

Syntheses and crystal structures of diorganotin (IV) moieties with 3-hydroxy-2-pyridinecarboxylic acid

Rufen Zhang^a, Guangru Tian^a, Chunlin Ma^{a,b,*}

^a Department of Chemistry, Liaocheng University, Liaocheng, Shandong 252059, PR China

^b Taishan University, Taian 271021, PR China

Received 26 April 2005; received in revised form 25 May 2005; accepted 3 June 2005

Available online 11 July 2005

Abstract

A series of new organotin (IV) complexes with 3-hydroxy-2-pyridinecarboxylic acid (3-OH-2-picH) of two types: $R_2SnCl(3-OH-2-pic)$ (I) (R = Me **1**, *n*-Bu **2**, Ph **3**, PhCH₂ **4**) and $R_2Sn(3-OH-2-pic)_2$ (II) (R = Me **5**, *n*-Bu **6**, Ph **7**, PhCH₂ **8**) have been synthesized by reactions of diorganotin (IV) dichloride with 3-hydroxy-2-pyridinecarboxylic acid in the presence of sodium ethoxide. All complexes are characterized by elemental analyses, IR spectra and NMR spectra analyses. Among them, complexes **1**, **5**, **6** and **7** are also characterized by X-ray crystallography diffraction analyses. Complex **1** is a 1D polymeric chain with six-coordinate tin atoms and the packing of complex **1** is stabilized by the C–H···Cl intermolecular weak interactions, thus a 2D network of **1** is formed. Complex **5** is also a 1D polymeric chain with seven-coordinate tin atoms. Complex **6** is a zigzag polymeric chain linked by Sn···O intermolecular weak interactions. Complex **7** is a monomeric complex with distorted octahedral geometry.

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Keywords: 3-Hydroxy-2-pyridinecarboxylic acid; Organotin (IV); Weak interactions

1. Introduction

Metal-directed self-assembly of organic ligands and metal ions or organometallic substances with various intriguing topologies have been extensively studied [1,2]. An important objective is the synthesis of new higher soluble metal complexes useful for testing the distinctive reactivity patterns of the multimetallic systems. In recent years, organotin (IV) carboxylates have been the subjects of interest for some time because of their biochemical and commercial applications [3]. In general, the biochemical activity of organotin (IV) carboxylates is greatly influenced by the structure of the molecule and the coordination number of the tin atoms [4–6].

Therefore, recognition of the importance between the biological properties and the structure of organotin (IV) carboxylates [7], have together spurred on the study of carboxylate of tin. Crystallographic studies reveal that organotin (IV) carboxylates adopt structure which are dependent on both the nature of the alkyl (or aryl) substituent bound to the tin atom and the type of carboxylate ligand [8–10]. Studies on organotin (IV) complexes having carboxylate ligands with additional donor atoms, such as a nitrogen, available for coordination to Sn, have revealed new structural types which may lead to complexes with different activity, such as pyridine-2, 6-dicarboxylic acid and pyridinecarboxylic acid.

In our previous work, we have reported several novel molecular structures of organotin (IV) complexes with 2-pyrazinecarboxylic acid [11]. As an extension of this research program and in connection with our current interest in the coordination chemistry of organotin (IV) complexes with heterocyclic ligands, we choose

* Corresponding author. Tel.: +86 635 825 8579; fax: +86 538 671 5521/635 823 8274.

E-mail address: macl@lctu.edu.cn (C. Ma).

another fascinating ligand: 3-hydroxy-2-pyridinecarboxylic acid (3-OH-2-picH). This ligand is interesting because of its hydroxyl in the pyridine ring. With the introduction of hydroxyl, the solubility of the complexes may be increased. Although its analogical ligand, such as pyridinedicarboxylic acid have been extensively studied before [12], to our knowledge, no organotin (IV) derivatives of 3-hydroxy-2-pyridinecarboxylic acid have been reported so far. Therefore, one of the aims of this work is to investigate and characterize the structures of new organotin (IV) derivatives of 3-hydroxy-2-pyridinecarboxylic acid, and to investigate whether or not the existence of hydroxyl will influence the coordination modes.

The above considerations stirred our interest in some detailed syntheses, structure patterns for diorganotin (IV) derivatives of the ligand. Finally, we obtained a series of diorganotin (IV) complexes by reaction of diorganotin (IV) dichloride with 3-hydroxy-2-pyridinecarboxylic acid in the presence of sodium ethoxide. When using 1:1:1 molar ratio of R_2SnCl_2 :(3-OH-2-picH):EtONa, we obtained polymeric complexes **1–4** of the type $R_2SnCl(3-OH-2-pic)$ ($R = Me$ **1**, $n-Bu$ **2**, Ph **3**, $PhCH_2$ **4**) and with 1:2:2 molar ratio, another four monomeric or polymeric complexes were obtained and the general formula is $R_2Sn(3-OH-2-pic)_2$ ($R = Me$ **5**, $n-Bu$ **6**, Ph **7**, $PhCH_2$ **8**). Determinations by elemental analyses, IR and NMR spectra analyses of all the complexes are given. Among them, complexes **1**, **5**, **6** and **7** are also characterized by X-ray crystallography diffraction analyses.

2. Experimental

2.1. Materials and measurements

Diphenyltin dichloride, di-*n*-butyltin dichloride, dimethyltin dichloride and 3-hydroxy-2-pyridinecarboxylic acid were commercially available, and they were used without further purification. Dibenzyltin dichloride was prepared by a standard method reported in the literature [13]. The melting points were obtained with Kofler micro melting point apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. 1H , ^{13}C and ^{119}Sn NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for 1H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses (C, H, N) were performed with a PE-2400II apparatus.

2.2. Syntheses

The general route of synthesis is shown in the following. The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. The 3-hydroxy-2-pyridinecarboxylic acid and sodium ethoxide were added to the solution of benzene, the mixture was stirred for 30 min, and then added organotin (IV) chlorides to the mixture, continuing the reaction about 12 h at 40 °C. After cooling down to room temperature, filtered it. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The details of synthetic experiments of complexes **1–8** were shown in Scheme 1.

