

Preparation and structural studies on dibutyltin(IV) complexes with pyridine mono- and dicarboxylic acids

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Abstract

A number of organotin(IV) complexes with pyridine mono- and dicarboxylic acids (containing ligating –COOH group(s) and aromatic {N} atoms) were prepared in the solid state. The bonding sites of the ligands were determined by means of FT-IR spectroscopic measurements. It was found that in most cases the –COO[–] groups form bridges between two central {Sn} atoms, thereby leading to polymeric (oligomeric) complexes. On this basis, the experimental ¹¹⁹Sn Mössbauer spectroscopic data were treated with partial quadrupole splitting approximations. The calculations predicted the existence of complexes with octahedral (oh) and trigonal-bipyramidal (tbp) structures, but the formation of complexes with pentagonal-bipyramidal (pbp) structures could not be ruled out. Single-crystals of 2-picolinic and pyridine-2,6-dicarboxylic acid Bu₂Sn(IV)²⁺ complexes were obtained. The X-ray diffraction studies revealed that the central {Sn} atoms are in a pbp environment with bond distances characteristic of organotin(IV) compounds. The two butyl groups are located in *axial* positions. ¹¹⁹Sn NMR measurements in dmsO solution and in the solid state indicated that the polymeric structures of the complexes are not retained in solution. The results of the solid-state ¹¹⁹Sn NMR measurements for compounds **1a**, **2a** and **6a** are in agreement with the structures predicted by Mössbauer spectroscopy and revealed by X-ray diffraction.

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1. Introduction

Organotin(IV) complexes have been demonstrated to exhibit relatively high antitumour activity, as emphasized in recent surveys [1,2]. To date, several papers have dealt with the structures of organotin(IV) carboxylates containing a {N} donor atom in an aromatic ring.

Pyridine-2,6-dicarboxylic acid (or dipicolinic acid) forms stable chelates with simple metal ions and oxo-metal cations and can display widely varying coordination behaviour, functioning as a multidentate ligand.

Like picolinic acid, dipicolinic acid can stabilize unusual oxidation states. The other isomeric pyridine-dicarboxylic acids, e.g. pyridine-2,3-, 2,4- and 2,5-dicarboxylic acids, behave like picolinic acid and act as bidentate (chelating) N,O donors.

A very important characteristic of these ligands is their diverse biological activity. Pyridine-2,3-dicarboxylic acid is an intermediate in the tryptophan degradation pathway and is a precursor for NAD [3].

The reaction of Me₂Sn(IV)²⁺ with pyridoxine [3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine, PN, vitamin B₆] yields three complexes, one with the composition [SnMe₂(PN-H)]NO₃ · 2H₂O. This complex is polymeric. Each monoprotonated pyridoxine

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coordinates to one {Sn} atom via the phenolic {O} and a deprotonated CH₂OH group {O} and to the other via the latter group alone. In each dimeric unit, the {Sn} atom is coordinated to two methyl groups, the phenolic {O} atom, the {O} atoms of two deprotonated –CH₂OH groups, and the {O} atom of the non-deprotonated –CH₂OH group [4]. Further work has been published on the interaction of the same ligand and Et₂Sn(IV)²⁺ in an 80:20 (v/v) ethanol:water mixture containing different anions in various molar ratios [5]. Three complexes are also formed in this system. The structure of one of the compounds was determined by X-ray diffraction and was found to involve dimeric [SnEt(PN–H)]₂²⁺ units (in which two bridging-chelating hydrogen pyridoxinate anions link pentacoordinated Sn(IV) atoms and hydrogen-bonded Cl[–]). This is similar to the system discussed above. Other work on similar systems was published in [6,7].

On the basis of its ¹¹⁹Sn CP/MAS NMR chemical shift ($\delta = -424.9$ ppm), the {Sn} in bis(dicyclohexylammonium) bis(2,6-pyridinedicarboxylato)dibutylstannate is considered to be heptacoordinated. The assignment has been corroborated by crystal structure determination of its monohydrate, in which the {Sn} atom has pentagonal-bipyramidal (pbp) *trans*-C₂SnNO₄ geometry [Sn–C = 204.0, 206.7 pm, C–Sn–C = 168.9°]. One carboxylato group chelates to the {Sn} atom (Sn–O = 223.4, 226.0 pm; Sn–N = 227.9 pm), whereas the other binds through only one carboxyl end (Sn–O = 241.6, 244.1 pm). The anhydrous compound displays higher in vitro antitumour activity than that of cisplatin or carboplatin [8].

The diorganotin(IV) pyridine-2,6-dicarboxylates exhibit in vitro antitumour activities [9]. Atassi assumed that water-soluble organotin(IV) compounds are probably more active than complexes soluble only in organic solvents [10]. Therefore, Gielen et al. [8,11] prepared tetraethylammonium diorganohalogenopyridine-2,6-dicarboxylatostannates (halogeno = Cl, F) whose water solubilities under physiological conditions are higher than those of the parent compounds. The desired compounds were obtained via a similar procedure as in the case of the analogous tetraethylammonium diorganohalogenothiosalicylatostannates [12]. The Mössbauer parameters ($|A| = 3.50\text{--}4.23$ mm s^{–1}) suggested that the heptacoordination around the {Sn} atom in the parent compounds [13,14] is maintained in the salts.

2. Experimental

2.1. Materials

The Bu₂SnO and the ligands (2-picolinic acid **1**, nicotinic acid **2**, iso-nicotinic acid **3**, pyridine-2,4-dicarboxylic acid (or lutidinic acid) **4**, pyridine-2,5-dicarboxylic acid **5**, pyridine-2,6-dicarboxylic acid **6**,

pyridine-3,4-dicarboxylic acid (or cincomeronic acid) **7**, pyridine-3,5-dicarboxylic acid **8**, and pyridine-2,3-dicarboxylic acid (or quinolinic acid) **9** were Fluka products. They were not purified before use.

The complexes were obtained as previously described [15]. Compounds **1a–9a** were prepared by method **a**, refluxing appropriate quantities of **1–9** and Bu₂SnO in methanol for 3 h. Compounds **1a**, **2a**, **3a** and **6a** were crystallized out after slow evaporation of the solvent at room temperature, then washed with methanol. Compounds **4a**, **5a**, **8a** and **9a** precipitated immediately from the mixture, while compound **7a** was obtained after removal of the solvent by rotary evaporation, then recrystallized from methanol. Compound **9b** was obtained by method **b**, where Bu₂SnO was refluxed in methanol–*n*-propanol (4:1, 250 cm^{–3}) for 5 h. The oxide reacted with *n*-propanol, giving di-*n*-butyltin(IV) propoxide and water. From the solvent mixture the water distils off as an azeotrope. After its removal and cooling, an equimolar quantity of **9**, dissolved in methanol, was added to the solution of di-*n*-butyltin(IV) propoxide with vigorous stirring. Compound **9b** precipitated during the stirring. The compounds **9a** and **9b**, obtained by the two different preparation modes had the same composition and structure.

