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Preparation and structural studies on the $^{t}Bu_2Sn(IV)$ complexes with aromatic mono- and dicarboxylic acids containing hetero {N} donor atom

Attila Szorcsik [a], László Nagy [b,*], Andrea Deák [c], Michelangelo Scopelliti [d], Zoltán A. Fekete [e], Ágota Császár [b], Claudia Pellerito [d], Lorenzo Pellerito [d]

[a] *Bioinorganic Research Group of Hungarian Academy of Sciences, Department of Inorganic and Analytical Chemistry, University of Szeged, P.O. Box 440, H-6701 Szeged, Hungary*

[b] *Department of Inorganic and Analytical Chemistry, University of Szeged, P.O. Box 440, H-6701 Szeged, Hungary*

[c] *Institute of Chemistry, Chemical Research Center of the Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary*

[d] *Dipartimento di Chimica Inorganica e Analitica Chimica "Stanislao Canizzaro", Universitá di Palermo, Viale delle Scienze, Parco d'Orleans, 90128 Palermo, Italy*

[e] *Department of Physical-Chemistry, University of Szeged, P.O. Box 105, H-6701 Szeged, Hungary*

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Abstract

Nine complexes of $^{t}Bu_2Sn(IV)^{2+}$ were obtained in the solid state with ligands containing –COOH group(s) and aromatic {N} donor atom. The binding sites of the ligands were identified by FT-IR spectroscopic measurements. It was found that in most cases the $–COO^-$ groups are co-ordinated in monodentate manner. Nevertheless, in some of our complexes, the $–COO^-$ group forms bridges between two central {Sn} atoms resulting in the formation of an oligomeric structure, a motif that is characteristic only to the nicotinate compound. These pieces of information and the rationalisation of the experimental ^{119}Sn Mössbauer nuclear quadrupole splittings, Δ, – according to the point charge model formalism – support the formation of octahedral (O_h) or trigonal bipyramidal (TBP) molecular structures. The X-ray diffraction analysis of one complex obtained as single crystal revealed the distortion of the TBP geometry towards square pyramidal (SP) one. This was rationalised by PM3 molecular modelling of the $^{t}Bu_2Sn(pdc)$ complex. In the asymmetric unit, the two chemically similar but symmetry independent molecules form pseudo-dimers, in which the Sn···Sn separation amounts to ca. 6.4 Å. The crystal lattice is stabilised by C–H···O hydrogen bonding between individual molecules.

Keywords: Organotin(IV); FT-IR; Mössbauer spectroscopy; X-ray diffraction; Molecular modelling

1. Introduction

It is well known that organotin(IV) complexes exhibit high biological activity (for example antitumor and fungicide) activity [1,2]. Organotin(IV) carboxylates containing aromatic {N} donor atom represent an interesting class of such complexes; however, up to now only a few papers deal with their molecular structures. Bis(dicyclohexylammonium)bis(2,6-pyridinedicarboxylato)dibutylstannate was assigned to have sevenfold co-ordination at tin on the basis of its ^{119}Sn CP/MAS NMR chemical shift ($\delta = -424.9$ ppm). The assignment has been corroborated by crystal structure determination of its monohydrate, whose

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[*] Corresponding author. Tel.: +36-62-544-340; fax: +36-62-420-505.
E-mail address: laci@chem.u-szeged.hu (L. Nagy).

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tin atom exhibits *trans*-C_2SnNO_4 pentagonal bipyramidal geometry [Sn–C = 2.04, 2.067 Å, C–Sn–C = 168.9°]. In this compound, one 2,6-pyridinedicarboxylato ligand chelates to the tin atom, while another binds through only one carboxylate end. The anhydrous compound showed higher in vitro antitumour activity than those of cisplatin or carboplatin [3].

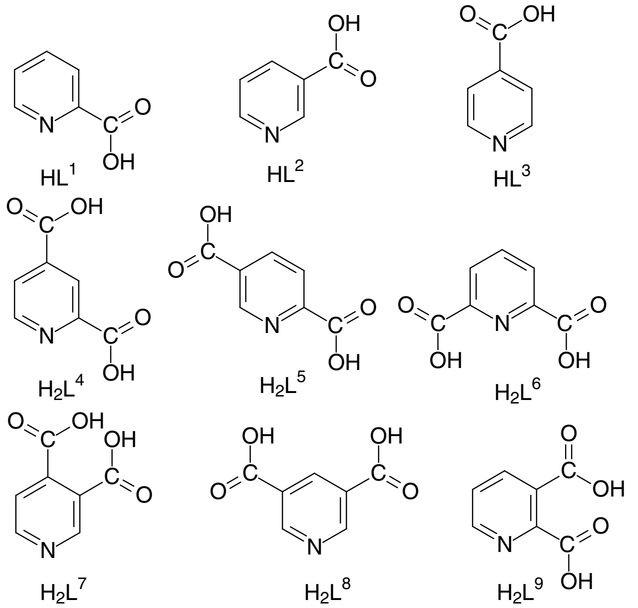
The $R_2Sn(IV)$-2,6-pyridinedicarboxylates exhibit antitumor activity in vitro [4]. Atassi assumed that water-soluble organotin(IV) compounds are likely to be more active than complexes that are soluble only in organic solvents [5]. Gielen and co-workers [3,6] prepared some tetraethylammonium (diorgano)-halogeno(2,6-pyridinecarboxylato)stannates, (halogeno = Cl^-, F^-) whose water solubility under physiological conditions is higher with respect to their parent compounds. The desired compounds were obtained using a similar procedure as in the case of the analogous tetraethylammonium diorgano(halogeno)thiosalicylatostannates [7]. In the parent compound, the experimental Mössbauer parameter nuclear quadrupole splitting ($\Delta \approx 4.2$ mm s^{-1}) suggested hepta-coordination around the tin atom [8]; this type of geometry is maintained in its salts.

