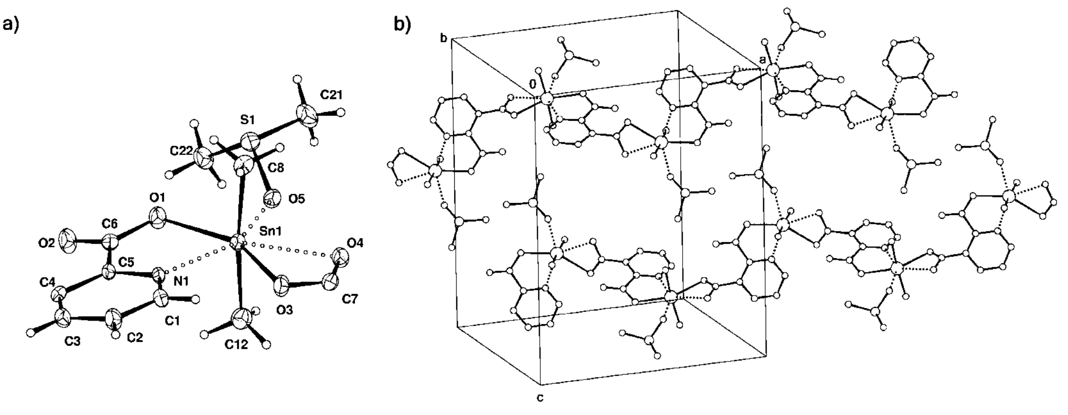


Figure 1. (a) Fragment of the polymeric structure of **1**-DMSO showing the distorted bipyramidal pentagonal coordination geometry of the tin atom. (b) Section of the crystal lattice of **1**-DMSO showing the shape and mutual orientation of the helicoidal polymers.

and the repeating fragments in their polymeric structures are shown in Figs 1 and 2, respectively. Selected bond lengths, bond angles and torsion angles are collected in Table 3.

The chain propagation in polymers **1**-DMSO, **2**-H_2O and **2**-MeOH is induced by the circumstance that the two carboxylate groups of the ligand are coordinated to two different tin atoms, thus each tin atom is surrounded by two covalently bound ligand molecules and vice versa. Apparently, two reasons can be given for this coordination behavior: first, the formation of a five-membered chelate ring with a N → Sn coordinative bond that removes the tin atom form the second carboxylate group; and second, steric crowding between the two neighboring carboxylate groups, which inhibits a simultaneous coordination to one and the same tin atom.