The complexes appeared to be stable in the solid state.

(**1a**) [Bu₂Sn(picolate)₂]_{*n*}: Anal. Calc. for C₂₀H₂₆N₂O₄Sn: C, 50.31; H, 5.49; N, 5.87; Sn, 24.88. Found: C, 50.12; H, 5.22; N, 6.21; Sn, 24.94%. (**2a**) [Bu₂Sn(nicotinate)₂]_{*n*}: Anal. Calc. for C₂₀H₂₆N₂O₄Sn: C, 50.31; H, 5.49; N, 5.87; Sn, 24.88. Found: C, 50.05; H, 5.14; N, 6.32; Sn, 24.57%. (**3a**) [Bu₂Sn(iso-nicotinate)₂]_{*n*}: Anal. Calc. for C₂₀H₂₆N₂O₄Sn: C, 50.31; H, 5.49; N, 5.87; Sn, 24.88. Found: C, 50.16; H, 5.08; N, 6.50; Sn, 25.06%. (**4a**) [Bu₂Sn(pyridine-2,4-dicarboxylic acid)(H₂O)]_{*n*}: Anal. Calc. for C₁₅H₂₃NO₅Sn: C, 43.31; H, 5.57; N, 3.37; Sn, 28.53. Found: C, 43.07; H, 5.34; N, 4.16; Sn, 28.67%. (**5a**) [Bu₂Sn(pyridine-2,5-dicarboxylic acid)(H₂O)]_{*n*}: Anal. Calc. for C₁₅H₂₃NO₅Sn: C, 43.31; H, 5.57; N, 3.37; Sn, 28.53. Found: C, 43.23; H, 5.19; N, 4.02; Sn, 28.87%. (**6a**) [Bu₂Sn(pyridine-2,6-dicarboxylic acid)(H₂O)]₂: Anal. Calc. for C₁₅H₂₃NO₅Sn: C, 43.31; H, 5.57; N, 3.37; Sn, 28.53. Found: C, 43.28; H, 5.49; N, 3.68; Sn, 28.59%. (**7a**) [Bu₂Sn(pyridine-3,4-dicarboxylic acid)(H₂O)]_{*n*}: Anal. Calc. for C₁₅H₂₃NO₅Sn: C, 43.31; H, 5.57; N, 3.37; Sn, 28.53. Found: C, 42.87; H, 5.10; N, 4.09; Sn, 28.14%. (**8a**) [Bu₂Sn(pyridine-3,5-dicarboxylic acid)(H₂O)]_{*n*}: Anal. Calc. for C₁₅H₂₃NO₅Sn: C, 43.31; H, 5.57; N, 3.37; Sn, 28.53. Found: C, 43.02; H, 5.17; N, 4.15; Sn, 28.92%. (**9a**) [Bu₂Sn(pyridine-2,3-dicarboxylic acid)(H₂O)]_{*n*}: Anal. Calc. for C₁₅H₂₃NO₅Sn: C, 43.31; H, 5.57; N, 3.37; Sn, 28.53. Found: C, 43.17; H, 5.31; N, 4.03; Sn, 28.76%. (**9b**) [Bu₂Sn(pyridine-2,3-dicarboxylic acid)(H₂O)]_{*n*}: Anal. Calc. for C₁₅H₂₃NO₅Sn: C, 43.31; H, 5.57; N, 3.37; Sn, 28.53. Found: C, 43.19; H, 5.28; N, 4.07; Sn, 28.81%.

Microanalyses were performed at the Department of Organic Chemistry, University of Szeged. The Sn contents were measured by inductively coupled plasma atomic emission spectrometry [16] and found to correspond to the theoretically calculated values.

2.2. Structure determination

Diffraction data were collected at 294 K with a Bruker-AXS SMART 2K CCD area detector diffractometer equipped with an Oxford Cryostream N₂ cooling device. Crystal parameters and refinement results are presented in Table 1. Empirical absorption corrections were carried out with the program SADABS [17]. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 . All non-hydrogen atoms were anisotropically refined. Hydrogen atoms bound to carbon were included at idealized positions in the models, while those bound to oxygen (water) were located in Fourier difference maps. All hydrogen atoms were refined according to the riding model. Refinement converged at a conventional R value of 0.0447 for **1a**.

Data collection and data reduction were performed with the programs SMART and SAINT [18]. All other calculations were performed with the programs SHELXS 86, SHELXL 93 and XP [19]. CCDC No. is 213526.

2.3. FT-IR and Raman spectroscopic measurements

The FT-IR spectra of the ligands and the complexes in KBr pellets were measured on BioRad Digilab Division FTS-40 and FTS-65A instruments in the range 4400–200 cm⁻¹. The FT Raman spectra were recorded

with a BioRad Digilab Division FT Raman spectrometer. The samples were in glass cells.

2.4. Mössbauer spectroscopic measurements

Mössbauer spectroscopic measurements were performed as described in [20]. Comparison of the experimental $|Δ|$ values with those calculated on the basis of the point-charge model [21] permits determination of the steric arrangements of the complexes formed, for tetrahedral (teth), trigonal-bipyramidal (tbp) and octahedral (oh) geometries. For calculations, we used the pqs values of different functional groups [22–24] as follows: $\{R\}^{\text{teth}} = -1.37$, $\{R\}^{\text{tbpa}} = -0.94$, $\{R\}^{\text{tbpe}} = -1.13$, $\{R\}^{\text{oh}} = -1.03$, $\{-\text{COO}^-\}^{\text{teth}} = -0.15_{(\text{monodentate})}$, $\{-\text{COO}^-\}^{\text{tbpa}} = 0.075_{(\text{bidentate})}$, $\{-\text{COO}^-\}^{\text{tbpe}} = 0.293_{(\text{bidentate})}$, $\{-\text{COO}^-\}^{\text{tbpa}} = -0.10_{(\text{monodentate})}$, $\{-\text{COO}^-\}^{\text{tbe}} = 0.06_{(\text{monodentate})}$, $\{-\text{COO}^-\}^{\text{oh}} = -0.11_{(\text{monodentate})}$, $\{-\text{COO}^-\}^{\text{oh}} = 0.083_{(\text{bidentate})}$, $\{N_{\text{pyridine}}\}^{\text{teth}} = -0.138$, $\{N_{\text{pyridine}}\}^{\text{tbpa}} = -0.035$, $\{N_{\text{pyridine}}\}^{\text{tbpe}} = 0.147$, $\{N_{\text{pyridine}}\}^{\text{oh}} = -0.10$, $\{H_2O\}^{\text{oh}} = 0.20$, $\{H_2O\}^{\text{tbpa}} = 0.18$, and $\{H_2O\}^{\text{tbpe}} = 0.43$ mm s⁻¹, where tbpa = trigonal-bipyramidal axial and tbe = trigonal-bipyramidal equatorial position.