We have recently demonstrated that the reaction of titled ligands with $^{n}Bu_2Sn(IV)^{2+}$ results in polymeric complexes. By means of X-ray diffraction measurements, it was found that the 2-picolinic and the pyridine-2,6-dicarboxylic acid complexes contain the Sn central atom in a pentagonal bypiramidal co-ordination environment [9]. Now we have synthesised the $^{t}Bu_2Sn(IV)$ complexes of 2-picolinic acid (**1**), nicotinic acid (**2**), iso-nicotinic acid (**3**), pyridine-2,4- (**4**), pyridine-2,5- (**5**), pyridine-2,6- (**6**), pyridine-3,4- (**7**), pyridine-3,5- (**8**), as well as pyridine-2,3-dicarboxylic acid (**9**). These complexes were prepared to study the influence of various mono- and dicarboxylato ligands containing hetero {N} donor atom to the co-ordination sphere of the $^{t}Bu_2Sn(IV)^{2+}$ cation. The X-ray diffraction analysis of the [$^{t}Bu_2Sn(pdc)$] complex (**6**) [pdc = pyridine-2,6-dicarboxylato anion] revealed that the Sn atom is penta-coordinated in slightly distorted SP fashion.

2. Experimental

2.1. Starting materials

The $^{t}Bu_2SnCl_2$ was purchased from Sigma–Aldrich. Ligands such as 2-picolinic (HL^1), nicotinic (HL^2), iso-nicotinic (HL^3), pyridine-2,4- (H_2L^4), pyridine-2,5- (H_2L^5), pyridine-2,6- (H_2L^6), pyridine-3,4- (H_2L^7), pyridine-3,5- (H_2L^8) and pyridine-2,3-dicarboxylic (H_2L^9) acids were purchased from Fluka. All the starting reagents are of A.R. grade and were used as purchased. The structures of the ligands are shown in Scheme 1.



Scheme 1. Structures of the HL^1–H_2L^9 ligands.

2.2. Syntheses

Complexes **1**–**9** were prepared as described in [10], however, some modifications were applied (Scheme 2). The 1:2 complexes of **1**–**3** and 1:1 complexes of **4**–**9** were prepared in two steps. First, the sodium salt of the ligands was prepared by adding solid NaOH (4 mmol) to a dry methanolic solution (50 cm^3) containing 4 mmol of the monobasic (HL^{1-3}) and 2 mmol of the dibasic (H_2L^{4-9}) ligands. The resulting solutions were refluxed for 2 h. Then methanolic solutions of $^{t}Bu_2SnCl_2$ (2 mmol) were added to the solution of sodium salt of the ligands and were refluxed for another 2 h.

Compounds **1**, **3**, **6** and **7** were obtained via slow evaporation of the solvent at room temperature and were separated by filtration and washed with dry methanol. Compounds **4**, **5** and **8** precipitated immediately from the mixture, while compounds **2** and **9** were obtained after removal of the solvent under reduced pressure by rotary evaporation. They were recrystallised from methanol. The obtained compounds were white

$$\mathrm{nNaOH + H_nL \xrightarrow{\substack{\text{MeOH}\\ \text{2 h reflux}}} Na_nL + nH_2O}$$

$$\mathrm{Na_nL + m^tBu_2SnCl_2 \xrightarrow{\substack{\text{MeOH}\\ \text{2 h reflux}}} (^tBu_2Sn)_mL + nNaCl}$$

n = 1 for HL^1-HL^3; 2 for H_2L^4-H_2L^9
m = 0.5 for HL^1-HL^3, 1 for H_2L^4-H_2L^9

Scheme 2. Preparation of the complexes.

