

Preparation and structural characterization of $[\text{Ph}_3\text{Sn(IV)}]^+$ complexes with pyridine-carboxylic acids or hydroxypyridine, -pyrimidine and -quinoline

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Abstract

A number of $[\text{Ph}_3\text{Sn(IV)}]^+$ complexes formed with ligands containing $-\text{OH}$ ($-\text{C}=\text{O}$), or $-\text{COOH}$ group(s) and aromatic {N} donor atom have been prepared. The binding sites of the ligands were identified by FT-IR spectroscopic measurements. In the complexes containing hydroxy and carboxylate functions, the carboxylate group is coordinated to the organotin(IV) centres in monodentate or bridging bidentate manner. It was also found that in the hydroxypyridine and -pyrimidine complexes the $[\text{Ph}_3\text{Sn(IV)}]^+$ moiety in most cases reacts with the phenolic form of the ligands. The rationalisation of the experimental ^{119}Sn Mössbauer nuclear quadrupole splittings, $|\Delta_{\text{exp}}|$ – according to the point charge model formalism – together with the FT-IR data support the formation of trigonal bipyramidal (Tbp) or octahedral (O_h) molecular structures. Furthermore, X-ray diffraction analysis has been performed on the triphenyltin(IV)-3-phenolato-2(1*H*)-pyridinone-*O,O'* single crystals. The penta-coordinated tin center exhibits a Tbp geometry. In case of 2-picolinic acid, a *trans*-phenylation was observed during the complexation, resulting $[\text{Ph}_2\text{Sn(IV)}]^{2+}$ complex and $\text{Ph}_4\text{Sn(IV)}$.

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1. Introduction

It is well known that organotin(IV) compounds exhibit high biological (for example fungicide and antitumor) activity [1,2]. Organotin(IV) complexes with ligands containing phenolic $-\text{OH}$ or $-\text{COOH}$ group(s), as well as, aromatic {N} donor atom represent an interesting class of such complexes, however, up to now only a few works have dealt with the molecular structures of them.

It has recently been demonstrated that the reaction of pyridine mono- and dicarboxylate anions with $[\text{Bu}_2\text{Sn(IV)}]^{2+}$ [3] and $[\text{Bu}_2\text{Sn(IV)}]^{2+}$ -cations [4] results in the formation of polynuclear complexes. In these di-*n*-butyltin(IV) and di-*t*-butyltin(IV) 2-picolinate and pyridine-2,6-dicarboxylate complexes the central tin(IV)-ion is hepta- and penta-coordinated in pentagonal-bipyramidal (Pbp) [3] and in square-pyramidal (Sp) [4] environment. Later, a systematically designed series of complexes containing $[\text{Bu}_2\text{Sn(IV)}]^{2+}$ and $[\text{Bu}_2\text{Sn(IV)}]^{2+}$ ions and hydroxypyridine, hydroxypyrimidine and hydroxyquinoline ligands have also been prepared. The structural data obtained reveal the influence of the nature and steric position of donor atoms on the

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coordination sphere of the tin center. Accordingly, the molecular structures of the complexes were established by FT-IR and Mössbauer-spectroscopy. Single-crystals of complexes of 8-hydroxyquinolinate with $[\text{Bu}_2\text{Sn(IV)}]^{2+}$ and $[\text{Bu}_2\text{Sn(IV)}]^{2+}$ were prepared. The X-ray diffraction studies revealed that the central {Sn} atoms are in *cis*- O_h environment [5].

Therefore, as organic continuation of former works the goal of present paper to demonstrate the influence on the structure of the bulky $[\text{Ph}_3\text{Sn(IV)}]^{+}$ moiety within the complexes formed.

2. Experimental

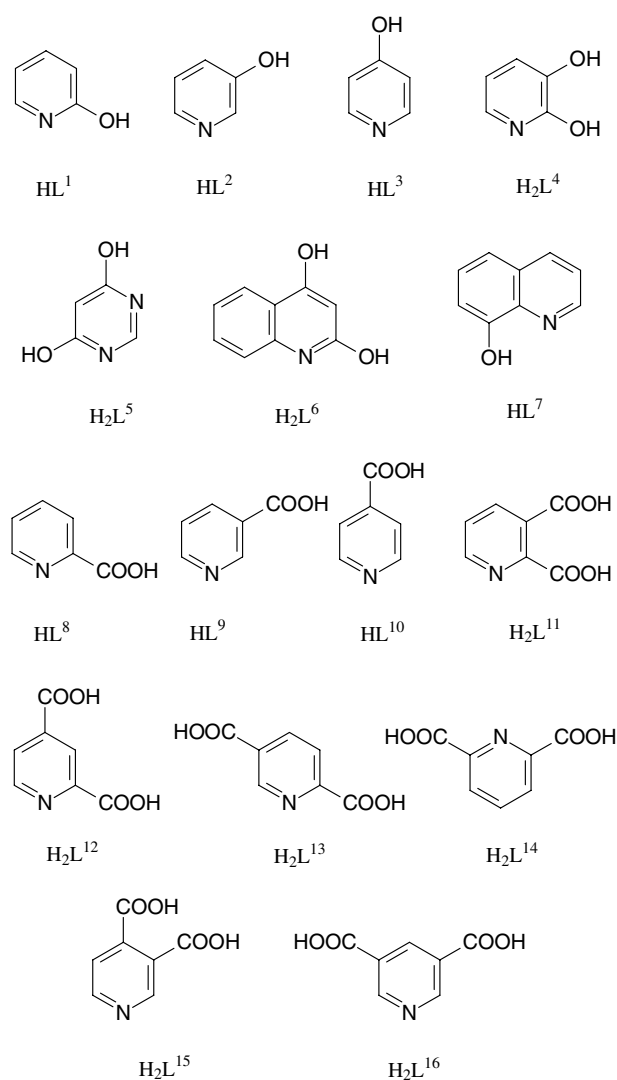
2.1. Starting materials

The triphenyltin-hydroxide (Ph_3SnOH) and ligands 2-hydroxypyridine $\{\text{HL}^1\}$, 3-hydroxypyridine $\{\text{HL}^2\}$, 4-hydroxypyridine $\{\text{HL}^3\}$, 2,3-dihydroxypyridine $\{\text{H}_2\text{L}^4\}$, 4,6-dihydroxypyrimidine $\{\text{H}_2\text{L}^5\}$, 2,4-quinolinediol $\{\text{H}_2\text{L}^6\}$ and 8-hydroxyquinoline $\{\text{HL}^7\}$ were purchased from Sigma–Aldrich. Ligands containing $-\text{COOH}$ group(s) as 2-picolinic (HL^8), nicotinic (HL^9), *iso*-nicotinic (HL^{10}), pyridine-2,3- (H_2L^{11}) pyridine-2,4- (H_2L^{12}), pyridine-2,5- (H_2L^{13}), pyridine-2,6- (H_2L^{14}), pyridine-3,4- (H_2L^{15}) and pyridine-3,5-dicarboxylic (H_2L^{16}) 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.