2.5. ¹¹⁹Sn, ¹³C and ¹H NMR measurements

NMR spectra were recorded on a Varian UNITY 300 spectrometer. For liquid-phase measurements (in dmsod₆): ¹¹⁹Sn, 111.81 MHz ¹³C, 75.42 MHz and ¹H 300 MHz, Varian 5 mm BB probe. For solid-state measurements: ¹¹⁹Sn, 111.81 MHz Doty XC5 probe, sample quantities 80–110 mg, rotation speed 5000–10,000 Hz, MAS experiments. Reference external K₂Sn(OH)₆ = -570 ppm relative to Me₄Sn.

Table 1
Crystal data and structure refinement for [Bu₂Sn(picolate)₂]_n (**1a**)

	1a
Empirical formula	C ₂₀ H ₂₆ N ₂ O ₄ Sn
Formula weight	477.12
Temperature (K)	294(2)
λ (Å)	0.71073
Space group	P ₁ /n
a (Å)	12.5862(12)
b (Å)	9.0517(8)
c (Å)	18.111(2)
β (°)	94.502(1)
V (Å ³)	2056.9(3)
Z	4
ρ (Mg m ⁻³)	1.541
μ (mm ⁻¹)	1.269
Max 2θ (°)	51.5
Reflections collected/unique	22803
Independent reflections	3794 [R _{int} = 0.1303]
Reflections with I > 2σ(I)	2275
Data/restraints/parameters	3402/0/244
Goodness-of-fit, S, on F ²	0.891
R[I > 2σ(I)]	0.0447
R _w [I > 2σ(I)]	0.0895

3. Results and discussion

The analytical data on the complexes revealed the formation of compounds with a 1:2 metal-to-ligand ratio for the pyridine-monocarboxylic acids, and with a 1:1 ratio for the pyridine-dicarboxylic acids. None of the compounds were soluble in water. It is a general phenomenon that oligomeric or polymeric organotin(IV) complexes can undergo depolymerization in donor solvents. The coordination number of the central {Sn} atom is changed due to solvation. A comparison of the solid-state structure with that in solution therefore runs into difficulty [1].

3.1. X-ray crystallography

[Bu₂Sn(picolate)₂]_n (**1a**). The building block (the asymmetric unit) of this polynuclear compound is shown in Fig. 1a. These units are connected into chains

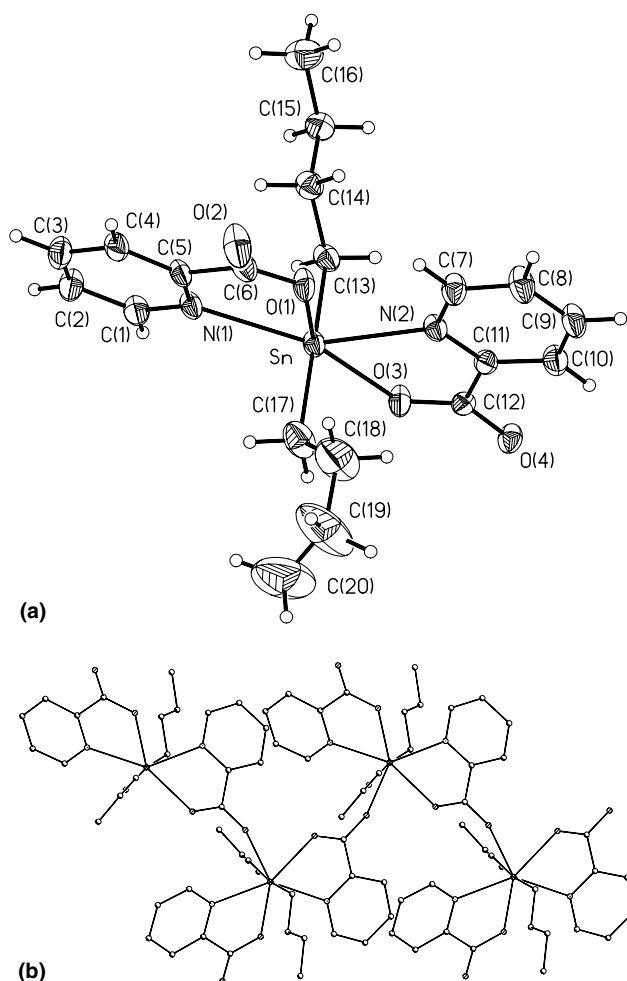


Fig. 1. (a) The asymmetric unit in $[\text{Bu}_2\text{Sn}(\text{picolate})_2]_n$ (**1a**) showing the atomic numbering scheme. Thermal ellipsoids are plotted at the 30% probability level. Symmetry code $a: -x + 1/2, y - 1/2, -z + 1/2$. (b) Chain structure of $[\text{Bu}_2\text{Sn}(\text{picolate})_2]_n$ (**1a**), four repeating units being shown.

(Fig. 1b), one of the picolate moieties serving as bridge between Sn atoms by chelating to one Sn through one carboxylate oxygen [O(3)] and the heterocyclic nitrogen atom [N(2)], and binding monodentately through the other carboxylate oxygen [O(4)] to the neighbour Sn. There are hence two crystallographically distinct picolate moieties in the structure, the bridging one mentioned above, and the second one being terminal and chelating to the Sn through one carboxylate oxygen [O(1)] and a nitrogen [N(1)]. The chain extends along the crystallographic twofold screw axis, displaying a zig-zag feature. The *intra* chain Sn...Sn distance across the picolate bridge is 6.286(1) Å and the Sn...Sn...Sn angle 92.11(1)°.

Sn is heptacoordinated in a distorted pentagonal bipyramidal geometry (pbp), where the butyl carbon atoms are found in the *ax* positions [Sn–C = 2.107(7) and 2.113(6) Å] and picolate oxygen and nitrogen atoms form the *eq* plane [Sn–O = 2.188(4), 2.376(4) and

2.392(4) Å, Sn–N = 2.473(4) and 2.481(4) Å] (Fig. 1b and Table 2). It may be noted that the shorter one of the Sn–O bonds involves the terminal (non-bridging) carboxylate group. The atoms defining the equatorial plane are close to coplanar (maximum atomic deviation 0.123 Å), and the range of O(N)–Sn–O(N) bond angles within the plane is 69.5–77.2°, reflecting the essentially pbp coordination geometry of Sn.