Table 1
Physical and analytical data for ^{t}BuSn(IV) complexes of ligands containing {O,N} donor atoms

Complex	Analysis (%)				Colour	Yield (%)	M.p. (°C)
	C	H	N	Sn			
^{t}Bu$_2$Sn(picolinate)$_2$ (**1**)	50.05 (50.31)	5.49 (5.45)	6.02 (5.87)	23.92 (24.89)	Colourless	65	214
[^{t}Bu$_2$Sn(nicotinate)$_2$]$_n$ (**2**)	49.78 (50.31)	5.32 (5.45)	6.28 (5.87)	24.27 (24.89)	White	52	120–124
[^{t}Bu$_2$Sn(iso-nicotinate)$_2$]$_n$ (**3**)	50.21 (50.31)	5.12 (5.45)	5.98 (5.87)	24.08 (24.89)	Colourless	68	176–178
[^{t}Bu$_2$Sn(pyridine-2,4-dicarboxylate)(H$_2$O)]$_n$ (**4**)	43.16 (43.27)	5.98 (5.53)	3.75 (3.36)	28.05 (28.54)	White	72	>300
[^{t}Bu$_2$Sn(pyridine-2,5-dicarboxylate)(H$_2$O)]$_n$ (**5**)	43.01 (43.27)	5.41 (5.53)	3.53 (3.36)	27.78 (28.54)	Yellow	76	>300
[^{t}Bu$_2$Sn(pyridine-2,6-dicarboxylate)] (**6**)	45.43 (45.23)	5.17 (5.28)	3.78 (3.52)	29.10 (29.83)	Colourless	71	297–298
[^{t}Bu$_2$Sn(pyridine-3,4-dicarboxylate)]$_n$ (**7**)	45.12 (45.23)	5.49 (5.28)	3.84 (3.52)	29.34 (29.83)	White	72	183
[^{t}Bu$_2$Sn(pyridine-3,5-dicarboxylate)(H$_2$O)]$_n$ (**8**)	43.15 (43.27)	5.19 (5.53)	3.42 (3.36)	27.93 (28.54)	White	60	>300
[^{t}Bu$_2$Sn(pyridine-2,3-dicarboxylate)(H$_2$O)]$_n$ (**9**)	43.07 (43.27)	5.75 (5.53)	3.18 (3.36)	27.23 (28.54)	White	55	180–182

solids, except **5**, which was yellow. All of them were insoluble in water and benzene. Complexes **1** and **6** were soluble in CHCl$_3$, while complexes **2** and **9** only in DMSO. Compounds **1** and **6** were obtained as single crystals, while the others were amorphous solids. The synthesis and spectroscopic and X-ray diffraction analysis of **1** were already reported [11,12]. The X-ray diffraction analysis of **1** showed that the Sn(IV) is hexa-coordinated in highly distorted O$_h$ environment, in which the bulky ^{t}butyl groups are apically positioned.

The analytical data are presented in Table 1 together with other characteristic physical constants. Microanalyses were performed at the Department of Organic Chemistry, University of Szeged. The Sn contents were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) and found to correspond to the theoretically calculated values.

2.3. X-ray crystallography

Crystal data for [^{t}Bu$_2$Sn(pdc)] (**6**): C$_{15}$H$_{21}$NO$_4$Sn, $M_r = 398.04$, orthorhombic, space group *Pbca* (No. 61), with $a = 10.675(1)$ Å, $b = 13.751(2)$ Å, $c = 46.489(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 6824.2(13)$ Å^3, $Z = 16$, $\rho_{\text{calc}} = 1.550$ Mg/m^3, $F(000) = 3200$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, μ (Mo Kα) = 1.511 mm^{-1}, crystal size 0.45×0.30×0.30 mm. Intensity data of 12017 reflections were measured ($2.45° \leqslant \Theta \leqslant 31.96°$) on an Enraf-Nonius CAD-4 diffractometer (ω–2Θ scans) of which 11727 were independent ($R_{\text{int}} = 0.0124$). The intensities of the standard reflections indicated a crystal decay of 15%, which was corrected. A semi-empirical (ψ-scan) absorption correction was also applied (min/max transmission: 0.5496/0.6599). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) [13]. 11727 reflections were employed in the structure refinement (379 parameters, 0 restraints). The final R values were $R_1 = 0.0419$ ($I > 2\sigma(I)$) and $wR_2 = 0.1319$ (all data); min/max residual electron density −1.233/0.835 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. Hydrogen atomic positions were generated from assumed geometries. A riding model refinement was applied for the hydrogen atoms.

Table 2
Partial quadrupole splitting (pqs) values of the functional groups used in the calculations (in mm s^{-1})

	T$_d$	TBP$_a$	TBP$_e$	O$_h$
{R}	−1.37	−0.94	−1.13	−1.03
{COO$^-$}$_m$	−0.15	−0.1	0.06	−0.11
{COO$^-$}$_b$	0.114	0.075	0.293	0.083
{N}	–	−0.035	0.147	−0.1
{H$_2$O}	–	0.18	0.43	0.2

Abbreviations. T$_d$, tetrahedral; TBP$_a$, trigonal-bipyramidal axial; TBP$_e$, trigonal-bipyramidal equatorial; O$_h$, octahedral; m, monodentate; b, bidentate.

2.4. FT-IR, Raman and Mössbauer spectroscopic measurements

The FT-IR spectra of the ligands and the complexes were measured on Bio-Rad Digilab Division FTS-40 and FTS-65A instruments in the range 4400–400 cm^{-1} in KBr pellets. The FT-Raman spectra were recorded with a Bio-Rad Digilab Division FT-Raman spectrometer. Mössbauer spectroscopic measurements were performed as described in [10]. To determine the steric arrangement of the Sn(IV) co-ordination sphere, the experimental quadrupole splitting (Δ) values were calculated on the basis of a simple, but general molecular orbital model, according to the pqs concept [14] for all the possible symmetries of tetra-, penta- and hexa-coordinated Sn(IV) binding involving two alkyl groups. The pqs values of the different functional groups [15,16] are given in Table 2.