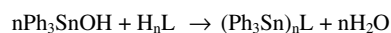
2.2. Syntheses

The complexes were prepared as described in [3], according to the reaction described in Scheme 2. First, the appropriate quantity of Ph_3SnOH (2 mmol) was dissolved and refluxed in dry methanol (50 cm^3) for 1 h. Then methanolic solution (50 cm^3) containing 2 mmol of the monobasic ($\text{HL}^{1-3,7-10}$) or 1 mmol of the dibasic ($\text{H}_2\text{L}^{4-6,11-16}$) ligand was added to the solution of the Ph_3SnOH and refluxed for another 2 h. In the case of dibasic ligands ($\text{H}_2\text{L}^{4-6,11-16}$) we have been used two different, 1:1 and 2:1 starting metal to ligand molar ratios for the preparation of the compounds. The analytical and spectroscopic studies reveal formation of complexes with 1:1 M:L for ligands $\text{H}_2\text{L}^{4-6,14}$ and 2:1 for the rest dibasic ligands.

Compounds **1**, **4–8**, and **13–16** were obtained via slow evaporation of the solvent at room temperature and were separated by filtration and washed with dry methanol. The other compounds precipitated immediately from the reaction mixture. The complexes were recrystallized from methanol. The obtained compounds were white solids, except **2**, **7**, **13** and **15**, which were yellow, **4** and **6**, which were light-brown. All of them were insoluble in water and benzene. Compounds **1**, **4**, and **7–10** were obtained as single crystals, while the others are amorphous solids. The synthesis and X-ray diffraction analysis



Scheme 1. Structure of the ligands studied.



Scheme 2. Preparation of the complexes.

of **8–10** were already reported [6–8]. The X-ray diffraction analysis of **9** and **10** showed that the Sn(IV) is penta-coordinated in distorted Tbp environment, in which the bulky phenyl groups are in equatorial positions. The complexes have a chain-like polymeric structure, where the monodentately co-ordinated $-\text{COO}^-$ group and the pyridine {N} atom act as bridges between the neighbouring {Sn} atoms.

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) and found to correspond to the theoretically calculated values.

Table 1
Physical and analytical data [calculated % values in parentheses] on $[\text{Ph}_3\text{Sn}(\text{IV})]^+$ complexes studied

Complex	Analysis (%)				Colour	M.p. (°C)
	C	H	N	Sn		
$[\text{Ph}_3\text{Sn}(2\text{-hpy})]_n$ (1)	61.29 (62.16)	4.15 (4.28)	3.05 (3.15)	25.93 (26.74)	White	119–121
$[\text{Ph}_3\text{Sn}(3\text{-hpy})]_n$ (2)	63.53 (62.16)	4.36 (4.28)	3.21 (3.15)	27.27 (26.74)	Light-yellow	204–207
$[\text{Ph}_3\text{Sn}(4\text{-hpy})]_n$ (3)	62.78 (62.16)	4.24 (4.28)	3.18 (3.15)	26.47 (26.74)	White	270–273
$\text{Ph}_3\text{Sn}(2,3\text{-dhpy})$ (4)	59.43 (60.03)	4.09 (4.13)	3.07 (3.04)	25.54 (25.80)	Light-brown	173–176
$[\text{Ph}_3\text{Sn}(4,6\text{-dhpym})(\text{H}_2\text{O})]_n$ (5)	54.04 (55.15)	4.09 (4.17)	5.73 (5.84)	24.28 (24.78)	White	99–101
$[\text{Ph}_3\text{Sn}(2,4\text{-dhq})]_n$ (6)	63.43 (63.56)	4.09 (4.12)	2.76 (2.74)	23.03 (23.27)	Light-brown	105–108
$\text{Ph}_3\text{Sn}(8\text{-hq})$ (7)	65.29 (65.62)	4.16 (4.25)	2.78 (2.83)	23.54 (24.02)	Yellow	130–132
$\text{Ph}_2\text{Sn}(\text{pica})_2$ (8)	55.37 (55.74)	3.46 (3.48)	5.37 (5.41)	22.62 (22.96)	Colourless	>300
$[\text{Ph}_3\text{Sn}(\text{nica})]_n$ (9)	61.74 (61.05)	4.13 (4.24)	3.03 (2.96)	24.93 (25.14)	White	180–184
$[\text{Ph}_3\text{Sn}(\text{inica})]_n$ (10)	60.69 (61.05)	4.02 (4.24)	2.76 (2.96)	25.07 (25.14)	White	192–196
$[(\text{Ph}_3\text{Sn})_2\text{-}2,3\text{-pydca}]_n$ (11)	58.90 (59.69)	3.79 (3.81)	1.55 (1.62)	27.13 (27.44)	White	>300
$[(\text{Ph}_3\text{Sn})_2\text{-}2,4\text{-pydca}]_n$ (12)	60.58 (59.69)	3.95 (3.81)	1.66 (1.62)	27.29 (27.44)	White	>300
$[(\text{Ph}_3\text{Sn})_2\text{-}2,5\text{-pydca}]_n$ (13)	58.91 (59.69)	3.42 (3.81)	1.57 (1.62)	27.08 (27.44)	Yellow	132–136
$[\text{Ph}_3\text{Sn}-2,6\text{-pydca}]_n$ (14)	57.79 (58.17)	3.38 (3.49)	2.59 (2.71)	22.92 (23.00)	White	148–152
$[(\text{Ph}_3\text{Sn})_2\text{-}3,4\text{-pydca}]_n$ (15)	58.38 (59.69)	3.73 (3.81)	1.59 (1.62)	27.25 (27.44)	Yellow	136–140
$[(\text{Ph}_3\text{Sn})_2\text{-}3,5\text{-pydca}]_n$ (16)	60.01 (59.69)	3.83 (3.81)	1.64 (1.62)	27.87 (27.44)	White	232–235

2.3. X-ray crystallography

Crystal data and refinement parameters of complex **4** are summarised in Table 2. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using the ω - 2θ scan technique. Three standard reflections were monitored every hour; these remained constant within experimental error. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) [9]. All non hydrogen atoms were refined anisotropically in F^2 mode. The H(1) hydrogen

atom on the N(1) nitrogen was found in the difference map, and its position was refined. All other hydrogen atomic positions were generated from assumed geometries and a riding model was applied.