Compound **1a** has a chain structure analogous to that of $[\text{Me}_2\text{Sn}(\text{picolate})_2]_n$ [25]. The features of the Sn coordination spheres in the two structures are in generally good agreement, with close to pbp geometry, and with the Sn–O bond of the non-bridging carboxylate being much shorter than those involving the bridging group. It is notable that the C–Sn–C angle is slightly larger in the $\text{Me}_2\text{Sn}(\text{IV})$ compound [174.5(3)°] than in the $\text{Bu}_2\text{Sn}(\text{IV})$ compound **1a** [169.9(2)°]. The structural type observed in these two compounds, arises as a result of the participation of the heterocyclic {N} atoms in the bonding to the {Sn} atoms.

The X-ray structure of $[\text{Bu}_2\text{Sn}(\text{pyridine-2,6-dicarboxylato})(\text{H}_2\text{O})_2]_n$ (**6a**) has earlier been reported by Huber et al. [26]. We have studied this compound for a second

Table 2
Selected bond lengths [Å] and angles [°] for $[\text{Bu}_2\text{Sn}(\text{picolate})_2]_n$ (**1a**) {Sn} coordination sphere

Bond lengths	
Sn–C(17)	2.107(7)
Sn–C(13)	2.113(6)
Sn–O(1)	2.188(4)
Sn–O(3)	2.376(4)
Sn–O(4a)	2.392(4)
Sn–N(1)	2.473(4)
Sn–N(2)	2.481(4)
Bond angles	
C(17)–Sn–C(13)	169.9(2)
C(17)–Sn–O(1)	91.2(2)
C(13)–Sn–O(1)	98.7(2)
C(17)–Sn–O(3)	87.9(2)
C(13)–Sn–O(3)	85.7(2)
O(1)–Sn–O(3)	140.85(14)
C(17)–Sn–O(4a)	84.9(2)
C(13)–Sn–O(4a)	85.8(2)
O(1)–Sn–O(4a)	146.18(14)
O(3)–Sn–O(4a)	72.70(13)
C(17)–Sn–N(1)	93.7(2)
C(13)–Sn–N(1)	88.0(2)
O(1)–Sn–N(1)	69.49(14)
O(3)–Sn–N(1)	149.63(14)
O(4a)–Sn–N(1)	77.23(14)
C(17)–Sn–N(2)	93.8(2)
C(13)–Sn–N(2)	90.8(2)
O(1)–Sn–N(2)	74.15(14)
O(3)–Sn–N(2)	66.87(13)
O(4a)–Sn–N(2)	139.57(14)
N(1)–Sn–N(2)	142.99(15)

Symmetry transformation used to generate equivalent atoms a: $-x + 1/2, y - 1/2, -z + 1/2$, b: $-x + 1/2, y + 1/2, -z + 1/2$.

time by X-ray diffraction, and additionally by means of FT-IR and Mössbauer spectroscopy in the solid state, and by means of multinuclear NMR spectroscopy in dmsO solution. For the benefit of clarifying the discussion of the spectroscopic results (see below) we here briefly describe the X-ray structure. The compound is dinuclear, the two Sn atoms being joined through pairs of Sn–O(carboxylate)–Sn bridges (Fig. 2), the Sn···Sn distance across this bridge being 4.420(1) Å. It is to be noted that while the carboxylate group in **1a** bridges in a bidentate fashion, a monodentate bridging mode is adopted in **6a**. The Sn–O–Sn bridge is markedly asymmetric, with Sn–O distances of 2.442 and 2.802 Å, respectively. Sn has a distorted pbp coordination geometry in **6a**, with butyl carbon atoms in the *ax* positions, as in **1a**. The known Me₂Sn(IV)-pyridine-2,6-dicarboxylate complex [27] also has a similar structure).

Apart from the particular structural features, these compounds deserve attention as they are examples of the organotin(IV) compounds containing heptacoordinated tin [28].

3.2. FT-IR spectroscopic measurements

The coordination sites of the ligands were determined by means of FT-IR spectroscopy. For comparison, the spectra of the starting materials and their Na(I) salts were also recorded.

For analysis of the IR spectra of the compounds, there are good approximations with which to investigate the absorption bands of the –COO[−] groups.

A range of different coordination modes exists in the pyridine carboxylic acid complexes, depending on whe-

ther the anionic or the protonated form of the ligands are coordinated to the metal ion (Scheme 1, coordination modes A–I) [29].

Deacon et al. [30] have studied the IR spectra of acetato and trifluoroacetato metal complexes. The following conclusions were drawn: (i) When the –COO[−] group coordinates to the metal ion in a monodentate manner, the difference between the wavenumbers of the (structure A) asymmetric and symmetric carboxylate stretching bands, $\Delta\nu = (\nu_{\text{as}}\text{COO}^- - \nu_{\text{sym}}\text{COO}^-)$, is larger than that observed for ionic compounds. (ii). When the ligand chelates (structure F), $\Delta\nu$ is considerably smaller than that observed for ionic compounds, but for asymmetric bidentate coordination the value is in the range characteristic of monodentate coordination. (iii). The characteristic $\Delta\nu$ for structures G and H is larger than that for chelated ions and nearly the same as that observed for ionic compounds.

On the above basis, it was possible to distinguish between the –COO[−] group coordination modes.

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 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 and Na(I) salts were assigned (Table 3).

The $\nu(\text{=CH})$ vibrations of the pyridines and their derivatives are found in the range 3070–3020 cm^{−1}. The skeleton vibrations of the pyridine ring appear at about 1615 cm^{−1}. On salt formation or quaternarization, they shift to higher frequencies (1625 cm^{−1}).

The 2:1 complex formed between 2-picolinic acid and Bu₂SnO has a polymeric chain structure, where the two ligand molecules coordinate to the {Sn} in different manners: one of the –COO[−] groups is in monodentate form, and the second is in bidentate form, serving as a bridge between the {Sn} atoms. For this complex, two $\nu_{\text{as}}\text{COO}^-$ values were observed, at 1670 and 1564 cm^{−1}, and two $\nu_{\text{s}}\text{COO}^-$ values, at 1384 and 1347 cm^{−1}. The

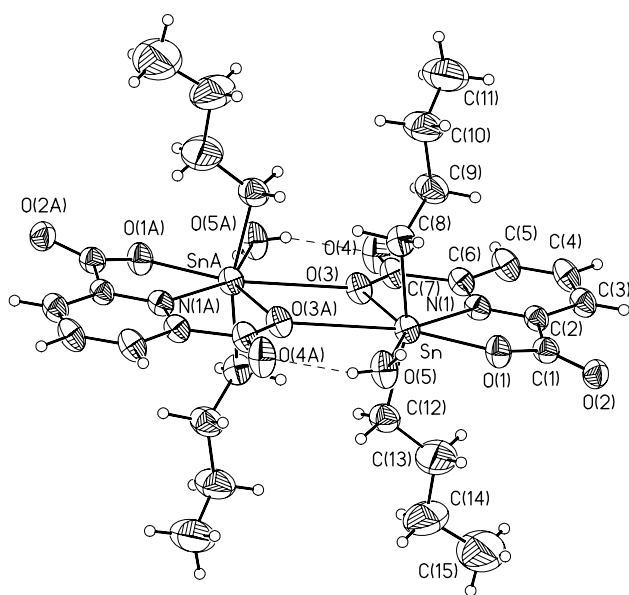
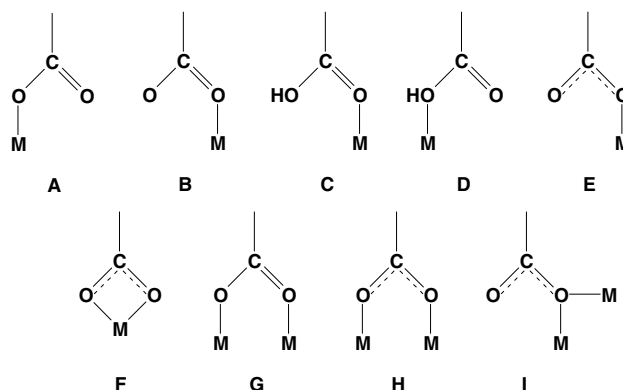