3. Results and discussion

3.1. X-ray structural studies

The asymmetric unit of [^{t}Bu$_2$Sn(pdc)] complex (**6**), established by single-crystal X-ray diffraction analysis, is shown in Fig. 1 with the atom numbering schemes. The relevant geometric parameters are collected in Table 3.

The single-crystal X-ray analysis revealed that there are two structurally similar but symmetry independent molecules (denoted as **6A** and **6B**) in the asymmetric unit. In both **6A** and **6B**, penta-coordinated C_2SnO_2N cores are formed by the O_2N donor set of the pdc anion, as well as, by the two carbon atoms of the ^{t}butyl groups. For penta-coordinated complexes the corresponding TBP or SP co-ordination geometries can be described by the τ factor, where $\tau = 0$ or 1 being indicative of perfect SP or TBP geometries, respectively [17]. The calculated $\tau = 0.14$ reveals a strong SP character of the Sn(IV) centres co-ordination environment [18]. The $–COO^-$ groups of the tridentate pdc anion are unidentate, and therefore form a fused five-membered O–C–Sn–C–N chelate ring with the tin centre ($\underline{A}_5$–$\underline{A}'_5$ and $\underline{B}_5$–$\underline{B}'_5$, respectively, see Fig. 1.) with practically unaltered bite angles: O(1*L*)–Sn(1*L*)–N(1*L*) [72.3(1)° for A_5 and 72.8(1)° for B_5] and O(3*L*)–Sn(1*L*)–N(1*L*) [73.1(1)° for $\underline{A}'_5$ and 72.5(1)° for $\underline{B}'_5$] (Table 3). The π electrons of these five-membered chelate rings, on their turns, interact with the H atoms of ^{t}butyl groups forming weak C–H···π bonds (Table 4). The lengths of the two Sn–O bonds formed with tridentate pdc anions in **6A** are nearly equal ($\Delta = 0.007$ Å), while those in **6B** are slightly differing ($\Delta = 0.015$ Å). The Sn–N bond length of 2.168(3) Å in **6A** is slightly longer than the 2.158(3) Å in **6B**.

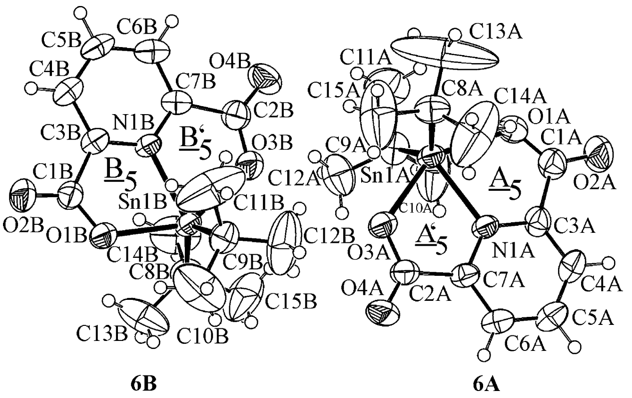


Fig. 1. ORTEP diagram for complex [^{t}Bu$_2$Sn(pdc)] (**6**), showing the two chemically similar but symmetry independent molecules in the asymmetric unit.

Table 3
Selected interatomic bond distances (Å) and bond angles (°) for [^{t}Bu$_2$Sn(pdc)] (**6**)

	L = *A*	*L* = *B*
Sn(1*L*)–O(1*L*)	2.186(3)	2.180(2)
Sn(1*L*)–O(3*L*)	2.171(3)	2.187(3)
Sn(*L*)–N(1*L*)	2.168(3)	2.158(3)
Sn(*L*)–C(8*L*)	2.169(4)	2.165(4)
Sn(*L*)–C(9*L*)	2.170(4)	2.171(4)
O(1*L*)–Sn(X)–N(1*L*)	72.3(1)	72.8(1)
O(3*L*)–Sn(X)–N(1*L*)	73.1(1)	72.5(1)
O(1*L*)–Sn(X)–O(3*L*)	145.3(1)	145.4(1)
C(8*L*)–Sn(X)–C(9*L*)	136.9(2)	133.4(2)

Table 4
Selected interatomic distances (Å) and angles (°) for the hydrogen bonding and C–H···π interactions in [^{t}Bu$_2$Sn(pdc)] (**6**)[a]

D–H···A	H···A (Å)	D···A (Å)	D– H···A (°)
C(10A)–H(10B)···π ($\underline{A}_5$)	2.88	3.19	100.2
C(14A)–H(14A)···π ($\underline{A}_5$)	2.96	3.30	101.9
C(10A)H(10A)···π ($\underline{A}'_5$)	3.28	3.72	110.2
C(14A)H(14B)···π ($\underline{A}'_5$)	2.83	3.41	120.5
C(11B)–H(11E)···π ($\underline{B}_5$)	2.89	3.34	110.1
C(14B)–H(14F)···π ($\underline{B}_5$)	3.26	3.67	107.9
C(14B)H(14E)···π ($\underline{B}'_5$)	2.84	3.27	108.7
C(11B)H(11F)···π ($\underline{B}'_5$)	2.93	3.42	113.0
C(4°)–H(4°)···O(1A)^{i}	2.36	3.21	151.8
C(4B)–H(4B)···O(2B)^{ii}	2.36	3.19	148.1
C(6B)–H(6B)···O(4A)^{iii}	2.23	3.04	145.2

[a] Symmetry codes: (i) $-1/2 + x$, y, $1/2 - z$; (ii) $2 - x$, $-y$, $-z$; (iii) $1 + x$, y, z.