2.2.1. $Me_2SnCl(3-OH-2-pic)$ (**1**)

Recrystallized from dichloromethane–hexane. M.p. 212–215 °C. Yield, 74%. Anal. Calc. for $C_8H_{10}ClNO_3$ -Sn: C, 29.81; H, 3.13; N, 4.35. Found: C, 29.65; H, 3.10; N, 4.27%. IR (KBr, cm^{-1}): 1628 ($\nu_{as}COO$), 1452 (ν_sCOO), 1591 (C=N), 583 (Sn–C), 476 (Sn–O), 457 (Sn–N), 270 (Sn–Cl), 3427 (O–H). 1H NMR ($CDCl_3$, ppm): δ 1.43(s, 6H, $^2J_{SnH} = 94.6Hz$, Me), 7.29–8.70 (br, 3H, ligand). ^{13}C NMR ($CDCl_3$, ppm): δ 10.2 ($^1J(^{119}Sn-^{13}C)$, 893 Hz, Me), 149.6 (C2, ligand), 121.2 (C3), 137.5 (C4), 124.6 (C5), 147.1 (C6), 166.7 (COO). ^{119}Sn NMR ($CDCl_3$, ppm): –223.2.

2.2.2. $Bu_2SnCl(3-OH-2-pic)$ (**2**)

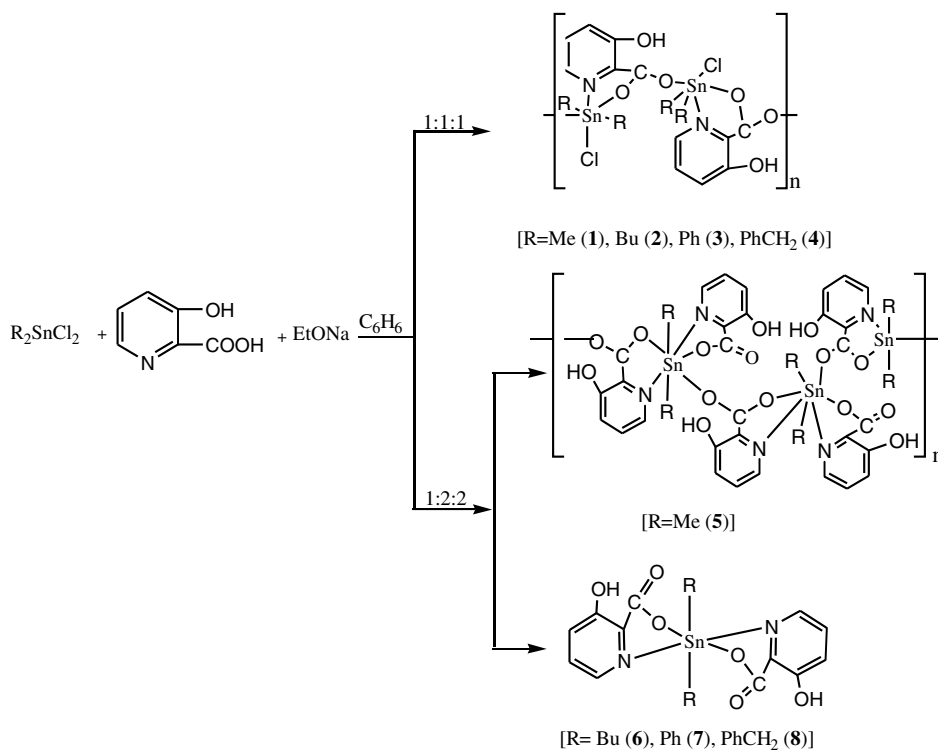
Recrystallized from dichloromethane–hexane. M.p. 52–54 °C. Yield, 78%. Anal. Calc. for $C_{14}H_{22}ClNO_3$ -Sn: C, 41.37; H, 5.46; N, 3.45. Found: C, 41.27; H, 5.51; N, 3.37%. IR (KBr, cm^{-1}): 1622 ($\nu_{as}COO$), 1448 (ν_sCOO), 1595 (C=N), 558 (Sn–C), 475 (Sn–O), 458 (Sn–N), 263 (Sn–Cl), 3429 (O–H). 1H NMR ($CDCl_3$, ppm): δ 0.91–2.11(m, 18H, nBu), 7.28–8.65 (br, 3H, ligand). ^{13}C NMR ($CDCl_3$, ppm): δ 28.0, 27.5, 26.1, 13.4 (nBu), 149.5 (C2, ligand), 121.1 (C3), 137.4 (C4), 124.3 (C5), 146.8 (C6), 167.0 (COO). ^{119}Sn NMR ($CDCl_3$, ppm): –341.6.

2.2.3. $Ph_2SnCl(3-OH-2-pic)$ (**3**)

Recrystallized from dichloromethane–hexane. M.p. 80–82 °C. Yield, 71%. Anal. Calc. for $C_{18}H_{14}ClNO_3$ -Sn: C, 48.42; H, 3.16; N, 3.14. Found: C, 48.21; H, 3.07; N, 3.15. IR (KBr, cm^{-1}): 1634 ($\nu_{as}COO$), 1445 (ν_sCOO), 1597 (C=N), 558 (Sn–C), 481 (Sn–O), 457 (Sn–N), 267 (Sn–Cl), 3425 (O–H). 1H NMR ($CDCl_3$, ppm): δ 7.47–7.80 (m, 10H, Ph), 7.29–8.65 (br, 3H, ligand). ^{13}C NMR ($CDCl_3$, ppm): δ 136.9 (*o*-C), 124.7 (*m*-C), 129.6 (*p*-C), 146.5 (*i*-C), 149.0 (C2, ligand), 121.3 (C3), 137.5 (C4), 124.5 (C5), 147.0 (C6), 167.1 (COO). ^{119}Sn NMR ($CDCl_3$, ppm): –371.5.