2.4. FT-IR and Mössbauer spectroscopic measurements

The FT-IR spectra of the ligands and those of the complexes were measured on BioRad Digilab Division FTS-65A instrument in the range 4400–400 cm^{-1} in KBr pellets.

Mössbauer spectroscopic measurements were performed as described in [3,4]. To determine the steric arrangement of the Sn(IV) coordination sphere, the experimental quadrupole splitting ($|\Delta_{\text{exp}}|$) values were calculated on the basis of a simple, but general molecular orbital model, according to the pqs concept [10] for all the possible symmetries of tetra-, penta- and hexa-coordinated Sn(IV) binding involving three phenyl groups. The pqs values of the different functional groups [11,12] are given in Table 3.

3. Results and discussion

3.1. X-ray structural studies

The molecular structure of **4** is shown in Fig. 1, selected bond lengths and angles are listed in Table 4. The coordination geometry around the Sn(IV) center is a distorted trigonal bipyramidal ($\tau = 0.64$) with the O(1) atom of the ligand and C(1A) atom of the phenyl-group occupying the axial positions of the coordination sphere [the O(1)–Sn(1)–C(1A) angle is $161.6(1)^\circ$]. The other two phenyl rings are in the equatorial plane, with C(1C)–Sn(1)–C(1B) angle close to 120° (Table 4). The third equatorial position is occupied by deprotonated oxygen O(2) atom of the ligand. The 3-phenolato-2(1H)-pyridinone-O,O' anion is coordinated to the metal center in a bidentate chelating fashion leading to a five-membered SnO_2C_2 ring with an O(1)–Sn(1)–O(2) bite angle of $73.3(1)^\circ$.

Table 2
Crystal data and structure refinement parameters for complex **4**

Empirical formula	$\text{C}_{23}\text{H}_{19}\text{N}_1\text{O}_2\text{Sn}$
Formula mass	460.08
Crystal size [mm]	$0.20 \times 0.50 \times 0.55$
Colour	Colourless
Crystal system	Monoclinic
Space group	$P2_1/c$
θ Range for data collection ($^\circ$)	$2.47 \leq \theta \leq 34.95$
a [Å]	10.916(1)
b [Å]	11.012(1)
c [Å]	16.723(2)
β [$^\circ$]	98.85(1)
V [Å 3]	1986.3(4)
Z	4
D_{calc} [Mg/m 3]	1.539
μ [mm $^{-1}$]	1.303
$F(000)$	920
Index ranges ($^\circ$)	$0 \leq h \leq 17$; $0 \leq k \leq 17$; $-26 \leq l \leq 26$
No. of reflections collected	9576
No. of independent reflections/ R_{int}	8710/0.0300
No. of observed reflections $I > 2\sigma(I)$	5600
No. of parameters	248
Goodness-of-fit	0.958
R_1 (observed data)	0.0466
wR_2 (all data)	0.1241

Table 3
Partial quadrupole splitting (pqs) values of the functional groups used in the calculations (in mms^{-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
{-C=O}	0.24	0.16	0.407	0.177
{N _{pyridine} }	-0.46	-0.035	0.147	-0.1
{N _{heterocycle} }	-0.46	-0.035	0.147	-0.1
{OH}	-0.40	-0.13	0.02	-0.14
{O ⁻ }	-0.37	-0.21	-0.09	-0.27
{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.

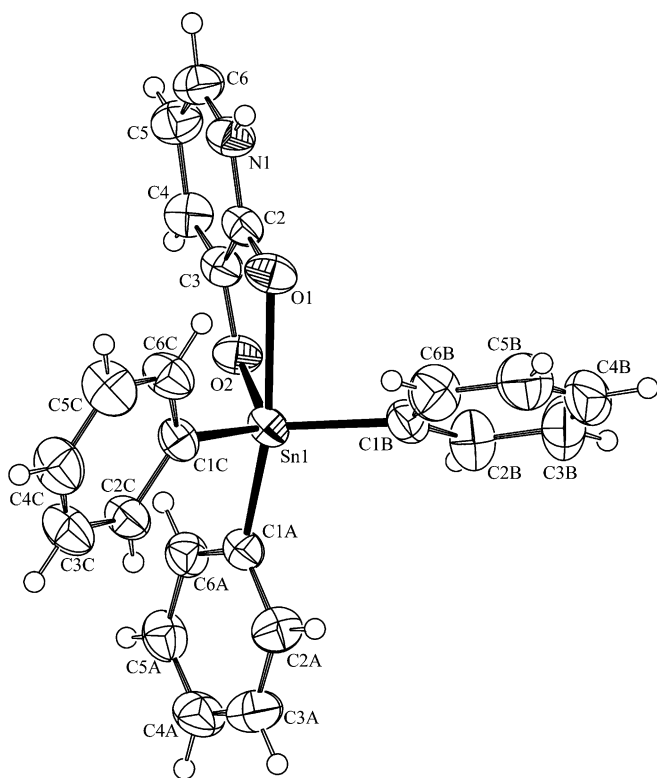


Fig. 1. A view of the molecular structure of complex **4** showing the atom-numbering scheme. Non-hydrogen atoms are shown as 50% probability ellipsoids and hydrogen atoms are shown as open circles.