It should be mentioned here that the pdc ligand with ^{n}Bu$_2$Sn(IV) cation forms hepta-coordinated [^{n}Bu$_2$Sn(pdc)(H$_2$O)]$_2$ dimers [8], or higher oligomers [^{n}Bu$_2$Sn(pdc)(H$_2$O)]$_{2n}$ [9], with additional H_2O molecules completing the co-ordination sphere. In both molecules, the two [^{n}Bu$_2$Sn(pdc)(H$_2$O)] units are linked via triconnective bridged carboxylato {O} atoms, generating four-membered stannoxanic Sn_2O_2 ring. In complex **6**, the carboxylato {O} atoms of pdc ligand could not participate in stannoxanic Sn–O bond formation owing to the bulkiness of the ^{t}Bu-groups, nevertheless, the symmetry independent **6A** and **6B** molecules are arranged in pseudo-dimeric manner. In this pseudo-dimeric arrangement the carboxylato O(3A) and O(3B) atoms and the {Sn} centres form a planar Sn_2O_2 ring [torsion angle: O(3A)–Sn(1B)–O(3B)–Sn(1A) 0.3°] with asymmetric Sn···O distance [4.55 and 4.84 Å, respectively, which is longer than the sum of the van der Waals radii (3.57 Å)] and a Sn···Sn separation of 6.4 Å. The crystal lattice of the complex **6** reported in this work, in addition, is stabilised by the aid of the C–H···O hydrogen bonding between individual molecules (Table 4).

In order to rationalise the difference between the behaviour of ^{t}butyl and ^{n}butyl groups, molecular modelling was performed on the respective complex monomers. The semi-empirical quantum chemical method PM3 [19a] was used, as implemented in the program MOPAC 6.0 [19b] version 6. First the structures of isolated ^{t}Bu$_2$Sn(pdc) and ^{n}Bu$_2$Sn(pdc) were optimised. Then, applying non-linear parameter estimation in conjunction with the co-ordinates so obtained, we determined the smallest cones which have their apex at the Sn atom and enclose all the atoms (as represented by spheres of their van der Waals radius) in the butyl groups. This geometrical description measures the space excluded from other ligands by the alkyl substituents, i.e. their steric effect: the conic half-angle for ^{n}butyl groups is 54° while for the bulkier ^{t}butyl groups it is 64°. It is interesting to note that the two cones in the latter case overlap slightly (with about 5° angle of intersection), which means that the two ^{t}butyl groups can only rotate in a concerted cogwheel fashion. The space-filling display of this structure shows how much the central Sn atom is shielded.

Beside the sheer bulkiness of the substituents, it is apparent that their facility of movement (i.e. rearrangement to the axial position in a bipyramidal structure) also determines the possibility of extra complexation above penta-coordinated. To characterise this readiness, the energies were calculated for the strained structures in which the C(Bu)$\cdots$Sn$\cdots$C(Bu) angle was restrained to its value taken in the crystalline state. The $^{t}Bu_2Sn$(pdc) conformation where this angle is increased to 162.5° [corresponding to the $^{n}Bu_2Sn$(pdc) crystal with its hepta-coordinated Sn] has 76 kJ/mol higher energy than the stable penta-coordinated conformer. This indicates a significant barrier against opening up the structure to allow higher co-ordination. In comparison, increasing the angle to 136.7° [corresponding to the $^{t}Bu_2Sn$(pdc) crystal with its penta-coordinated tin] requires only 21 kJ/mol, while the analogous energy difference between crystalline $^{n}Bu_2Sn$(pdc) and its penta-coordinated conformer in isolation is 46 kJ/mol. Thus, even this simple model calculation that only includes intramolecular interaction energy reveals the different tendency for co-ordination in the pdc complexes with the two isomer butyl substituents.

3.2. FT-IR spectroscopic characterisation

The FT-IR spectra of the complexes **1**–**9** were recorded in the 4400–400 cm^{-1} spectral range. The observed characteristic bands as well as the vibrational assignments are summarised in Table 5.