2.2.4. $PhCH_2)_2SnCl(3-OH-2-pic)$ (**4**)

Recrystallized from dichloromethane–hexane. M.p. 114–116 °C. Yield, 81%. Anal. Calc. for $C_{20}H_{18}ClNO_3$ -



Scheme 1.

Sn: C, 50.62; H, 3.82; N, 2.95. Found: C, 50.71; H, 3.68; N, 2.87%. IR (KBr, cm^{-1}): 1625 ($\nu_{\text{as}}\text{COO}$), 1454 ($\nu_{\text{s}}\text{COO}$), 1601 (C=N), 528 (Sn–C), 478 (Sn–O), 463 (Sn–N), 265 (Sn–Cl), 3430 (O–H). ^1H NMR (CDCl_3 , ppm): δ 7.32–7.86 (m, 10H, Ph), 3.50 (s, 4H, $\text{CH}_2\text{-Ph}$), 7.25–8.69 (br, 3H, ligand). ^{13}C NMR (CDCl_3 , ppm): δ 136.8 (*o*-C), 124.8 (*m*-C), 129.7 (*p*-C), 146.0 (*i*-C), 38.2 (CH_2Ph), 149.2 (C2, ligand), 120.9 (C3), 137.1 (C4), 124.7 (C5), 146.7 (C6), 166.8 (COO). ^{119}Sn NMR (CDCl_3 , ppm): -305.1 .

2.2.5. $\text{Me}_2\text{Sn}(3\text{-OH-2-pic})_2$ (5)

Recrystallized from dichloromethane–hexane. M.p. 154–156 °C. Yield, 84%. Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_6\text{Sn}$: C, 39.50; H, 3.32; N, 6.59. Found: C, 39.27; H, 3.45; N, 6.47%. IR (KBr, cm^{-1}): 1629 ($\nu_{\text{as}}\text{COO}$), 1453 ($\nu_{\text{s}}\text{COO}$), 1597 (C=N), 543 (Sn–C), 480 (Sn–O), 444 (Sn–N), 3426 (O–H). ^1H NMR (CDCl_3 , ppm): δ 1.42 (s, 6H, Me), 7.28–8.71 (br, 6H, ligand). ^{13}C NMR (CDCl_3 , ppm): δ 10.3 (Me), 149.2 (C2, ligand), 121.5 (C3), 136.9 (C4), 123.7 (C5), 146.2 (C6), 166.5 (COO). ^{119}Sn NMR (CDCl_3 , ppm): -226.7 .

2.2.6. $\text{Bu}_2\text{Sn}(3\text{-OH-2-pic})_2$ (6)

Recrystallized from dichloromethane–hexane. M.p. 194–196 °C. Yield, 75%. Anal. Calc. for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_6\text{Sn}$: C, 47.18; H, 5.15; N, 5.50. Found: C, 47.21; H, 5.13; N, 5.29. IR (KBr, cm^{-1}): 1651 ($\nu_{\text{as}}\text{COO}$), 1340 ($\nu_{\text{s}}\text{COO}$), 1603 (C=N), 536 (Sn–C), 475 (Sn–O), 455 (Sn–N),

3425 (O–H). ^1H NMR (CDCl_3 , ppm): δ 0.90–2.10 (m, 18H, ^nBu), 7.28–8.63 (br, 6H, ligand). ^{13}C NMR (CDCl_3 , ppm): δ 28.1, 27.2, 26.3, 13.5 (^nBu), 149.5 (C2, ligand), 121.3 (C3), 137.7 (C4), 124.5 (C5), 146.2 (C6), 167.1 (COO). ^{119}Sn NMR (CDCl_3 , ppm): -221.4 .

2.2.7. $\text{Ph}_2\text{Sn}(3\text{-OH-2-pic})_2$ (7)

Recrystallized from dichloromethane–hexane. M.p. 215–218 °C. Yield, 73%. Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_6\text{Sn}$: C, 52.49; H, 3.30; N, 5.10. Found: C, 52.41; H, 3.41; N, 5.21%. IR (KBr, cm^{-1}): 1645 ($\nu_{\text{as}}\text{COO}$), 1341 ($\nu_{\text{s}}\text{COO}$), 1607 (C=N), 550 (Sn–C), 471 (Sn–O), 451 (Sn–N), 3426 (O–H). ^1H NMR (CDCl_3 , ppm): δ 7.46–7.81 (m, 10H, Ph), 7.26–8.61 (br, 6H, ligand). ^{13}C NMR (CDCl_3 , ppm): δ 137.1 (*o*-C), 125.6 (*m*-C), 130.0 (*p*-C), 146.4 (*i*-C), 148.9 (C2, ligand), 120.9 (C3), 137.2 (C4), 124.7 (C5), 146.8 (C6), 167.0 (COO). ^{119}Sn NMR (CDCl_3 , ppm): -386.7 .

2.2.8. $\text{PhCH}_2)_2\text{Sn}(3\text{-OH-2-pic})_2$ (8)

Recrystallized from dichloromethane–hexane. M.p. 102–104 °C. Yield, 86%. Anal. Calc. for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_6\text{Sn}$: C, 54.10; H, 3.84; N, 4.85. Found: C, 54.13; H, 3.72; N, 4.68%. IR (KBr, cm^{-1}): 1652 ($\nu_{\text{as}}\text{COO}$), 1440 ($\nu_{\text{s}}\text{COO}$), 1596 (C=N), 540 (Sn–C), 472 (Sn–O), 454 (Sn–N), 3429 (O–H). ^1H NMR (CDCl_3 , ppm): δ 7.32–7.86 (m, 10H, Ph), 3.51 (s, 4H, $\text{CH}_2\text{-Ph}$), 7.21–8.62 (br, 6H, ligand). ^{13}C NMR (CDCl_3 , ppm): δ 136.8 (*o*-C), 124.5 (*m*-C), 129.2 (*p*-C), 146.1 (*i*-C), 38.0 (CH_2Ph), 149.3