Fig. 2. The dinuclear [Bu₂Sn(pyridine-2,6-dicarboxylate)(H₂O)]₂ unit (**6a**).



Scheme 1. Possible coordination modes of the –COO[−] groups.

Table 3

Assignment of characteristic FT-IR and Raman vibrations (cm^{-1}) for $\text{Bu}_2\text{Sn(IV)}$ complexes and Na(I) salts of pyridine-carboxylic and -dicarboxylic acids (dca)

Compositions	$\nu_a \text{COO}^-$	$\nu_s \text{COO}^-$	$\Delta\nu \text{COO}^-$	$\nu_{a,s} \text{C}=\text{C}/\text{N}=\text{C}$	$\beta \text{C}=\text{N}$	$\nu \text{Sn}-\text{C}$	$\nu \text{Sn}-\text{O}$
(1a) $[\text{Bu}_2\text{Sn}(\text{picolinate})_2]_n$	1670 vs, 1564 s	1347 s, 1384 m	323 180	1628 s, 1609 w, 1550 s, 1469 w, 1442 w	635 m	542 w	455 w
Na-picolinate	1607 vs	1411 s	196	1584 vs, 1565 vs, 1474 w, 1438 m	–	–	–
(2a) $\text{Bu}_2\text{Sn}(\text{nicotinate})_2$	1610 s	1436 m	174	1630 sh, 1592 s, 1549 m, 1444 m	–	519 w	427 w
Na-nicotinate	1615 vs	1409 s	206	1603 s, 1591 m, 1557 m, 1420 sh	–	–	–
(3a) $\text{Bu}_2\text{Sn}(\text{i-nicotinate})_2$	1636 m, 1594 s	1424 sh, 1396 w	212 198	1617 m, 1549 s, 1491 w, 1404 vs	–	610 m	415 m
Na(i-nicotinate)	1588 vs	1412 s	176	1640 w, 1545 vs, 1490 sh, 1400 sh	–	–	–
(4a) $\text{Bu}_2\text{Sn}(\text{p-2,4-dca})$	1634 vs, 1625 s	1388 vs, 1361 s	246 264	1597 vs, 1547 s, 1477 w, 1400 sh	689 m	506 w	402 s
$\text{Na}_2(\text{p-2,4-dca})$	1608 vs	1388 s	220	1593 s, 1551 s, 1475 w, 1435 m	–	–	–
(5a) $\text{Bu}_2\text{Sn}(\text{p-2,5-dca})$	1617 vs	1340 s	277	1640 s, 1590 sh, 1540 sh, 1482 w, 1393 s	658 w	533 w	400 s
$\text{Na}_2(\text{p-2,5-dca})$	1602 vs	1405 s	197	1640 sh, 1555 w, 1476 w, 1356 m	–	–	–
(6a) $\text{Bu}_2\text{Sn}(\text{p-2,6-dca})$	1656 s, 1623 vs	1358 m, 1373 s	298 250	1590 m, 1573 m, 1460 w, 1424 m	673 m	530 w	458 w
$\text{Na}_2(\text{p-2,6-dca})$	1607 vs	1386 vs	221	1622 s, 1578 s, 1443 m	–	–	–
(7a) $\text{Bu}_2\text{Sn}(\text{p-3,4-dca})$	1637 s	1396 s	241	1664 m, 1580 s, 1492 w, 1416 s	–	610 m	423 w
$\text{Na}_2(\text{p-3,4-dca})$	1578 vs	1418 s	160	1617 s, 1542 m, 1490 w, 1400 m	–	–	–
(8a) $\text{Bu}_2\text{Sn}(\text{p-3,5-dca})$	1612 vs	1376 s	236	1582 w, 1568 m, 1445 m, 1422 m	–	533 w	450 w
$\text{Na}_2(\text{p-3,5-dca})$	1640 s	1444 m	196	1605 s, 1575 m, 1547 m, 1416 s	–	–	–
(9a) $\text{Bu}_2\text{Sn}(\text{p-2,3-dca})$	1649 s, 1585 vs	1390 m, 1356 s	259 229	1608 m, 1550 sh, 1536 w, 1444 w	670 w	550 w	462 w
(9b) $\text{Bu}_2\text{Sn}(\text{p-2,3-dca})$	1649 s, 1585 vs	1390 m, 1356 s	259 229	1607 m, 1550 sh, 1535 sh, 1444 w	669 w	550 w	461 w
$\text{Na}_2(\text{p-2,3-dca})$	1593 vs	1394 s	199	1573 s, 1563 vs, 1455 w, 1448 w	–	–	–

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

corresponding $\Delta\nu$ data are 323 and 180 cm^{-1} , confirming the monodentate and bidentate coordination modes, respectively, of the $-\text{COO}^-$ groups. The intensities of these bands suggest a ratio of about 1:1 for the different $-\text{COO}^-$ groups in the molecule. This is in good agreement with the results obtained from X-ray diffraction measurements. The Bu groups are in *ax* positions (as shown by the X-ray diffraction and NMR measurements; see later), while the two {N} and the carboxylic {O} atoms occupy the *eq* plane. In this way, two five-

membered rings are formed, stabilizing the structure. Further, only one Sn–C stretching vibration was observed, and consequently the C–Sn–C bond angle is close to 180°.

In the $\text{Bu}_2\text{Sn(IV)}$ complexes of nicotinic and isonicotinic acids, double chelate ring formation as shown above is not possible. The νOH of the $-\text{COOH}$ appears as broad bands which disappear after complex formation, indicating deprotonation of the $-\text{COOH}$ group and reaction with $\text{Bu}_2\text{Sn(IV)}$. The $\Delta\nu$ value in the case of the

nicotinate is 174 cm^{-1} . This means that in this complex the $-\text{COO}^-$ group is bonded to the $\{\text{Sn}\}$ in a bidentate manner and the two $\{\text{O}\}$ atoms of the $-\text{COO}^-$ group bridge two organotin(IV) centres (see Fig. 1b).