The characteristic bands of the C=O group were assigned in the spectra of the neutral H_2L^5 and H_2L^6 ligands in the 1794–1703 cm^{-1} spectral range. The presence of broad and irregularly shaped bands in the 3500–2500 cm^{-1} spectral region shows that the –COO^{-} groups are involved in intra- and intermolecular hydrogen bonding [20]. These characteristic vibrational modes are absent in the spectra of complexes **1**–**9** indicating the co-ordination of the –COO^{-} group(s) to the central Sn(IV) atom. Deacon shows that the magnitude of the $\Delta\nu$ [$\Delta\nu = \nu_a(COO^-) - \nu_s(COO^-)$] can be correlated with the co-ordination modes of this anion [21]. The $\Delta\nu$ values of the studied complexes (**1**–**9**) were compared with that of the sodium salts of HL^1–H_2L^9 ligands [9] (Table 5). For complexes **1** and **3**–**9** these $\Delta\nu$ values reflect the monodentate co-ordination mode of the –COO^{-} group, while for complex **2** being indicative of bridging bidentate and monodentate co-ordination mode.

Further characteristic FT-IR bands of the complexes **1**–**9** are in good agreement with the recently published data [9]. In accord with the C–O–Sn bond formation, the ν(C–OH) vibration (spectral range 1290–1210 cm^{-1}) is shifted to lower frequencies of about 20–70 cm^{-1}. The presence of the ν (Sn–O) vibrational mode in the 500–390 cm^{-1} spectral range also confirms the co-ordination of the –COO^{-} groups to Sn(IV) centre. The presence of new broad band with medium intensity in the

Table 5
Assignment of characteristic FT-IR and Raman vibrations (cm^{-1}) of complexes **1**–**9**

Complex	ν(CO)[a]	ν(OH)	$\nu_a(COO)^-$	$\nu_s(COO)^-$	$\Delta\nu$	$\nu_{a,s}$(C=C/N=C)	ν(Sn–C)	ν(Sn–O)
1	1721 m	–	1672 vs	1327 s	345	1593 m, 1567 m 1475 m, 1435 m	542 w, 528 w	431 m
2	1708 m	–	1618 sh 1594 vs	1352 m 1401 s	266 193	1552 s, 1534 m 1482 m, 1422 s	624 w, 536 w 568 w, 522 w	456 m
3	1712 m	–	1647 s	1346 s	301	1600 m, 1559 m 1493 w, 1411 m	522 m, 502 w	422 m
4	1794 m	3451 mb	1617 s	1357 m	260	1628 m, 1593 vs 1544 m, 1457 w	504 w	442 w
5	1730 s	3430 mb	1647 s	1336 s	311	1616 s, 1591 m 1562 m, 1475 w	567 w	479 w
6	1703 s	–	1682 vs	1335 s	347	1620 sh, 1597 w 1562 w, 1420 w	589 w, 531 w	437 w
7	1712 m	–	1651 s 1618 s	1359 s 1331 s	292 287	1597 m, 1558 m 1488 w, 1457 m	532 m, 472 w	402 m
8	1721 m	3450 m, 3409 m	1641 m 1602 vs	1384 m 1341 s	277 261	1583 m, 1552 m 1444 m, 1409 m	551 w, 503 w	438 w
9	1712 m	3454 mb	1666 vs 1658 vs	1347 s 1330 sh	319 328	16 5 sh, 1585 m 1470 m, 11454 w	555 m, 489 w 533 m, 459 w	398 m

Abbreviations. s, strong; m, medium; w, weak; vs, very strong; sh, shoulder; b, broad.

[a] Carbonyl stretching vibrations of free ligands.

3500–3400 cm^{-1} region strongly suggests the presence of co-ordinated water molecule for complexes **4**, **5**, **8** as well as **9**. No information on the possible occurrence of N → Sn bond can be extracted from $\nu_{as,s}$(C=C/C=N) vibrational modes, as these bands were shifted only by 4–22 cm^{-1} towards the higher frequencies. For complexes **1**, **4**–**6** and **9**, the observed 30–50 cm^{-1} red shift of the in plane deformation of the pyridine ring (near 650 cm^{-1}) suggests that the pyridine {N} atom is involved in co-ordination [22]. Only one Sn–C stretching vibration could be observed in the spectra of complexes **4** and **5**, which suggests that the C–Sn–C bond angle is close to 180°. The presence of two Sn–C vibrations in the spectra of complexes **1**, **3**, **6**–**8** is indicative of the non-linearity of the C–Sn–C bonds, however, the presence of two pairs of Sn–C vibrations in the spectra of complexes **2** and **9** strongly suggest two different co-ordination geometry around Sn(IV) centre. This observation is in good agreement with the results of Mössbauer spectroscopic investigations.

3.3. Mössbauer spectroscopic characterisation

Mössbauer parameters are helpful in determining the co-ordination number and the structure of the Sn compounds. The experimental δ and $|\Delta|$ parameters are summarised in Table 6, which clearly indicate the presence of organotin(IV) species. The spectra of compounds **1** and **3**–**8** comprised only one, well-developed doublet (the narrowness of the full width at half of the resonance peaks being average), which suggests the presence of completely equivalent Sn environments in these compounds. An unsymmetric doublet with the line width greater than 1.0 was observed in the spectra of compounds **2** and **9**, suggesting the presence of Sn in two different co-ordination environments. These doublets were deconvoluted into two dublets.