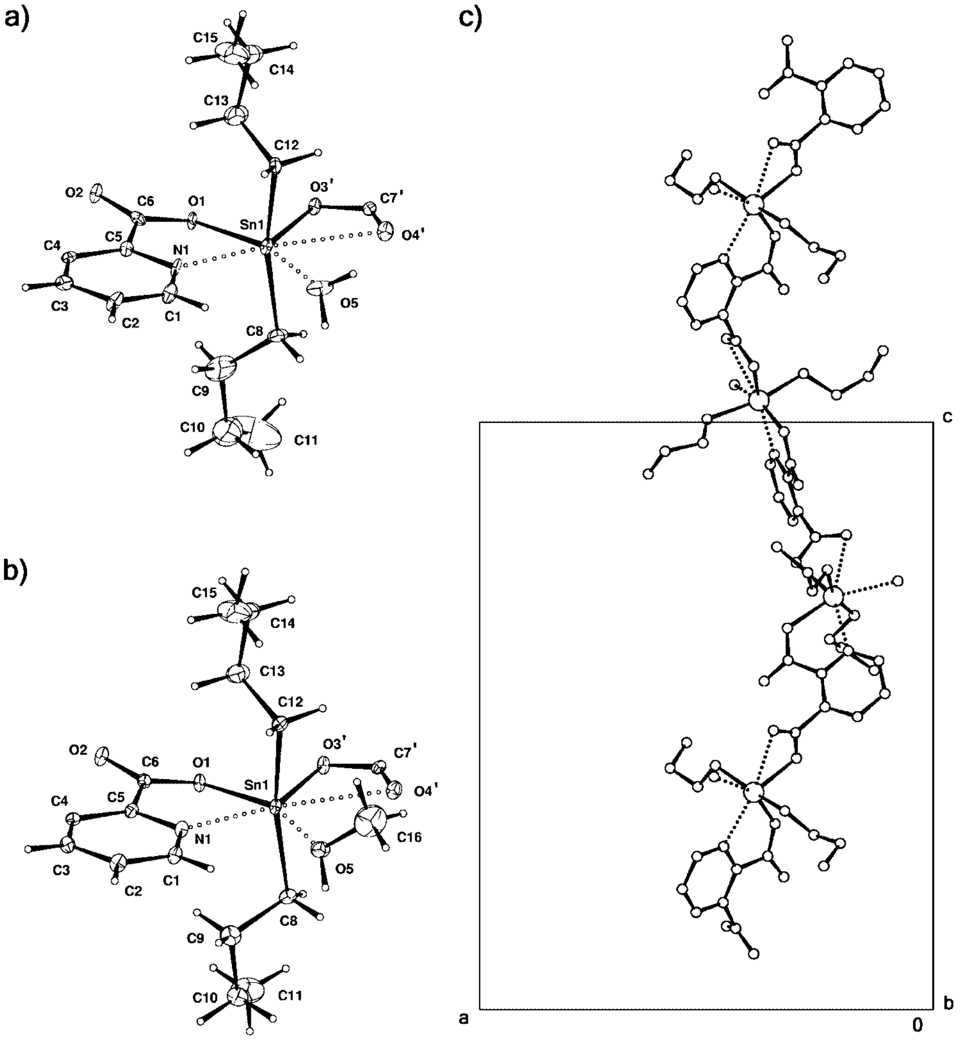


Figure 2. (a) and (b) Fragment of the polymeric structures of **2**-H_2O and **2**-MeOH, showing the distorted bipyramidal pentagonal coordination geometries of the tin atoms. (c) Section of the crystal lattice of **2**-H_2O showing the propagation of the helicoidal chain in *c*-direction. The polymeric structure of **2**-MeOH is very similar.

As can be seen from Figs 1 and 2, in all cases the coordination environment of the tin atoms is distorted bipyramidal–pentagonal, the axial positions being occupied by the organic substituents and the equatorial positions being shared by the coordinating atoms of the ligand as well as one solvent molecule (DMSO in **1**-DMSO, H_2O in **2**-H_2O and MeOH **2**-MeOH). It is interesting to note that the crystal structures of **2**-H_2O and **2**-MeOH are very similar, the difference being mainly the type of solvent coordinated to the tin atoms (compare the crystal lattice parameters in Table 2). Because of the chelate ring formation, the carboxylate group in position 2 is monodentate, while that in position 3 is anisobidentate, as commonly observed for diorganotin(IV) dicarboxylates.[29–35,46–48] However, a closer view of the distribution of the bonds in the pentagonal plane reveals a significant difference between the two polymers **1**-DMSO and **2**-H_2O, **2**-MeOH. In **1**-DMSO the two covalent Sn–O bonds are in an approximate *trans*-orientation, O–Sn–O = 147.0(2)°, while in **2**-H_2O and **2**-MeOH they are *cis*-orientated, O–Sn–O = 79.3(2) and 78.6(1)°. Owing to this arrangement, the solvent molecules are located approximately *trans* to the pyridine nitrogen atom in **1**-DMSO, N1–Sn–O5 = 149.2(2)°, but *cis* in **2**-H_2O and **2**-MeOH, N1–Sn–O5 = 85.3(3) and 81.8(2)°. The different basicities and steric requirements of the coordinated solvent molecules seem to be responsible for further distortions in the coordination environment, mainly with respect to the anisobidentatively coordinated carboxylate groups and the organic substituents, e.g. the C–Sn–C bond angle changes from 173.8(4)° in **1**-DMSO to 162.7(4) and 165.3(2)° in **2**-H_2O and **2**-MeOH. The $O_{solvent} \rightarrow Sn$ bond length is 2.306(6) Å in **1**-DMSO, 2.561(8) Å in **2**-H_2O and 2.502(4) Å **2**-MeOH, indicating that DMSO coordinates significantly more strongly to the tin atom in these complexes than methanol and water.

Table 3. Selected bond lengths (Å), bond angles (deg) and torsión angles (deg) for **1**-DMSO, **2**-H_2O and **2**-MeOH