The spectra of the complexes formed with the pyridine-dicarboxylic acids are rather complicated. Here, it is important that there is a $-\text{COO}^-$ in the *ortho* position relative to the ring $\{\text{N}\}$ atom, which allows the formation of a stable chelate ring. Moreover, depending on the location of the second $-\text{COO}^-$ group, dimeric or oligomeric complexes can form.

For doubly deprotonated pyridine-2,6-dicarboxylic acid, resonance stabilization is expected to preserve a planar configuration and result in its functioning as a tridentate ligand. In the FT-IR spectrum of the ligand, there is a very strong absorption band of the $\nu\text{C=O}$ stretch of the free $-\text{COOH}$ group at 1702 cm^{-1} [31]. The presence of the $-\text{COOH}$ group involved in the intramolecular hydrogen bonding is evident from the broad and irregularly shaped bands in the region $3500\text{--}2500\text{ cm}^{-1}$. In the FT-IR spectrum of the complex, new bands appear at 1656 and 1623 cm^{-1} and at 1373 and 1358 cm^{-1} , corresponding to the $\nu_{\text{as}}\text{COO}^-$ and $\nu_{\text{s}}\text{COO}^-$ modes of the coordinated carboxyl group. The considerable differences between them (298 and 250 cm^{-1}) indicate strong coordination of the $-\text{COO}^- \{\text{O}\}$ to the $\text{Bu}_2\text{Sn(IV)}$ acceptor. The former $-\text{COO}^-$ groups coordinate to the $\{\text{Sn}\}$ in a monodentate fashion, while the other bridges two $\{\text{Sn}\}$ centres. This is in good agreement with two pairs of observed $-\text{COO}^-$ stretching vibrations. In this case, therefore, the dicarboxylate ligand is tetradentate, forming three bonds to one $\{\text{Sn}\}$ atom and at the same time bridging to a second $\{\text{Sn}\}$ atom.

For the other pyridine-2,*x*-carboxylic acid complexes, it is obvious that the two $-\text{COO}^-$ groups are in different surroundings, in spite of the fact that both are coordinated monodentately. In all cases, two pairs of $\nu_{\text{as}}\text{COO}^-$ and $\nu_{\text{s}}\text{COO}^-$ bands are observed, $\Delta\nu$ in the interval $200\text{--}300\text{ cm}^{-1}$. In the region $1600\text{--}1400\text{ cm}^{-1}$ includes bands

extracted from the vibration modes $\nu_{\text{as,s}}\text{C=C/C=N}$. These bands are shifted by only $5\text{--}40\text{ cm}^{-1}$ to higher frequencies. Coordination of the pyridine $\{\text{N}\}$ is indicated by a red shift by $10\text{--}40\text{ cm}^{-1}$ of the pyridine ring in-plane deformation vibration ($\beta\text{C=N}$) observed near $690\text{--}600\text{ cm}^{-1}$ [32].

In the FT-IR spectra of the organotin(IV) complexes formed with pyridine-3,4- and -3,5-dicarboxylic acids, only one $-\text{COO}^-$ stretching vibration band pair was assigned. The $\Delta\nu$ values are between 230 and 250 cm^{-1} , indicating monodentate coordination. This is evidence that these compounds have oligomeric or polymeric structures. No indication is found of any $\nu\text{Sn-N}$ mode around 400 cm^{-1} .

From the FT-IR measurements, it was not possible unequivocally to confirm the coordination of the $\{\text{N}\}$ atom of the ligands, and consequently Mössbauer and NMR spectroscopic measurements were performed.

3.3. Mössbauer spectroscopy

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. Some of the spectra indicated the presence of two overlapping quadrupole doublets, the two outer and the two inner lines being associated, while others furnished only one doublet. The experimental δ and $|A|$ parameters determined by computer evaluation are presented in Table 4. All of them are characteristic for the $\{\text{Sn}\}$ atom of the organotin(IV) moiety within the complexes.

The $|A|$ values in Table 4 fall in the range $2.90\text{--}4.31\text{ mm s}^{-1}$, and are not sufficient to characterize a Sn(IV) complex as either tetra-, penta-, hexa-, or heptacoordinated [33]. However, a successful correlation has been reported between the quadrupole splitting and the structure of differently coordinated Sn(IV) , using either a simple point-charge approach [34] or a more elaborate

Table 4
Experimental and calculated Mössbauer spectroscopic parameters of the complexes

Complexes	R	δ_1	$ A _{1m}$	Γ_1	δ_2	$ A _{2m}$	Γ_2	$ A _{1c}$	$ A _{2c}$	θ
(1a) $[\text{Bu}_2\text{Sn}(\text{picolinate})_2]_n$	2:1	1.45	4.26	1.0	–	–	–	–	–	(169.9)
(2a) $\text{Bu}_2\text{Sn}(\text{nicotinate})_2$	2:1	1.50	4.20	0.95	–	–	–	4.45	–	164.4
(3a) $\text{Bu}_2\text{Sn}(\text{i-nicotinate})_2$	2:1	1.31	2.90	1.0	1.35	3.87	0.99	2.98	3.70	–
(4a) $\text{Bu}_2\text{Sn}(\text{p-2,4-dca})$	1:1	1.50	4.18	0.99	–	–	–	4.03	–	163.0
(5a) $\text{Bu}_2\text{Sn}(\text{p-2,5-dca})$	1:1	1.31	3.12	0.87	1.51	4.23	0.86	3.06	4.03	166.4
(6a) $\text{Bu}_2\text{Sn}(\text{p-2,6-dca})$	1:1	1.47	4.17	0.89	–	–	–	–	–	(162.5)
(7a) $\text{Bu}_2\text{Sn}(\text{p-3,4-dca})$	1:1	1.33	3.12	1.0	1.51	4.31	0.94	3.06	4.03	175.5
(8a) $\text{Bu}_2\text{Sn}(\text{p-3,5-dca})$	1:1	1.51	4.07	0.97	–	–	–	4.35	–	157.2
(9a) $\text{Bu}_2\text{Sn}(\text{p-2,3-dca})$	1:1	1.50	4.12	1.0	–	–	–	4.03	–	159.7
(9b) $\text{Bu}_2\text{Sn}(\text{p-2,3-dca})$	1:1	1.49	4.11	0.95	–	–	–	4.03	–	159.2

R = metal:ligand ratio; δ , $|A|$ and Γ given in mm s^{-1} ; θ is the C–Sn–C angle, given in $^\circ$, calculated for pbp geometry; values in parentheses were obtained from X-ray diffraction measurements. dca = pyridine-*x,y*-dicarboxylic acid.

hybridization treatment [24]. Our evaluation of the Mössbauer spectroscopic measurements by means of the pqs concept, taking into account the mono- or bidentate coordination mode of the COO^- , demonstrated that the Sn(IV) could be present only in a *tbp*, *oh*, or *pbp* environment. The $|\Delta|_{\text{exp}}$ values suggested configurations where the Bu groups are located mostly in *ax* positions. Linear oligomerization occurred through the monodentate COO^- groups from two different ligand molecules, except for compounds **1a** and **2a**, where bidentate COO^- groups form bridges between the two {Sn} centres. Other coordination sites are occupied by the {N} atom of the pyridine ring or H_2O .