Table 1
Crystal data and structure refinement parameters for **1**, **5**, **6** and **7**

	1	5	6	7
Empirical formula	C ₈ H ₁₀ ClNO ₃ Sn	C ₁₄ H ₁₄ N ₂ O ₆ Sn	C ₂₀ H ₂₆ N ₂ O ₆ Sn	C ₂₄ H ₁₈ N ₂ O ₆ Sn
<i>M</i>	322.31	424.96	509.12	549.09
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.888(2)	13.927(5)	30.80(3)	11.700(7)
<i>b</i> (Å)	11.062(3)	9.101(4)	9.277(7)	10.762(6)
<i>c</i> (Å)	10.728(3)	13.767(5)	20.609(19)	18.153(11)
α (°)	90.00	90.00	90.00	90.00
β (°)	104.011(3)	116.777(5)	124.14(2)	93.704(9)
γ (°)	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	1138.5(5)	1557.8(10)	4874(7)	2281(2)
<i>Z</i>	4	4	8	4
μ (mm ⁻¹)	2.461	1.673	1.082	1.163
Reflections collected	5856	7833	11974	8477
Independent reflections	2013	2746	4220	3142
<i>R</i> _{int}	0.0338	0.0264	0.0971	0.0888
Goodness-of-fit on <i>F</i> ²	1.010	1.004	1.010	1.026
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0318, 0.0624	0.0231, 0.0586	0.0680, 0.1514	0.0682, 0.1407
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0569, 0.0733	0.0309, 0.0637	0.1327, 0.1876	0.1067, 0.1568

(C2, ligand), 121.2 (C3), 136.8 (C4), 124.9 (C5), 147.0 (C6), 166.3 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): -334.8.

2.3. X-ray Structure Analyses of **1**, **5**, **6** and **7**

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart-1000 CCD area-detector with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against *F*² by full matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations of **1**, **5**, **6** and **7** are listed in Table 1.

3. Results and discussion

All complexes **1–8** are stable in the air and soluble in most organic solvents, such as CH₂Cl₂, THF, EtOH, DMF, DMSO, etc. And due to the existence of the hydroxyl in the ligand, all complexes are also soluble in the mixture of DMSO and water (*V*:*V* = 1:1).

3.1. Spectra

The stretching frequencies of interest are those associated with the acid COO, Sn–C, Sn–O and Sn–N groups. The spectra of all the complexes show some common characters. The explicit feature in the infrared spectra of all complexes is that, strong absorption appears at about 477 cm⁻¹ in the respective spectra of the complexes, which is absent in the free ligand, is as-

signed to the Sn–O stretching mode of vibration. The ν (C=N) band, occurring in the range of 1591–1607 cm⁻¹, is considerably shifted towards lower frequencies with respect to that of the free ligand 1610 cm⁻¹, confirming the coordination of the heterocyclic N to the tin. The stretching frequency is lowered owing to the displacement of electron density from N to Sn atom, thus resulting in the weakening of the C=N bond as reported in the literature [14]. So that the weak- or medium-intensity band in the region 444–463 cm⁻¹ can be assigned to Sn–N stretching vibrations. All these values are consistent with that detected in a number of organotin (IV) derivatives [15,16].

Some obvious differences among the spectra of the complexes are also observed. A strong band at about 268 cm⁻¹ for complexes **1–4** is assigned to ν (Sn–Cl) stretching mode of vibration. Besides, in organotin (IV) carboxylate complexes, the IR spectra can provide useful information concerning the coordinate formation of the carboxyl. The magnitude of $\Delta\nu$ ($\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) of about 170–190 cm⁻¹ for complexes **1–5** is comparable to those for the corresponding sodium salts, which indicates the presence of bidentate carboxyl groups [17]. Moreover, the magnitude of $\Delta\nu$ of 311, 304, 212 cm⁻¹ for complex **6**, **7** and **8**, respectively, indicates that the carboxylate ligand function as monodentate ligand under the conditions employed [6b,18], which is also confirmed by X-ray structure analyses.

In ¹H NMR spectra of the free ligand, single resonance is observed at 7.46 ppm, which is absent in the spectra of the complexes, indicating the replacement of the carboxylic acid proton by a diorganotin moiety. The spectra shows that the chemical shifts of the methyl groups, 1.42–1.43, 0.90–2.11 ppm for the butyl group,

7.46–7.81 ppm for the phenyl group and the benzyl group in 3.50–3.51 and 7.32–7.86 ppm. All upfield shifts are compared with those of their corresponding precursors. The $^2J_{\text{SnH}}$ of dimethyltin derivative **1** has a value of 95.6 Hz, comparable with those previously reported for six-coordinate octahedral tin (IV) adducts [19].

The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonance, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor. Although at least two different types of carboxyl groups are present, only single resonance are observed for the COO group in the ^{13}C spectra. The possible reason is that either accidental magnetic equivalence of the carbonyl carbon atoms or the separation between the two sets of resonance is small to be resolved. Complementary information is given by the values of the coupling constant. The $^1J_{\text{SnC}}$ value for **1** is 893 Hz, similar to that of the hexa-coordinate complex, and the calculated $\theta(\text{C}–\text{Sn}–\text{C})$ by the Holeček and Lyèka equation [20] are 163.9° , which is close to the angles observed in the solid state for complex **1**.

The ^{119}Sn NMR data show the complexes **1–4** only one signal, typical of a six-coordinate species, has been found in accordance with the structure of solid state [21]. However, The chemical shift for complex **7** shows -386.7 ppm. Although $\delta(^{119}\text{Sn})$ is influenced by several factor, including the aromatic or aliphatic of the group R bound to the tin atom (and possibly the type of donor atoms of the ligand), it may be used with cation to infer the coordination number of the tin atom [21b]. In the case of diphenyltin (IV) complexes different coordination numbers are clearly associated with different range of $\delta(^{119}\text{Sn})$ values, and the chemical shift of complex **7** is well within the range corresponding to coordination number 6, -360 to -540 ppm [21b]. So it can reasonably be assumed that the structure in solution of complex **7** is likely different from that observed in the solid state.