Table 4
Selected interatomic bond lengths (Å) and bond angles (°) for complex **4**

Sn(1)–O(1)	2.358(2)	C(1B)–Sn(1)–C(1C)	116.9(1)
Sn(1)–O(2)	2.093(2)	O(1)–Sn(1)–O(2)	73.3(1)
Sn(1)–C(1A)	2.162(2)	O(1)–Sn(1)–C(1B)	84.1(1)
Sn(1)–C(1C)	2.137(2)	O(1)–Sn(1)–C(1C)	84.6(1)
Sn(1)–C(1B)	2.132(3)	O(1)–Sn(1)–C(1A)	161.6(1)
O(2)–C(3)	1.340(3)	O(2)–Sn(1)–C(1A)	89.0(1)
O(1)–C(2)	1.262(3)	O(2)–Sn(1)–C(1B)	111.8(1)
C(3)–C(2)	1.447(3)	O(2)–Sn(1)–C(1C)	123.4(1)
N(1)–C(2)	1.350(3)	C(1B)–Sn(1)–C(1A)	107.6(1)
N(1)–C(6)	1.364(4)	C(1C)–Sn(1)–C(1A)	101.7(1)

The Sn(1)–O(1) and the Sn(1)–O(2) bond distances are 2.093(2) and 2.358(2) Å, respectively. The axial C(1A)–Sn(1) bond distance [2.162(2) Å] is somewhat longer (by ~ 0.03 Å) than the Sn–C bond distances in the equatorial plane [2.137(2) and 2.132(3) Å]. The O(2) oxygen atom is engaged in N–H \cdots O hydrogen bonds (2.26 Å), which in their turn link the adjacent molecules into infinite chains. In addition, weak C–H \cdots O and C–H \cdots π interactions can also be observed (Table 5).

3.2. FT-IR spectroscopic characterization

Information on the nature of the tin–ligand bonds can be extracted from infrared absorption frequencies (Tables 6 and 7).

The bifunctional hydroxypyridine, hydroxypyrimidine and hydroxyquinoline ligands can [13] to be existing in different hydroxy or ketone form. They are predominantly in pyridone form in the solid state, but in complex formation the hydroxy is the preferred form [14–16]. In the FT-IR spectra of free HL¹, HL³, H₂L⁴, H₂L⁵ and H₂L⁶, there are characteristic medium and strong bands in the spectral regions 3210–3090 and 1680–1630 cm^{-1} of the –NH and –C=O groups (Table 6), respectively. These bands are absent from the spectra of HL² and HL⁷, because the tendency of tautomerization to their keto form is small. The broad ν OH absorption band in the region 3400–3200 cm^{-1} arises from the strong intra- and intermolecular hydrogen-bonding network of the free ligands.

In the spectrum of the free Ph₃SnOH the medium sharp band at 3618 cm^{-1} is attributed to $\nu(\text{Sn})\text{OH}$ vibration mode, which is absent from the spectra of the complexes, reflecting the deprotonation of this group in the complex-formation process. The four typical weak bands relating to the phenylic aromatic rings in the range 1762–1876 cm^{-1} in the spectra of the complexes clearly demonstrate the presence of the [Ph₃Sn(IV)]⁺ moiety in the complexes.

Most of the spectra exhibit well developed, sharp bands. However, the assignments are not always clear-cut because, due to complex formation, the positions of many of the

Table 5
Selected interatomic distances (Å) and angles (°) for the hydrogen bonding and C–H \cdots π interactions in complex **4**^a

D–H \cdots A	H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A (°)
N(1)–H(1) \cdots O(2) ^a	2.26	3.04	163
C(3C)–H(3C) \cdots O(1) ^b	2.60	3.40	145
C(3C)–H(3C) \cdots Cg3 ^b	3.18	3.72	119
C(5A)–H(5A) \cdots Cg1 ^c	3.28	3.60	103
C(6)–H(6) \cdots Cg2 ^a	3.39	4.17	143
C(6A)–H(6A) \cdots Cg4 ^c	3.37	4.03	130

Cg1, Cg2, Cg3 and Cg4 are the centroids of the Sn(1)/O(1)/C(2)/C(3)/O(2) (chelate), C(1A)/C(2A)/C(3A)/C(4A)/C(5A)/C(6A), C(1B)/C(2B)/C(3B)/C(4B)/C(5B)/C(6B) and C(1C)/C(2C)/C(3C)/C(4C)/C(5C)/C(6C) rings.

^a Symmetry codes: (a) $-x, -1/2 + y, 1/2 - z$; (b) $x, 3/2 - y, -1/2 + z$; (c) $-x, 2 - y, -z$.

Table 6
Assignment of characteristic FT-IR vibrations (cm^{-1}) of hydroxypyridines, hydroxypyrimidine and hydroxyoxyquinolines and their triphenyltin(IV) complexes

	νOH	νNH	$\nu\text{C}=\text{O}$	$\nu_{\text{a,s}} \text{C}=\text{C}/\text{N}=\text{C}$	$\nu\text{CO}(\text{Sn})$	$\gamma_{\text{Ph}}=\text{CH}$	$\nu_{\text{a}}\text{SnC}$	$\nu_{\text{s}}\text{SnC}$	νSnO
HL ¹	–	3150 m	1683 m, 1649 vs	1608 s, 1575 s, 1539 s, 1455 m	–	–	–	–	–
1	3436 w	–	–	1606 vs, 1542 m 1492 m, 1437 m	1155 w 1079 w	731 s 693 vs	562 w	516 w	446 m
HL ²	3424 w	–	–	1574 vs, 1540 sh, 1479 vs, 1445 sh	–	–	–	–	–
2	3432 w	–	–	1577 m, 1560 m 1479 s	1182 w 1127 w	730 m 697 s	582 m	–	454 m
HL ³	–	3205 m	1670 sh, 1633 vs	1548 s, 1507 vs, 1428 msh,	–	–	–	–	–
3	3421 w	–	–	1510 vs, 1480 m	1190 s	729 m 697 s	586 w	–	455 m
H₂L ⁴	3270 m	3240 m	1676 s, 1664 vs	1613 m, 1579 m, 1446 w, 1412 w	–	–	–	–	–
4	–	3245 w	1627 m	1550 m, 1479 w 1426 m	1155 w 1102 w	729 m 700 m	597 m	485 w	451 m 447 m
H₂L ⁵	–	–	1681 m, 1642 s	1607 vs, 1585 s, 1521 m, 1445 m	–	–	–	–	–
5	3424 w	3242 w	1650 s	1609 m, 1497 m 1428 m	1080 m 1063 m	730 m 693 m	628 w	539 m	451 m
H₂L ⁶	3380 w	3093 m	1689 vs	1610 s, 1594 vs, 1551 w, 1505 m, 1471 s, 1420 s	–	–	–	–	–
6	–	3343 w	1624 s	1593 vs, 1514 m	1106 w 1076 w	730 m 698 m	570 w	–	460 m 455 m
HL ⁷	3470 w	–	–	1580 m, 1509 vs, 1473 s, 1434 m	–	–	–	–	–
7	–	–	–	1575 m, 1496 s, 1465 s	1106 w	730 m 699 m	–	523 m	452 m 444 w