The experimental δ and $|\Delta|$ values in the complexes **4** and **5** (δ, 1.75; $|\Delta|$, 4.13, 3.97) fall in the range of those noted for the *trans* O_h complexes [23], with the two –COO^- groups, H_2O and pyridine {N} in equatorial position. These complexes are probably cyclic oligomers or very long chain-like compounds and have a structure similar to the earlier studied ^{n}Bu_2Sn(IV) complexes [9]. The proposed structures are depicted in Fig. 2.

According to the IR and solubility data, the compounds **7** and **8** must also have one-dimensional polymeric structure. The structural elucidation based on pqs concept has shown, that linear oligomerisation is occurred through the monodentate –COO^- groups from two different ligands. In complex **7**, the Sn centres are in T_d, while in **8** in distorted TBP co-ordination geometry. The latter one contains an additional co-ordinated H_2O molecule in the equatorial position of the TBP, furthermore, the ^{t}butyl groups are also arranged in equatorial plane (Fig. 2). The molecular structure of the **1** is already known [11,12] and the Sn(IV) centre proved to be hexa-coordinated in highly distorted O_h geometry with the two bulky ^{t}butyl groups in axial positions. Our results further confirm the published structure. In complex **3**, the two carboxylic oxygen and the two pyridine {N} atoms occupy the equatorial positions of a distorted O_h co-ordination site, as the C–Sn–C angle is estimated to be about 128°.

In some cases the differences between the calculated and observed $|\Delta|$ values are larger than the experimental error. This can be explained considering that the calculated value is given for the ideal co-ordination polyhedron. Deviation from the ideal geometry can be estimated on the basis of the Sham–Bancroft equation $\Delta = -4\{R\}[1-(3/4)\sin^2\theta]^{1/2}$ (where {R} denotes the pqs value of the ^{t}butyl group, and θ represents the C–Sn–C angle), taken from [23]. The C–Sn–C bond angle for complex **6** determined by X-ray diffraction method is 136.9° for **6A**, and 133.4° for **6B**, respectively (Table 1). Using the above mentioned equation and the pqs values, such as $\{R\} = -1.03$ mm s^{-1} [14] or -1.01 mm s^{-1} [24], the calculated C–Sn–C angles are 136° and 138°, respectively. These values agree excellently with the X-ray diffraction data, and confirm the validity of Sham–Bancroft equation.

Table 6
Experimental and calculated Mössbauer spectroscopic parameters of complexes **1**–**9**

Complex	δ_1	$\lvert\Delta\rvert_{1exp}$	$\lvert\Delta\rvert_{1cal}$	Γ_1	δ_2	$\lvert\Delta\rvert_{1exp}$	$\lvert\Delta\rvert_{2cal}$	Γ_2	I_1:I_2	Geometry	C–Sn–C
1[a]	1.53	3.31	3.30	0.92	–	–	–	–	–	O_h	140
2	1.55	3.59	3.60	0.87	1.49	2.90	2.97	0.97	2:1	O_h, TBP	142, 120
3	1.28	2.61	2.55	0.96	–	–	–	–	–	O_h	120
4	1.75	4.13	4.04	1.0	–	–	–	–	–	O_h	180
5	1.75	3.97	4.04	1.0	–	–	–	–	–	O_h	162
6	1.58	3.30	3.31	0.95	–	–	–	–	–	SP	138
7	1.32	2.72	2.82	1.03	–	–	–	–	–	T_d	120
8	1.67	3.40	3.36	0.93	–	–	–	–	–	TBP	138
9	1.57	3.49	3.50	0.81	1.36	2.72	2.60	1.17	3:4	TBP, O_h	138, 124

δ, $|\Delta|$ and Γ are given in mm s^{-1}, C–Sn–C bond angles are given in °.

[a] Structure is known, see [11].