3.2. Description of crystal structures

3.2.1. $\text{Me}_2\text{SnCl}(3\text{-OH-2-pic})$ (**1**)

Selected bond lengths and bond angles for **1** are given in Table 2, and its molecular structure and 1D polymeric chain and 2D network are shown in Figs. 1 and 2, respectively.

As shown in Fig. 2, complex **1** has been proved to be a 1D polymeric chain with 3-hydroxy-2-pyridinecarboxylic acid bridging the adjacent tin atoms with oxygen atoms of the carboxyl. The complex exists in a distorted octahedron geometry with six-coordinate tin atoms. The sum of the equatorial plane bond angles is 360.02° , indicating that Sn(1), N(1), Cl(1), O(1) and O(2)#1 $[-x + 3/2, y + 1/2, -z + 3/2]$ are in the same plane. The distortion comes from the axial angle: C(7)–Sn(1)–C(8) $157.8(3)^\circ$, which deviates markedly from standard 180° .

Table 2
Selected bond lengths (Å) and bond angles ($^\circ$) for **1**

Sn(1)–C(7)	2.097(5)
Sn(1)–C(8)	2.099(5)
Sn(1)–O(1)	2.193(4)
Sn(1)–Cl(1)	2.4247(16)
Sn(1)–O(2)#(1)	2.451(4)
Sn(1)–N(1)	2.452(4)
C(7)–Sn(1)–C(8)	157.8(3)
C(7)–Sn(1)–O(1)	98.86(19)
C(8)–Sn(1)–O(1)	96.7(2)
C(7)–Sn(1)–Cl(1)	98.21(18)
C(8)–Sn(1)–Cl(1)	98.03(18)
O(1)–Sn(1)–Cl(1)	88.24(10)
C(7)–Sn(1)–O(2)#1	83.70(19)
C(8)–Sn(1)–O(2)#1	83.0(2)
O(1)–Sn(1)–O(2)#1	171.98(12)
Cl(1)–Sn(1)–O(2)#1	83.86(10)
C(7)–Sn(1)–N(1)	84.77(19)
C(8)–Sn(1)–N(1)	85.61(19)
O(1)–Sn(1)–N(1)	70.46(13)
Cl(1)–Sn(1)–N(1)	158.69(11)
O(2)#1–Sn(1)–N(1)	117.46(13)

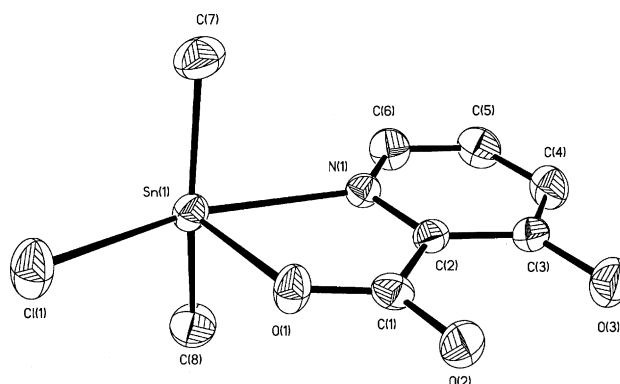


Fig. 1. Molecular structure of complex **1**.

The Sn(1)–N(1) bond length is $2.452(4)$ Å, which lies in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [22], slightly greater than the sum of the covalent radii of tin and nitrogen atoms (2.15 Å), but is considerably less than the van der Waals radii of the two atoms (3.74 Å) [23]. The carboxylate ligand chelated to two Sn atoms with asymmetric Sn–O bond distances. The difference between Sn–O bond distances for the carboxylate ligand is 0.258 Å (Sn(1)–O(1) $2.193(4)$ Å and Sn(1)–O(2)#1 $2.451(4)$ Å). Although both of the Sn–O bond lengths are longer than the sum of the covalent radii of the tin and oxygen 2.13 Å [24], they are similar to those reported in the literature [25]. The Sn–Cl bond length (Sn(1)–Cl(1) $2.4247(16)$ Å) lies in the range of the normal covalent radii of tin and chlorine atoms (2.37 – 2.60 Å) [22]. The Sn–C distances fall in a narrow range from $2.097(5)$ to $2.099(5)$ Å, typical of organotin (IV) derivatives.

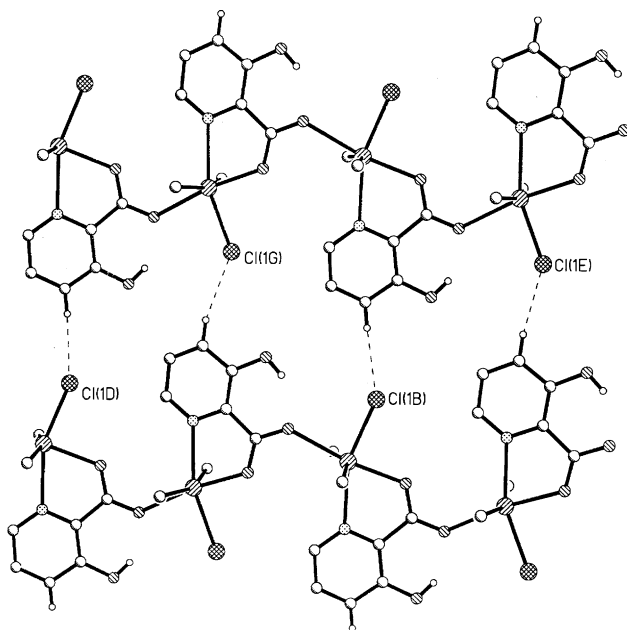


Fig. 2. The 2D network of complex **1** showing 1D polymeric chain and the C–H···Cl weak interactions.