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

Table 7
Assignment of characteristic FT-IR vibrations (cm^{-1}) of pyridine-carboxylic and -dicarboxylic acids (dca) and for $[\text{Ph}_3\text{Sn}(\text{IV})]^{+}$ complexes

	νOH	$\nu\text{C}=\text{O}$	$\nu_{\text{a}}\text{COO}^{-}$	$\nu_{\text{s}}\text{COO}^{-}$	$\Delta\nu\text{COO}^{-}$	$\nu\text{C}=\text{C}/\text{N}=\text{C}$	$\nu_{\text{a}}\text{SnC}$	$\nu_{\text{s}}\text{SnC}$	$\nu\text{Sn}-\text{O}$
HL ⁸	3443 bw	1721 bw	1594 m	1444 w	150	1607 m, 1528 w 1454 m	–	–	–
8	–	–	1679 vs	1332 m	347	1600 m, 1562 w 1467 w	–	530 w	446 m
HL ⁹	3462 bw	1707 m	–	–	–	1597 m, 1494 w 1417 m	–	–	–
9	3444 bw	–	1653 vs	1350 m	303	1596 m, 1550 w	574 w	–	450 m
HL ¹⁰	–	1712 bs	1616 m	1411 s	205	1562 w, 1425 w	–	–	–
10	–	–	1646 s	1348 m	298	1556 w, 1415 w	543 w	–	455 m
H₂L ¹¹	3453 gy	1711 gy	1606 s	1423 m	183	1587 e, 1478 e	–	–	–
11	3368 bw	–	1691 vs, 1658 s	1321 s, 1409 s	370 249	1620 w, 1587 m, 1458 w	551 w	487 w	452 w
H₂L ¹²	3523 bm	1794 bm	1611 s	1406 w	205	1519 w, 1465 m	–	–	–
12	–	–	1678 vs, 1661 s	1316 vs, 1409 s	362 252	1558 w, 1510 w	–	497 w	453 m
H₂L ¹³	–	1730 vs	1596 m	1407	189	1627 w, 1538 w	–	–	–
13	3417 bw	–	1642 vs, 1627 s	1333 m, 1407 m	309 220	1606 s, 1590 s	575 w	527 m	455 m
H₂L ¹⁴	3443 w	1702 vs	–	–	–	1575 m, 1459 m	–	–	–
14	3231 bw	1692 m	1625 vs	1430 s	195	1604 k, 1584 k 1556 s, 1480 k	585 w	534 w	446 w
H₂L ¹⁵	3428 w	1712 bm	1608 m	1409 m	201	1640 m, 1453 w	–	–	–
15	–	3419 bw	1678 s, 1661 vs	1340 s, 1316 vs	328 345	1617 m, 1559 m 1450 w	618 w	–	453 m
H₂L ¹⁶	–	1721 bs	–	–	–	1661 s, 1602 m 1584 m, 1466 w	–	–	–
16	–	–	1661 vs	1374 m	287	1647 m, 1601 m 1578 m, 1445 w	576 w	–	449 m

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

bands are shifted and some new bands appear. Consequently, only the most important bands in the spectra of the ligands and their organotin(IV) complexes were assigned (Tables 6 and 7).

In the spectra of the complexes **1** and **3**, the medium and strong bands of the $-\text{NH}$ and $-\text{C}=\text{O}$ groups characteristic of the keto tautomer have disappeared, due to the deprotonation of the ligands and the binding of the phenolate oxy-

gen(s) to the metal ion. We have been assigned these frequencies for complexes **4–6** (Table 6). This would imply that the ligands exist in phenolate and ketone form and only one of the two OH groups is deprotonated and bonded to the $[\text{Ph}_3\text{Sn}(\text{IV})]^{+}$ centre, in accordance with the analytical results.

The involvement of the aromatic nitrogen {N} in the coordination can be concluded from the absorption

frequencies of the $\nu_{\text{C}=\text{N}/\text{C}=\text{C}}$ bands. For **1–3,7**, and **8–14** these bands are shifted considerably towards lower frequencies with respect to the positions for the free ligands, confirming the coordination of the heterocyclic {N} to the triphenyltin(IV) moiety. The stretching frequency is lowered owing to the transfer of electron density from {N} to the {Sn} atom.

Triorganotin(IV) carboxylates may adopt in principle three idealised structures (Scheme 3). A T_h (A), in which the $-\text{COO}^-$ group is monodentately coordinated. In (B), distorted Tbp with facial organic groups and chelating carboxylate group, or a *trans* Tbp structure in which planar $\text{R}_3\text{Sn(IV)}$ units are linked by bidentate (C1) or anisobidentate (C2) carboxylate bridges. Additionally, there are more possibilities in the case of pyridine mono- and dicarboxylic acids, differing on the ring position of the carboxylic group (D and E).

For analysis of the IR spectra of the $[\text{Ph}_3\text{Sn(IV)}]^+$ –pyridine-carboxylate complexes, there are good approximations with which to investigate the absorption bands of the $-\text{COO}^-$ groups.

The FT-IR spectra of the $[\text{Ph}_3\text{Sn(IV)}]^+$ –pyridine-carboxylate complexes (Table 7) do not contain the characteristic bands of the $-\text{C}=\text{O}$ group of the free ligands. It can be, therefore, concluded that the $[\text{Ph}_3\text{Sn(IV)}]^+$ moieties are bound through every carboxylic group of the ligands, except **14**, where the presence of the $\nu_{\text{C}=\text{O}}$ band indicate free CO(OH) group in the complex.