In some cases, the differences between the calculated and measured $|\Delta|$ values are larger than the experimental error. This can be explained if it is borne in mind that the calculated value is given for the ideal structure. A distortion of $5\text{--}10^\circ$ results in the measured $|\Delta|$ value being $0.2\text{--}0.41\text{ mm}^{-1}$ greater than that calculated for ideal geometry (Table 4). For Sn(IV) complexes containing a $\text{R}_2\text{Sn(IV)}$ moiety, such a quadrupole splitting is dominated by highly covalent Sn–C bonds and, if the contributions of the other ligands are ignored, it can be shown that $|\Delta|$ is given [34] by

$$|\Delta| = -4[R][1 - (3/4)\sin^2\theta]^{1/2}, \quad (1)$$

where $[R]$ denotes the pqs value of group R, and θ is the C–Sn–C angle. Eq. (1) has been satisfactorily applied to penta- and hexacoordinated Sn(IV) compounds, using appropriate values of $[R]$ for each coordination number [23]. The value used for $[R]$ was -1.03 mm s^{-1} , but this value yields C–Sn–C angles which are in poor agreement with crystallographic observations on heptacoordinated complexes. Although few Mössbauer and structural (X-ray diffraction) data are available in the literature on heptacoordinated Sn(IV) compounds, the existing data point to reasonable and consistent behaviour for Eq. (1) [35].

As concerns complexes **1a** and **6a** [26] (we redetermined the structure of the latter, and the structural parameters obtained were completely the same as found in [26]), whose structures were determined by single-crystal X-ray diffraction, the pqs value for group R can be estimated. On inserting the values $|\Delta| = 4.26\text{ mm s}^{-1}$ and $\theta = 169.9^\circ$ for the heptacoordinated site of complex **1a**, and $|\Delta| = 4.17\text{ mm s}^{-1}$ and $\theta = 162.5^\circ$ for **6a**, into Eq. (1), we get $[R] = -1.08\text{ mm s}^{-1}$ for both compounds. This value agrees within an error of 1% with the value $[R] = -1.09\text{ mm s}^{-1}$ reported for heptacoordinated Sn(IV) complexes [36]. From the data in Table 4, it can be seen that there are numerous complexes with $|\Delta|_{\text{exp}}$ values higher than 4.00 mm s^{-1} . Therefore, it cannot be ruled out that in these compounds the central Sn(IV) atoms are also in heptacoordinated surroundings. Use of the pqs value calculated for the R = Bu group (-1.08 mm s^{-1}) and $|\Delta|_{\text{exp}}$ values higher than 4.00 mm s^{-1}

(complexes **2a**, **4a**, **5a**, **7a**, **8a**, **9a** and **9b**) with Eq. (1) allows a prediction of the C–Sn–C angles in the complexes (see Table 4).

The correlation between the Mössbauer and X-ray structural data, with use of the equation (1), gave a pqs value for butyl in excellent agreement with earlier reported ones. We consider that this correlation is important, with regard to the published structural data on heptacoordinated complexes as compared with penta- and hexacoordinated ones.

3.4. NMR spectroscopy

It is well established that organotin(IV) carboxylates often form polymeric structures in the solid phase and in concentrated organic solutions. Upon dilution of solution or solvation of the solid complexes, however, depolymerization usually occurs and oligomeric or monomeric species are produced [15].

For pure Bu_2SnO , one signal is observed in the solid state, at $\delta^{119}\text{Sn(isotropic)} = -177\text{ ppm}$ relative to external Me_4Sn . Because of the low solubility, solution-phase NMR data could not be obtained.

The complex $[\text{Bu}_2\text{Sn(picolate)}_2]_n$ (**1a**) in the solid state also gives one signal, with $\delta^{119}\text{Sn(isotropic)} = -475\text{ ppm}$ (line width $\Delta\nu_{1/2} = 414\text{ Hz}$). This chemical shift suggests a coordination number 7 [37], in line with the X-ray diffraction measurement data.

In solution direct ^{13}C observation was not possible due the low solubility of the complex in most organic solvents, but in dmsO it was sufficient for polarization transfer experiments, DEPT. The spectra indicate C_2 or higher symmetry, only one butyl and one picolinic acid group is observed.

Butyl groups: ^{13}C , $\text{C}_\alpha = 32.4\text{ ppm}$, $\text{C}_\beta = 27.1\text{ ppm}$, $\text{C}_\gamma = 25.2\text{ ppm}$, and $\text{C}_\delta = 13.2\text{ ppm}$. Weak satellites due to the one-, two- and three-bond $^{119}\text{Sn}\text{--}^{13}\text{C}$ couplings were observed in the DEPT spectrum.

The ^1H NMR measurements in dmsO resulted in a H_α multiplet at about 1.14 ppm (2H), $^2J(\text{Sn}\text{--}\text{C}\text{--}\text{H}) \cong 110\text{ Hz}$, $\text{C}_\beta = 0.94\text{ ppm}$ (multiplet, 4H), $\text{C}_\gamma = 0.90\text{ ppm}$ (sextet), and $\text{C}_\delta = 0.50\text{ ppm}$ (triplet, 3H).

For the picolinic acid moiety the ^1H NMR spectrum gave four multiplets at $\text{H}_6 = 9.24\text{ ppm}$, $\text{H}_4 = 8.24\text{ ppm}$, $\text{H}_3 = 8.18\text{ ppm}$, and $\text{H}_5 = 7.82\text{ ppm}$. No coupling of the H_6 proton to the ^{119}Sn was observed, which makes coordination of the nitrogen atom to the metal unlikely or very brief.

DEPT: $\text{C}_6 = 147.5\text{ ppm}$, $\text{C}_3 = 140.3\text{ ppm}$, $\text{C}_5 = 126.9^*\text{ ppm}$, and $\text{C}_4 = 124.4^*\text{ ppm}$. Protonated carbons of the pyridine ring do not exhibit satellites due to the couplings to the $^{119/117}\text{Sn}$ nuclei. Since the carbonyl signal does not appear in this spectrum, we have no direct confirmation for the carboxylate coordination either.

At ambient temperatures, the spectra clearly show a butyl/pyridine ratio of 1:1, i.e. for one metal atom we

have two pyridine rings, which confirms the formation of a complex with a metal:ligand ratio of 1:2.