Furthermore, as shown in Fig. 2, intermolecular C–H···Cl weak interactions are found between the 1D polymeric chains. Thus, this structural feature leads to an expansion of the supramolecular structure of **1** to a 2D network. The C···Cl and H···Cl distance and the C–H···Cl angle are 3.616 and 2.815 Å and 144.90°, respectively. All the values are smaller than those found in the literature (C···Cl 3.763(3) Å, H···Cl 2.90(2) Å and C–H···Cl 155(2)°) [26]. It is reported that the CH···X (halogen) hydrogen bond is more effective than the CH···π bond [27]. So, these weak interactions stabilize the self-assembly of complex **1**, effectively.

3.2.2. $\text{Me}_2\text{Sn}(3\text{-OH-2-pic})_2$ (**5**)

Selected bond lengths and bond angles for **5** are listed in Table 3, and its molecular structure and 1D polymeric chain are illustrated in Figs. 3 and 4, respectively.

As shown in Fig. 4, complex **5** exhibits a 1D polymeric chain with 3-hydroxy-2-pyridinecarboxylic acid bridging the adjacent tin atoms with oxygen atoms of the carboxyl. The complex contains a seven-coordinate tin atom and has a distorted pentagonal bipyramidal geometry with C(13) and C(14) atoms occupying the axial sites and the axial–Sn–axial, C(13)–Sn(1)–C(14) is 169.08(14)°. The tin atom lies in a crystallographic 2-fold structure, Sn(1), O(1), N(4), O(4), N(1) and O(5)#1 [$-x + 1, y - 1/2, -z + 1/2$] are completely coplanar with the tin atom existing in the plane. The sum of angles between the tin atom and the equatorial atoms is 350.40°, deviating greatly from the ideal value of 360°.

In the structure, two carbon atoms and two nitrogen atoms of 3-hydroxy-2-pyridinecarboxylic acid are cova-

Table 3
Selected bond lengths (Å) and bond angles (°) for **5**

Sn(1)–C(14)	2.097(3)
Sn(1)–C(13)	2.098(3)
Sn(1)–O(1)	2.175(2)
Sn(1)–O(4)	2.359(2)
Sn(1)–N(2)	2.431(2)
Sn(1)–O(5)#1	2.520(2)
Sn(1)–N(1)	2.530(2)
C(14)–Sn(1)–C(13)	169.08(14)
C(14)–Sn(1)–O(1)	97.64(12)
C(13)–Sn(1)–O(1)	92.82(13)
C(14)–Sn(1)–O(4)	85.82(11)
C(13)–Sn(1)–O(4)	87.66(12)
O(1)–Sn(1)–N(1)	68.72(8)
O(4)–Sn(1)–N(1)	147.86(8)
O(1)–Sn(1)–O(4)	143.19(8)
C(14)–Sn(1)–N(2)	93.72(11)
C(13)–Sn(1)–N(2)	91.97(12)
O(1)–Sn(1)–N(2)	75.07(8)
O(4)–Sn(1)–N(2)	68.13(8)
C(14)–Sn(1)–O(5)#1	84.62(10)
C(13)–Sn(1)–O(5)#1	84.97(12)
O(1)–Sn(1)–O(5)#1	145.92(8)
O(4)–Sn(1)–O(5)#1	70.82(7)
N(2)–Sn(1)–O(5)#1	138.93(7)
C(14)–Sn(1)–N(1)	85.16(12)
C(13)–Sn(1)–N(1)	95.81(12)
N(2)–Sn(1)–N(1)	143.24(8)
O(5)#1–Sn(1)–N(1)	77.66(8)

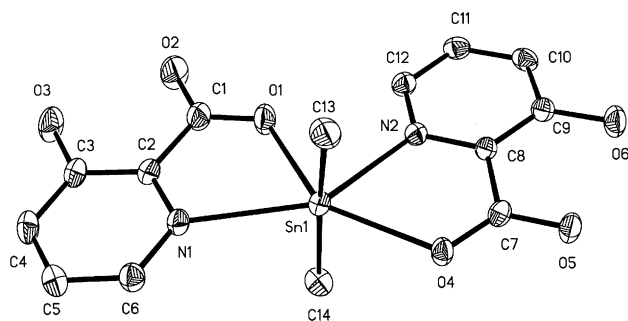


Fig. 3. Molecular structure of complex **5**.

lently linked to the tin. The Sn–N bond lengths (Sn(1)–N(1) 2.530(2) and Sn(1)–N(2) 2.431(2) Å) are shorter than those found in $(\text{CH}_3)_2\text{Sn}(\text{pca})_2 \cdot (\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ (Sn(1)–N(1) and Sn(1)–N(1)#1, 2.55(9) Å) [11], similar to those in $\text{Me}_2\text{Sn}(2\text{-Pic})_2$ (2.507 and 2.477 Å) [12b] and much shorter than the sum of the van der Waals radii of Sn and N, 3.74 Å [23]. The Sn–O bond lengths (Sn(1)–O(1) 2.175(2) and Sn(1)–O(4) 2.359(2) Å) are comparable with those found in $(\text{CH}_3)_2\text{Sn}(\text{pca})_2 \cdot (\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ (Sn(1)–O(3) 2.33(10) Å) [11] and below the sum of the van der Waals radii of these atoms, 3.68 Å [24]. Another Sn–O bond length (Sn(1)–O(5)#1 2.520(2) Å) is close to the distance between coordinated O atom and central Sn atom in other organotin complexes [28].

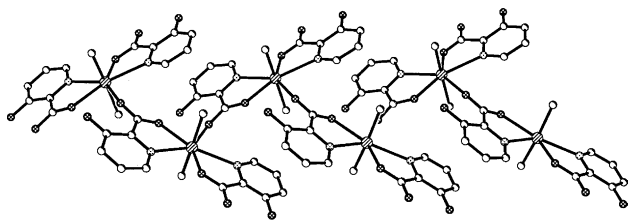


Fig. 4. 1D polymeric chain structure of complex 5.