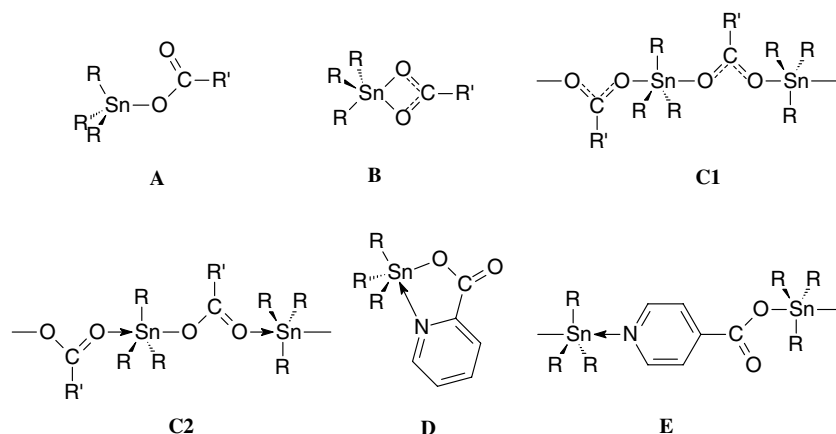
Deacon shows that the magnitude of the $\Delta\nu$ [$\Delta\nu = \nu_{\text{a}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$] can be correlated with the coordination modes of this anion [17]. The $\Delta\nu$ values (Table 7) of the studied complexes (**8–16**) were compared with that of the sodium salts of HL^8 – H_2L^{16} ligands [3]. For complexes **8–10** these $\Delta\nu$ values reflect the monodentate coordination mode of the $-\text{COO}^-$ group, while for complexes of dicarboxylic acids being indicative of bridging anisobidentate and monodentate coordination mode, depending on the location of the two $-\text{COO}^-$ groups relative to the ring {N} atom. In complexes **11–14** it is impor-

tant that there is a $-\text{COO}^-$ in the *ortho* position, which is monodentate and allows the formation of a stable five-membered chelate ring with the aromatic {N} atom. The $\Delta\nu$ values (220 – 252 cm^{-1}) of the second $-\text{COO}^-$ group in **11–13** (Table 7) indicate the bridging anisobidentate coordination mode, which allows the formation of linear polymeric compounds. Compound **14** may be also long chain-like polymer, such as above-mentioned complexes. In this case the oligomerization is occurred through bridging bidentate $-\text{COO}^-$ oxygen atoms. Although, the magnitude of the $\Delta\nu$ predict monodentate coordination mode in **15** and **16**, the solubility and the structural elucidation based on Mössbauer spectroscopic results showed polymer structure of the complexes.

The asymmetrical and the symmetrical stretching vibrations of the Sn–C bonds can be used to assign the geometries of the triorganotin(IV) derivatives [18,19]. In the IR spectra of **2, 3, 6, 9, 10, 15** and **16** only the $\nu_{\text{as}}\text{Sn–C}$ band can be observed (Tables 6 and 7), indicating trigonal-planar SnC_3 structures (local D_{3h} symmetry). In the case of the other complexes, the occurrence of the $\nu_{\text{s}}\text{Sn–C}$ band showed a significant deviation from planarity (local C_{3v} symmetry).

3.3. Mössbauer spectroscopic results

While the FT-IR data provide valuable information on the compositions of the adducts, they give no indication as to their structures. To address this latter question, we recorded ^{119}Sn Mössbauer spectra. An unsymmetric doublet with the line width greater than 1.0 mm s^{-1} was observed in the spectra of compounds **11–13**, suggesting the presence of Sn in two different coordination environments. These doublets were deconvoluted into two doublets. The experimental δ and $|\Delta|$ parameters determined by computer evaluation are presented in Table 8. All spectra of the complexes studied display typical $|\Delta|$ values of central organotin(IV), as well as the characteristic δ of $\text{R}_3\text{Sn(IV)}$ compounds, except **8** (0.88 mm s^{-1}) typical for $\text{R}_2\text{Sn(IV)}$ moiety.



Scheme 3. Structures of the triorganotin(IV) carboxylates.

Table 8
Experimental and calculated Mössbauer spectroscopic parameters of complexes studied

	δ_1	$ A_{\text{exp}1} $	$ A_{\text{cal}1} $	Γ_1	δ_2	$ A_{\text{exp}2} $	$ A_{\text{cal}2} $	Γ_2	$I_1:I_2$	Geom.1	Geom.2
1	1.22	2.93	2.86	1.00	–	–	–	–	–	Tbp1	–
2	1.20	2.89	2.86	0.98	–	–	–	–	–	Tbp1	–
3	1.21	2.94	2.86	0.95	–	–	–	–	–	Tbp1	–
4	1.09	1.99	1.97	0.92	–	–	–	–	–	Tbp2	–
5	1.30	3.30	3.20	1.02	–	–	–	–	–	O _h 1	–
6	1.16	2.82	2.76	0.88	–	–	–	–	–	Tbp3	–
7	1.03	1.68	1.55	0.86	–	–	–	–	–	Tbp4	–
8	0.88	1.92	1.96	0.90	–	–	–	–	–	O _h 2	–
9	1.23	2.89	3.02	0.94	–	–	–	–	–	Tbp5	–
10	1.26	3.00	3.02	1.05	–	–	–	–	–	Tbp5	–
11	1.16	2.82	3.06	0.87	0.98	1.71	1.80	1.00	1:1	Tbp6	Tbp7
12	1.25	3.15	3.06	0.80	1.02	2.04	1.80	0.80	1:1	Tbp6	Tbp7
13	1.27	3.66	3.06 ^a	1.09	1.07	2.71	2.70	1.10	1:1	Tbp6	Tbp7
14	1.24	3.54	3.60	1.16	–	–	–	–	–	O _h 3	–
15	1.24	2.81	3.06	1.02	–	–	–	–	–	Tbp6	–
16	1.28	3.04	3.06	0.99	–	–	–	–	–	Tbp6	–

δ , $|A|$ and Γ are given in mm s^{-1} ; Tbp, trigonal-bipyramidal; O_h, octahedral.

^a A distortion of 5–10° results in the measured $|A|$ value being 0.2–0.6 mm s^{-1} greater than that calculated for ideal geometry.