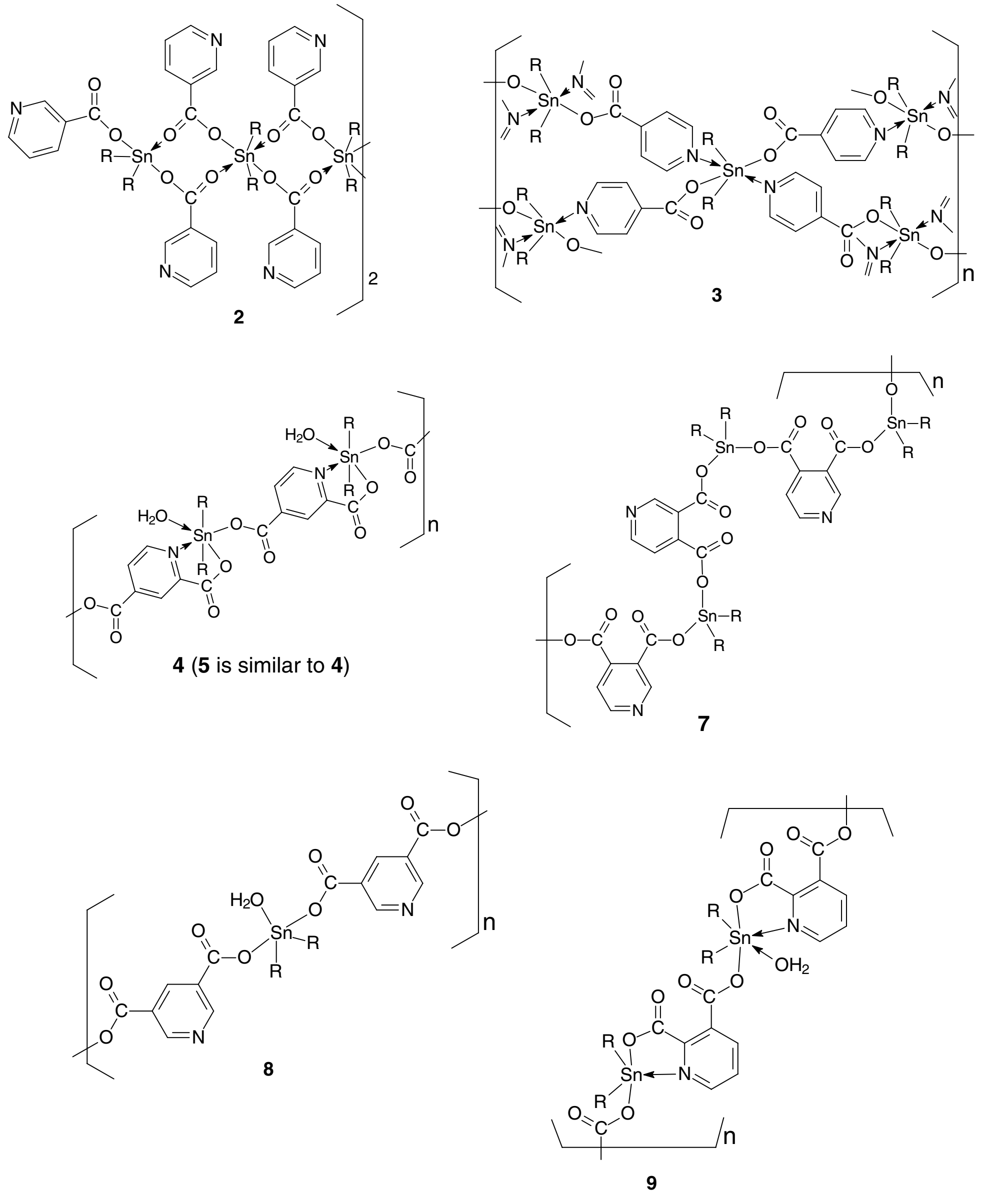


Fig. 2. Proposed structures of complexes **1**–**9**.

Complexes **2** and **9** contain organotin(IV) cations in two different stereochemical arrangement, thus, it is likely that these complexes have polymeric structures. With the assumption of chain-like oligomerisation, the ratio of terminal and in-chain organotin(IV) moieties can be calculated for each complex from the relative intensities of the corresponding Mösbauer spectra (Table 6). The complex **2** contains distorted O_h co-ordination site within the chain. Both ends of the chain are terminated by TBP moieties. In the O_h species the alkyl groups are located in axial positions and the oligomerisation is occured through the bridging bidentate –COO$^-$ groups in equatorial positions. In the terminal TBP species the chain is ended with monodentately co-ordinated –COO$^-$ group occupying the axial position, while the ^{t}butyl groups are located in equatorial positions (Fig. 2).

Compound **9** may be also cyclic oligomer or very long chain-like, such as complexes **4** and **5**. There are alternate TBP and O_h co-ordination geometries within the chain (Fig. 2). The alkyl groups are located in equatorial positions both in the TBP and O_h co-ordination sites. The additionally co-ordinated H_2O decrease the C–Sn–C bond angle in the O_h species by about 14°. The oligomerisation is occurred through the monodentate –COO$^-$ groups of different ligands. They have monodentate co-ordination mode within the TBP and O_h species in apical positions (Fig. 2).

4. Conclusions

The synthetic procedures used in this work resulted in the formation of ^{t}BuSn(IV) compounds with a 1:2 metal-to-ligand ratio for the pyridine-monocarboxylic acids (complexes **1**–**3**) and with a 1:1 ratio for the pyridine-dicarboxylic acids (complexes **4**–**9**). The analytical, FT-IR and Mössbauer spectroscopic data of these complexes revealed the formation of well-defined compounds. In polymeric complexes obtained with H_2L^4, H_2L^5 and H_2L^7–H_2L^9 dicarboxylic acids, polymerisation through carboxylato groups occurred, where the monodentately co-ordinated $-COO^-$groups act as bridges between the neighbouring Sn atoms. The X-ray diffraction analysis of complex **6** shows a seriously distorted TBP co-ordination sphere with equatorial ^{t}Bu groups. It was shown that the bulkiness of ^{t}Bu groups prohibits the formation of a hepta-coordinated geometry, which is observed for ^{n}BuSn(IV) complexes. The values of the C–Sn–C bond angles of complex **6** obtained from X-ray diffraction analysis are in good agreement with the values calculated on the basis of Mössbauer spectroscopic data.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 215838. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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