3.2.3. $Bu_2Sn(3-OH-2-pic)_2$ (**6**)

Selected bond lengths and bond angles for **6** are listed in Table 4, and its molecular structure and zigzag polymeric chain are illustrated in Figs. 5 and 6, respectively.

The central tin atom of complex **6** forms six primary bonds, two to butyl groups, two to nitrogen atoms and two to the carboxyl oxygen atoms of the ligand. Thus, complex **6** displays a distorted octahedron geometry with O(1), N(1), O(4) and N(2) defining the equatorial plane and the axial positions are occupied by C(13) and C(17). The sum of the equatorial plane bond angles is 360.3° , indicating that Sn(1), N(1), N(2), O(1) and O(4) are in the same plane. The distortion comes from the axial angle: C(17)–Sn(1)–C(13) $162.8(4)^\circ$, which deviates markedly from standard 180° .

The Sn–N distances (Sn(1)–N(1) 2.339(7) and Sn(1)–N(2) 2.500(7) Å) are comparable with those in complex **5**, and lie in the range recorded in the Cambridge Cryst-

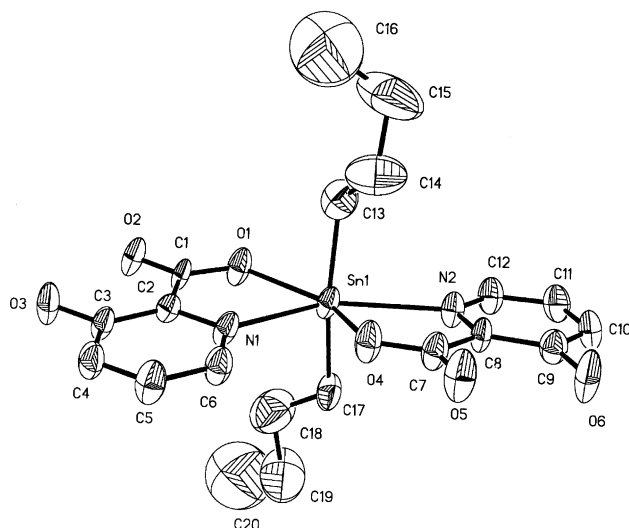


Fig. 5. Molecular structure of complex 6.

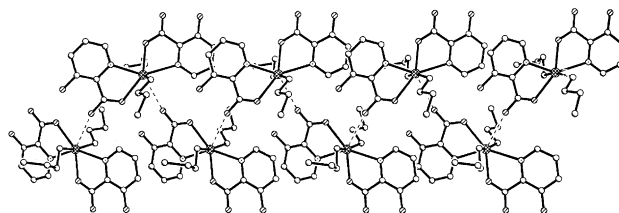


Fig. 6. 1D polymeric chain structure of complex 6 showing Sn...O weak interactions.

Table 4
Selected bond lengths (Å) and bond angles ($^\circ$) for **6**

Sn(1)–C(17)	2.084(10)
Sn(1)–C(13)	2.087(11)
Sn(1)–O(4)	2.164(6)
Sn(1)–O(1)	2.308(6)
Sn(1)–N(1)	2.339(7)
Sn(1)–N(2)	2.500(7)
Sn(1)–O(2)#1	2.808(6)
C(17)–Sn(1)–C(13)	162.8(4)
C(17)–Sn(1)–O(4)	96.5(4)
C(13)–Sn(1)–O(4)	96.0(4)
C(17)–Sn(1)–O(1)	92.9(3)
C(13)–Sn(1)–O(1)	83.2(4)
O(4)–Sn(1)–O(1)	146.5(2)
C(17)–Sn(1)–N(1)	93.3(4)
C(13)–Sn(1)–N(1)	101.0(4)
O(4)–Sn(1)–N(1)	77.6(2)
O(1)–Sn(1)–N(1)	69.8(2)
C(17)–Sn(1)–N(2)	86.0(3)
C(13)–Sn(1)–N(2)	87.3(4)
O(4)–Sn(1)–N(2)	69.3(2)
O(1)–Sn(1)–N(2)	143.6(2)
N(1)–Sn(1)–N(2)	146.5(2)
C(17)–Sn(1)–O(2)#1	81.5(3)
C(13)–Sn(1)–O(2)#1	81.4(3)
O(4)–Sn(1)–O(2)#1	145.8(2)
O(1)–Sn(1)–O(2)#1	67.4(2)
N(1)–Sn(1)–O(2)#1	136.5(2)
N(2)–Sn(1)–O(2)#1	76.5(2)

tallographic Database from 2.27 to 2.58 Å [22], and within the covalent radii (2.15 Å) and the van der Waals radii of the two atoms (3.74 Å) [23]. The Sn–O bond lengths (Sn(1)–O(1) 2.308(6) and Sn(1)–O(4) 2.164(6) Å) are shorter than that in complex (n -Bu₂Sn(2-pic)₂O)₂ (Sn(1)–O(2) 2.303(4) Å) [8], and a little longer than the covalent radii of tin and oxygen (2.13 Å) [24].

Interestingly, an additional intermolecular Sn(1)···O(2)#1 interaction between each tin and carboxylic oxygen of a neighboring molecule gives rise to a zigzag polymeric chain structure of complex **6**. The Sn···O distance is 2.808(6) Å, much shorter than the van der Waals radii of these atoms (3.68 Å) [24]. Therefore, including the intermolecular weak interaction, the coordination number of the central tin is seven.

3.2.4. $Ph_2Sn(3-OH-2-pic)_2$ (**7**)

Selected bond lengths and bond angles for **7** are listed in Table 5, and its molecular structure and cell packing diagram are illustrated in Figs. 7 and 8, respectively.