On the basis of experimental quadrupole splitting $|A|_{\text{exp}}$ values, the structure of triphenyltin(IV) complexes of HL^{1-3} and H_2L^6 in 1:1 metal to ligand molar ratio are very similar. The calculated Δ values agree very well with the measured ones (Table 8). These complexes have a distorted Tbp structure, where the phenyl groups are in *eq* positions (Fig. 2). The apical sites are occupied by a {O} of a deprotonated hydroxy group and the pyridine {N} and quinolone {O} in monohydroxypyridinato complexes and in the 4-quinolato-2(1*H*)-quinolone-*O,O'* complex, respectively. The O–Sn–X (X = N or O) bond angle is smaller than 180°.

Our evaluation of the Mössbauer spectroscopic measurements by means of the pqs concept, demonstrates that the coordination geometry of **4** and **7** may be also similar. On the base of the magnitude of experimental δ and $|A|$ values (δ : 1.09, 1.03; $|A|$: 1.99, 1.68, Table 8), we can rule out the planar triphenyltin(IV) configuration. The results of pqs calculations also reveal the formation of distorted *cis* Tbp structures, with two phenyl groups in *eq* and one in *ax* position with C–Sn–C bond angles less than 120°. The remaining *eq* site is occupied by the deprotonated OH group of ligands. In second *ax* position in the case of 2,3-dihydroxypyridine there is a pyridone {O} atom due to the tautomerization (Fig. 1). The protonated {N} atom is not coordinated. This is in accordance with the results of the X-ray structural characterisation. In 8-hydroxyquinoline (oxine) complex the {N} atom is located in the *ax* position and five membered chelate ring is formed (Fig. 3), in correspondence with the published structures of the investigated triorganotin(IV) complexes of oxin derivatives [20–23].

The Mössbauer spectrum of $\text{Ph}_3\text{Sn(IV)-4,6}$ -dihydroxypyrimidine complex is a symmetric doublet. According to the FT-IR measurements both tautomeric forms of the ligand are co-ordinated and polymeric compound is formed. The {N} atom does not co-ordinated (Fig. 3).

The δ_1 and $|A_{\text{exp}1}|$ values for the pyridine carboxylic acid complexes fall in the range 1.16–1.28 and 2.81–3.66 mm s^{-1} , except 2-picolinic acid with unexpected low values (0.88 and 1.92 mm s^{-1}). We were obtained **8** as single crystals. The preliminary X-ray diffraction investigation showed that in this case there is a $[\text{Ph}_2\text{Sn(IV)}]^{2+}$ complex formed. The molecular structure of the **8** is already known [6]. The isomer shift of $\text{Ph}_2\text{Sn(L}^8)_2$ is in the range typical of diorganotin(IV) derivatives [10]; $|A_{\text{exp}1}|$ is consistent with that of hexa-coordinated diorganotin(IV) complexes in highly distorted *cis*-O_h geometry with the two bulky phenyl groups in *ax* and *eq* positions [5] (Fig. 2). The $-\text{COO}^-$

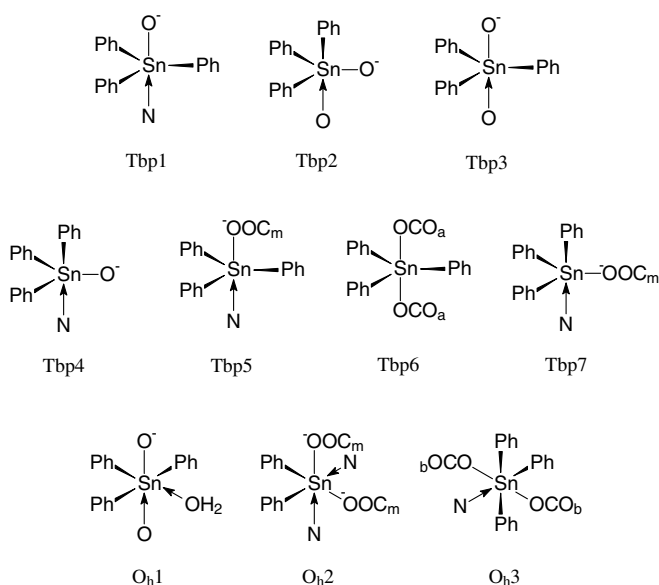


Fig. 2. Calculated quadrupole splitting values for the tin(IV) coordination spheres in different stereochemical arrangements. m, monodentate coordination mode; b, bidentate coordination mode; a, anisobidentate coordination mode.

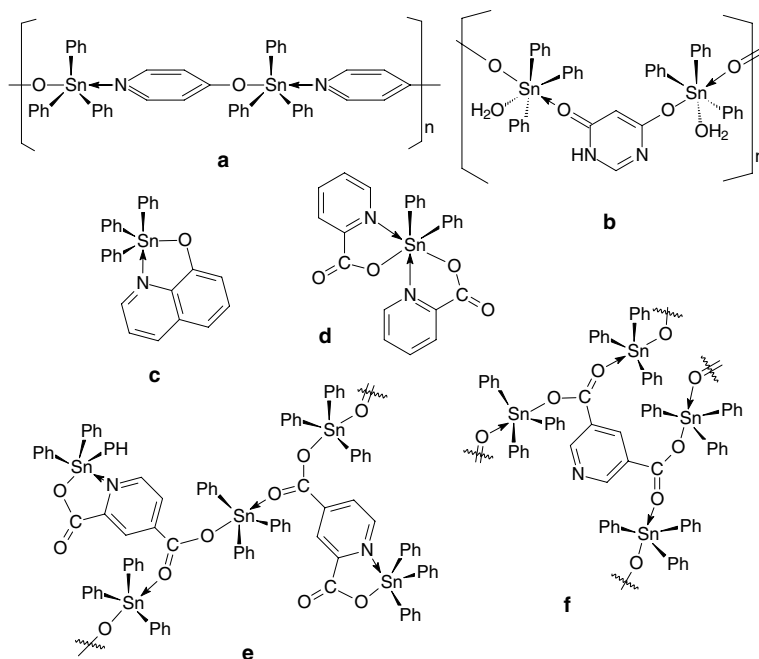
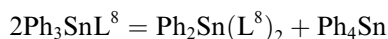
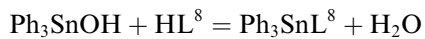


Fig. 3. Proposed structures for some selected complexes; a, b, e and f – repeating units of **3**, **5**, **12** and **16**, respectively, c and d – monomeric complexes of **7** and **8**.

groups of the two picolinate anions are unidentate, and therefore form with the hetero cyclic {N} atom five membered O–C–Sn–C–N chelate ring. Our results further confirm the published structure.