	1-DMSO	**2**-H_2O[a]	**2**-MeOH[a]
Bond lengths (Å)			
Sn1–O1	2.216(6)	2.142(6)	2.160(3)
Sn1–O3	2.376(6)	2.209(6)	2.224(3)
Sn1–O4	2.461(6)	2.680(6)	2.634(3)
Sn1–O5[b]	2.306(6)	2.559(8)	2.502(4)
Sn1–N1	2.393(7)	2.373(8)	2.403(3)
Sn1–C8	2.112(10)	2.120(10)	2.120(5)
Sn1–C12	2.101(10)	2.121(9)	2.127(5)
O1–C6	1.289(11)	1.278(11)	1.281(5)
O2–C6	1.213(11)	1.229(12)	1.236(6)
O3–C7	1.240(11)	1.277(11)	1.277(6)
O4–C7	1.276(12)	1.223(12)	1.233(6)
Bond angles (deg)			
O1–Sn1–O3	147.0(2)	79.3(2)	78.6(1)
O1–Sn1–N1	70.2(2)	72.0(2)	71.1(1)
O1–Sn1–O5	79.1(2)	157.2(3)	152.8(1)
O3–Sn1–O4	54.1(2)	52.4(4)	53.2(1)
O3–Sn1–O5	133.8(2)	123.4(3)	128.5(1)
O3–Sn1–N1	76.9(2)	151.1(3)	149.4(1)
O4–Sn1–N1	130.6(2)	155.6(4)	156.6(1)
O5–Sn1–N1	149.2(2)	85.2(3)	81.8(2)
C8–Sn1–O1	93.4(3)	98.3(4)	96.6(2)
C12–Sn1–O1	91.4(3)	99.0(3)	97.9(2)
C8–Sn1–O3	86.8(3)	93.1(4)	92.4(2)
C12–Sn1–O3	91.3(3)	91.7(4)	92.1(2)
C8–Sn1–O5	90.5(4)	83.1(4)	84.1(2)
C12–Sn1–O5	86.6(3)	80.4(3)	82.2(2)
C8–Sn1–N1	93.6(3)	94.8(4)	95.0(2)
C12–Sn1–N1	91.6(3)	89.0(3)	88.2(2)
C8–Sn1–C12	173.8(4)	162.7(4)	165.3(2)
O1–C6–C5	114.5(8)	116.3(9)	116.6(4)
N1–C5–C6	116.1(8)	115.3(8)	115.1(4)
Sn1–O1–C6	121.9(6)	122.3(6)	122.7(3)
Sn1–N1–C5	113.8(6)	112.8(6)	113.0(3)
Sn1–O5–S1	123.2(4)	—	—
Torsion angles (deg)			
O1–Sn–N1–C5	11.7(6)	4.7(6)	5.5(3)
Sn–N1–C5–C6	−6.2(10)	0.1(10)	−0.7(5)
N1–C5–C6–O1	−8.4(12)	−8.5(12)	−8.2(6)
C5–C6–O1–Sn	−21.0(11)	−14.1(11)	−14.6(5)
C6–O1–Sn–N1	18.2(7)	10.5(7)	11.1(3)
O3–C7–C4–C3	−95.7(12)	74.1(11)	72.7(6)

[a] Symmetry operator for O3, C7 and O4: $1/3 - y, 2/3 + x - y, -1/3 + z$.

[b] DMSO for **1**-DMSO, H_2O for **2**-H_2O and MeOH for **2**-MeOH.

As a consequence, the isobidentate character in the binding of the carboxylate group in β-position to the nitrogen atom is higher for **1**-DMSO than for **2**-H_2O and **2**-MeOH, as can be seen from the corresponding Sn–O and C–O bond lengths (see Table 3). A further interesting fact is that, for **1**-DMSO, the $O_{DMSO} \rightarrow Sn$ bond distance, 2.306(6) Å, is significantly shorter than the covalent Sn-O1 bond length, 2.376(6) Å. The lengths of the N → Sn coordinative bonds with values of 2.393(7) and 2.396(6) Å for **1** and **2**, respectively, are in the range of those found for other diorganotin(IV) pyridine derivatives.[32–35,41–43,49–54]

As already shown by Dakternieks *et al.*,[32] the organic substituents attached to the tin atoms influence the molecular structure and supramolecular association in organotin carboxylates. This and differences in the volumes of the coordinated solvent molecules should be responsible for the different shapes of the polymeric helicoidal chains of **1**-DMSO, **2**-H_2O and **2**-MeOH, which are outlined in Figs 1(b) and 2(c). From Fig. 1(b) it can be seen that for **1**-DMSO a complete turn of the helix is reached after two repeating units (orientation along a 2_1 axis in the crystal lattice), while in the case of **2**-H_2O and **2**-MeOH (Fig. 2(c)), three repeating units are required for each turn (orientation along a 3_1 axis). There remain small cavities in the crystal lattices of compound **1**-DMSO and **2**-H_2O, which are occupied by additional solvent molecules (DMSO and H_2O, respectively), whereby in the case of **2**-H_2O only smears of electron density could be detected in the channels along axis *c*. In the case of the **2**-MeOH derivative the voids are almost completely occupied by the methyl groups attached to the tin atoms, so that the achievement of optimal space-filling might be the explanation for why methanol coordinates when a MeOH/H_2O solvent mixture is used instead of EtOH/H_2O during the crystallization process.

CONCLUSIONS

In conclusion, this contribution has shown that the combination of 2,3-pyridinedicarboxylate with dimethyl- and di-*n*-butyltin(IV) results in complexes that have structural and electronic properties different from those of the analogous phthalates. These differences are a consequence of the formation of a coordinative N → Sn bond, which alters the coordination mode of the carboxylate groups from 2-fold anisobidentate to monodentate and iso- or anisobidentate. Apparently, the variation of the chemical environment enhances the Lewis acidity of the tin atoms, since in the two cases examined herein solvent molecules are coordinated both in solution and the solid state. The volume of the organic substituents and solvent molecules attached to the tin atoms have an important influence on the molecular and supramolecular structure of the complexes.

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