Complex **7** is a monomeric complex and the coordination mode of the ligand in complex **7** is similar as that in complex **6**. The central tin is six-coordinate with distorted octahedron geometry. The equatorial plane is defined by O(1), O(4), N(1) and C(19), and the sum of the

Table 5
Selected bond lengths (Å) and bond angles (°) for 7

Sn(1)–O(4)	2.112(6)
Sn(1)–C(13)	2.130(9)
Sn(1)–O(1)	2.131(6)
Sn(1)–C(19)	2.138(10)
Sn(1)–N(1)	2.321(8)
Sn(1)–N(2)	2.343(8)
O(4)–Sn(1)–C(13)	91.6(3)
O(4)–Sn(1)–O(1)	154.7(3)
C(13)–Sn(1)–O(1)	103.3(3)
O(4)–Sn(1)–C(19)	103.3(3)
N(1)–Sn(1)–N(2)	76.2(3)
C(13)–Sn(1)–C(19)	104.5(3)
O(1)–Sn(1)–C(19)	92.7(3)
O(4)–Sn(1)–N(1)	86.0(3)
C(13)–Sn(1)–N(1)	91.2(3)
O(1)–Sn(1)–N(1)	73.6(3)
C(19)–Sn(1)–N(1)	161.4(3)
O(4)–Sn(1)–N(2)	72.7(3)
C(13)–Sn(1)–N(2)	160.3(3)
O(1)–Sn(1)–N(2)	87.8(3)
C(19)–Sn(1)–N(2)	91.0(3)

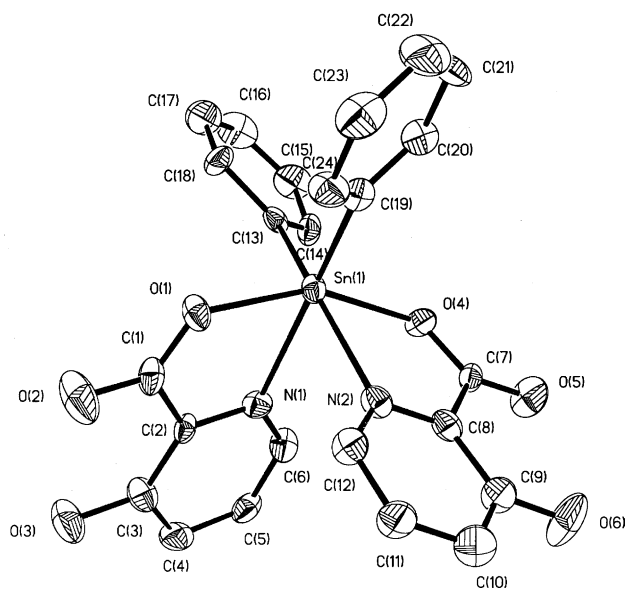


Fig. 7. Molecular structure of complex 7.

equatorial plane bond angles is 355.6° , indicating that Sn(1), N(1), C(19), O(1) and O(4) are almost in the same plane. The distortion comes from the axial angle: C(13)–Sn(1)–N(2) $160.3(3)^\circ$, which deviates markedly from standard 180° .

The Sn–N distances (Sn(1)–N(1) 2.321(8) and Sn(1)–N(2) 2.343(8) Å) are shorter than those found in $\text{Ph}_2\text{Sn}(\text{pca})_2$ (Sn(1)–N(1) 2.638(4) and Sn(1)–N(3) 2.396(5) Å) [11], which lie in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [22], slightly greater than the sum of the covalent radii of tin and nitrogen atoms (2.15 Å), but is consider-

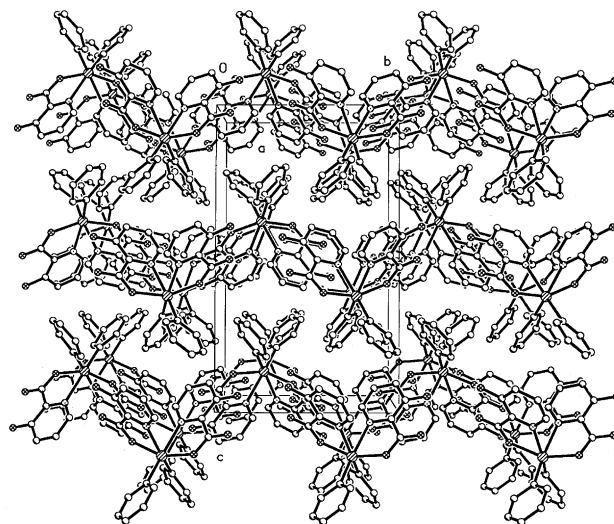


Fig. 8. Cell packing diagram of complex 7.

ably less than the van der Waals radii of the two atoms (3.74 Å) [23]. The Sn–O bond lengths (Sn(1)–O(1) 2.131(6) and Sn(1)–O(4) 2.112(6) Å) are also less than those found in $\text{Ph}_2\text{Sn}(\text{pca})_2$ (Sn(1)–O(1) 2.260(4) and Sn(1)–O(3) 2.180(4) Å) [11]. There is no significant weak interaction between those molecules in the packing diagram of 7.

4. Conclusions

The 3-hydroxy-2-pyridinecarboxylic acid has been shown to be able to form monomeric and polymeric complexes. The hydroxyl in the pyridine ring of the ligand has no obvious influence on the coordination to the central tin atom. High coordination number is found in all the complexes. The formation of monomeric molecules in the complex in question may be caused by steric hindrances due to the presence of bulky phenyl groups. Additionally, weak but significant intermolecular interactions (C–H \cdots Cl and Sn \cdots O) are observed. Therefore, multi-dimension self-assembly supramolecular structure is apt to form. Preliminary studies show that 3-hydroxy-2-pyridinecarboxylic acid has potential for the design of heterometallic systems containing both transition and post-transition metals.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper (1, 5, 6, 7) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-257753, 252044, 260189, 257757, respectively. Copies of the data can be obtained free of charge on application

to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgments

The authors thank the National Natural Science Foundation of China (20271025) and the Natural Science Foundation of Shandong Province for financial support.

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