$\text{Bu}_2\text{Sn}(\text{nicotinate})_2$ (**2a**): in the solid state a broad line ($\Delta\nu_{1/2} = 450$ Hz) was observed at $\delta^{119}\text{Sn}(\text{isotropic}) = -293$ ppm. This chemical shift suggests coordination number 5 or 6 in the solid state [37–39].

^{13}C NMR: butyl groups, $^1J(^{119}\text{Sn}-^{13}\text{C}_\alpha) =$ “not measurable” (broadened line), $^2J(^{119}\text{Sn}-^{13}\text{C}_\beta) = 38$ Hz, $^3J(^{119}\text{Sn}-^{13}\text{C}_\gamma) = 136$ Hz, and $^4J(^{119}\text{Sn}-^{13}\text{C}_\delta) = 0$ Hz. Chemical shifts: $\text{C}_\alpha = 29.7$ ppm, $\text{C}_\beta = 26.8$ ppm, $\text{C}_\gamma = 25.6$ ppm, and $\text{C}_\delta = 13.6$ ppm.

^1H NMR: $\text{H}_\alpha =$ broad signal at about 1.6 ppm, $^2J(\text{Sn}-\text{C}-\text{H})$ not available, $\text{H}_\beta = 1.54$ ppm (broadened multiplet), $\text{H}_\gamma = 1.26$ ppm (sextet), and $\text{H}_\delta = 0.86$ ppm (triplet).

Nicotinic acid: satellites due to $^{13}\text{C}-^{119}\text{Sn}$ couplings are not observed for either $-\text{C}=\text{O}$ or C_3 of the pyridine ring, but both signals are broadened. We interpret this as an indication that the carboxylate anion does coordinate temporarily to the metal, but the lifetime of the complex is not long enough for visualization of the scalar couplings. The protonated carbons do not exhibit satellites, therefore the nitrogen coordination is again unlikely or very short. Chemical shifts: $\text{C}_2 = 152.8$ ppm, $\text{C}_3 = 128.1$ ppm (broad), $\text{C}_4 = 136.8$ ppm, $\text{C}_5 = 123.9$ ppm, $\text{C}_6 = 150.2$ ppm, and $-\text{COO}^- = 170.2$ ppm (broad). ^1H NMR: $\text{H}_2 = 9.08$ ppm, $\text{H}_6 = 8.72$ ppm, and $\text{H}_4 = 8.24$ ppm, $\text{H}_5 = 5.52$ ppm.

In solution at ambient temperatures, the spectra clearly show a butyl/pyridine ratio of 1:1, i.e. for one metal we have two pyridine rings, similarly as in the 2-picolinic acid complex.

The complex $[\text{Bu}_2\text{Sn}(\text{pyridine-2,6-dicarboxylato})-(\text{H}_2\text{O})_2]$ (**6a**) in the solid state is an oligomer, as proved by the X-ray structure.

In the solid state [40], the ^{119}Sn isotropic shift is $\delta^{119}\text{Sn}(\text{isotropic}) = -375$ ppm (line width $\Delta\nu_{1/2} = 340$ Hz). This chemical shift again suggests a coordination number of seven in the solid state [37].

In dmsO solution, $\delta^{119}\text{Sn}(\text{isotropic}) = +47.2$ ppm relative to the SnMe_4 , with line width $\Delta\nu_{1/2} = 40$ Hz. This indicates a symmetric oligomer or, more likely, a monomer, since no $^{119}\text{Sn}-^{117}\text{Sn}$ coupling is observed. (For dimeric structures of $^{119}/^{117}\text{Sn}$ isotopomers, the observation of two-bond $^{119}\text{Sn}-^{117}\text{Sn}$ coupling is to be expected, the magnitude of which can vary widely, e.g. between 50 and 400 Hz for $\text{Sn}-\text{O}-\text{Sn}$ bonds; see [41].)

^{13}C NMR: at ambient temperatures, the spectrum clearly shows C_2 symmetry and a butyl/pyridine ratio of 1:2, i.e. one pyridine ring for one metal. This suggests the formation of a complex with a metal:ligand ratio of 1:1.

Butyl groups: $^1J(^{119}\text{Sn}-^{13}\text{C}_\alpha) = (-)970$ Hz, the predicted $\text{C}-\text{Sn}-\text{C}$ angle calculated from this value is about 175° , which shows that the two butyl groups are in *ax* positions [39]. $^2J(^{119}\text{Sn}-^{13}\text{C}_\beta) = 42$ Hz, $^3J(^{119}\text{Sn}-$

$^{13}\text{C}_\gamma) = 157$ Hz, and $^4J(^{119}\text{Sn}-^{13}\text{C}_\delta) = 8.4$ Hz. The relevant chemical shifts are as follows: $\text{C}_\alpha = 30.4$ ppm, $\text{C}_\beta = 26.9$ ppm, $\text{C}_\gamma = 25.6$ ppm, and $\text{C}_\delta = 13.5$ ppm.

Pyridine-2,6-dicarboxylic acid: two-bond coupling [$2J(^{119}\text{Sn}-^{13}\text{C}_{\text{beta}}) = 32$ Hz] is observed to the $-\text{C}=\text{O}$ carbon indicating that the carboxylate coordination to the metal (presumably as bidentate ligands) lasts long enough for the two-bond scalar couplings to be seen. Similar couplings to the ortho carbons of the pyridine ring are not observed, i.e. in solution the ring {N} atom does not coordinate to the central metal atom. Chemical shifts: $\text{C}_{2,6} = 146.7$ ppm, $\text{C}_4 = 144.6$ ppm, $\text{C}_{3,5} = 125.8$ ppm, and $-\text{COO}^- = 164.1$ ppm.

^1H NMR: Butyl groups, $\text{H}_\alpha =$ multiplet at about 1.38 ppm with satellites, $^2J(\text{Sn}-\text{C}-\text{H})$ is about 40 Hz, $\text{H}_\beta = 0.98$ ppm (multiplet), $\text{H}_\gamma = 0.96$ ppm (m), and $\text{H}_\delta = 0.86$ ppm (triplet).

Pyridine rings: $\text{H}_{3,5} = 8.3$ ppm (doublet), and $\text{H}_4 = 8.5$ ppm (triplet).

4. Conclusion

The procedures used resulted in the formation of complexes with a 1:2 metal-to-ligand ratio for the pyridine-monocarboxylic acids, and with a 1:1 ratio for the pyridine-dicarboxylic acids. The FT-IR, Mössbauer and NMR spectroscopic data on the complexes revealed the formation of polymeric compounds. The polymerization occurred through $-\text{COO}^-$ groups, which bridge two central {Sn} atoms. In most cases, the butyl groups are located in *ax* positions and the {Sn} are in *oh* or *pbp* stereochemical arrangements. The structure of one new compound was determined by means of X-ray diffraction measurements.

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