It is known, that in sea water the biologically active sediments convert trimethyltin(IV) hydroxyde to dimethyltin compound and to the volatile tetramethyltin(IV) [24]. The methyl group removal has been attributed to the action of UV light, chemical cleavage and biological degradation by bacteria, although its chemistry has never been elucidated. In our case a similar, phenyl migrational dismutation has been detected in methanolic solution of Ph_3SnOH –2-picolinic acid system according to the results of X-ray and Mössbauer spectroscopic measurements. For this reaction we propose the following mechanism:



This reaction is interesting because, to our knowledge, it is the first report of a Lewis base-induced redistribution of a triphenyltin(IV) compound.

In the $[\text{Ph}_3\text{Sn}(\text{IV})]^+$ complexes of nicotinic and isonicotinic acids, a five-membered chelate ring formation as shown above, is not possible. The structural elucidation based on pqs concept has shown, that linear oligomerization is occurred through the monodentate $-\text{COO}^-$ group and through the {N} atom from two different ligands. In complexes, the Sn centres are in distorted *trans* Tbp coordination geometry with phenyl groups in the equatorial positions (Fig. 2).

For the pyridine-dicarboxylic acid complexes, it is obvious that the two $-\text{COO}^-$ groups are in different surround-

ings. For $\text{H}_2\text{L}^{11-14}$, it is important to note that there is a $-\text{COO}^-$ group in the *ortho* position (relative to the ring {N} atom), which allows the formation of a stable five-membered chelate ring. The Mössbauer spectra of the $[\text{Ph}_3\text{Sn}(\text{IV})]^+$ complexes of $\text{H}_2\text{L}^{11-13}$ display two unsymmetrical doublets, indicating the presence of two different Sn(IV) environments within the complexes. Deconvolution of the spectra for the three cases resulted in one of the doublet with δ_1 and $|\Delta_{\text{exp}}|_1$ values (Table 8) characteristic of a *trans* Tbp and a second doublet with δ_2 and $|\Delta_{\text{exp}}|_2$ values (Table 8) characteristic of a *cis* Tbp Sn(IV) environment (Fig. 2). In the *trans* Tbp species the phenyl groups are located in *eq* positions and linear polymerisation is occurred through the bridging anisobidentate $-\text{COO}^-$ groups in *ax* positions. The pqs calculations lead to the finding, that the latter Sn(IV) moiety, with *cis* Tbp symmetry, involves two phenyl groups in *eq* and one in *ax* positions. The monodentately bounded carboxylate oxygen and the pyridine nitrogen formed five-membered chelate ring with the {Sn} centre (Fig. 3) The FT-IR measurements revealed the two type carboxylate coordination mode in these complexes, which is consistent with the conclusion from Mössbauer data.

$\text{Ph}_3\text{Sn}(\text{IV})$ -2,6-pyridine-dicarboxylato complex represents a more interesting case. The Mössbauer spectrum exhibits only one symmetric, unbroadened doublet, indicating only one type of environment around tin(IV) in the complex, with $|\Delta_{\text{exp}}|$ value of 3.54 mm s^{-1} . When the calculated quadrupole splitting values, based on different suggested stereochemistries of the tin(IV) surrounding were compared with the experimental one we got a good agreement with that suggesting an O_h symmetry of $\text{Ph}_3\text{Sn}(\text{IV})$ -2,6-pyridine-dicarboxylate involving *ax* and one *eq* phenyl

groups, with two bidentate carboxylate oxygens and pyridine nitrogen in the remaining *eq* positions (Fig. 2). Six-coordination is indicated also by IR spectra. The $\nu\text{C}=\text{O}$ absorption at 1692 cm^{-1} indicate that one of the two carboxylate groups remained free and involved in hydrogen bonding system, while the $\Delta\nu\text{COO}^-$ value (195 cm^{-1}) reveal bidentate mode for the second one.

The Mössbauer spectra of the $[\text{Ph}_3\text{Sn(IV)}]^+$ complexes formed with pyridine-3,4- and -3,5-dicarboxylic acids exhibit only one symmetrical doublet. The identical Mössbauer parameters of these two compounds suggest that the symmetry of the coordination sphere of the Sn(IV) is very similar. It can be seen that the experimental $|\Delta_{\text{exp}}|$ values of these compounds are close to that calculated for the ideal *trans* Tbp geometry (Figs. 2 and 3). Moreover, both the m.p. data and the low solubility of **15** and **16** suggest a long-chain polymeric structure of these compounds. There has been some disagreement concerning the magnitude of the $\Delta\nu$ values and the suggested structure. This can be elucidate by assumption, that the bounding of the $-\text{COO}^-$ groups is alternate between mono- and bidentate mode. Therefore, the oligomerization between tin(IV) centres is interpreted through anisobidentate $-\text{COO}^-$ groups of ligands.

4. Conclusions

The synthetic procedures used in this work resulted in the formation of $[\text{Ph}_3\text{Sn(IV)}]^+$ compounds with a 1:1 metal-to-ligand ratio for ligands containing a hetero {N} atom and a hydroxy group, for nicotinic, isonicotinic and dipicolinic acid, while for the pyridine dicarboxylic acid complexes 2:1. The X-ray diffraction analysis of complex **4** shows a distorted *cis* Tbp coordination sphere around the Sn(IV) center. In methanolic Ph_3SnOH 2-picolinic acid system, we have observed a phenyl migrational dismutation reaction, which resulted $\text{Ph}_2\text{Sn(pica)}_2$ and Ph_4Sn . The analytical, FT-IR and Mössbauer spectroscopic data of these complexes revealed the formation of well-defined compounds. The Mössbauer spectroscopic data for complexes **1–3**, **6**, **9–13**, **15** and **16** are indicative of trigonal-planar SnC_3 (i.e. *trans* Tbp) structures with the phenyl groups in *eq* positions. The Mössbauer spectra of the $[\text{Ph}_3\text{Sn(IV)}]^+$ complexes of $\text{H}_2\text{L}^{11-13}$ display two unsymmetrical doublets, indicating the presence two different (*trans* and *cis* Tbp) Sn(IV) environments in the complexes. In polymeric complexes the linear oligomerisation is occurred through the bridging anisobidentate $-\text{COO}^-$ groups in *ax* positions.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited

with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 286848. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk].

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