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Penta- and heptacoordinated tin(IV) compounds derived from pyridine Schiff bases and 2-pyridine carboxylate: Synthesis and structural characterization

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ABSTRACT

The synthesis of the Sn(IV)-complexed, Schiff base derivatives **1a**–**1l**, prepared in one pot by the reaction of 2-amino-4-R-phenol (R = H, Me, Cl, NO_2), 2-pyridinecarboxaldehyde, 2-picolinic acid and dimethyl-, dibutyl-, and diphenyltin oxides, is described. The complexes were characterized by IR, MS, ^{1}H, ^{13}C, ^{119}Sn NMR. Suitable crystals of **1e** and 1**h** enabled us to use X-ray diffraction to determine their molecular structures, which exhibited pentagonal–bipyramidal geometries where the butyl groups occupied the axial positions whereas the nitrogen and the oxygen atoms occupied the equatorial positions. The reaction of the Schiff base **2** with dibutyltin oxide led to the pentacoordinated complex, **2h**, through the addition of methanol to the C=N bond. An unusual reduction–oxidation reaction took place by the reaction of 2-amino-4-nitro-phenol, dibutyltin oxide and 2-pyridinecarboxaldehyde, which produced the corresponding amine, **3h,** and the amide, **4h,** tin(IV) derivatives. Both structures were established by X-ray crystallography and exhibited a distorted, bipyramidal trigonal (BPT) geometry.

1. Introduction

Organotin complexes have been studied in view of their structural diversity and their possible biological applications. In this regard, compounds which exhibit anti-microbial [1–5], anti-inflammatory [7–11], bactericidal [12,13], cardiovascular [1,5–14,15] biocidal [16], antitubercular [17,18], antifungal [19] and cytotoxic [20–23] biological activity have been described. Different complexes have been investigated in the search of treatments for diseases such as trypanosomiasis [24] and jaundice [25].

Pyridine ligands, which have been used in the coordination chemistry of a variety of metals [26–30], occupy a unique position in the synthesis of biologically active compounds [31]. The chemistry of organostannyl carboxylates is one of the more fascinating fields, and pyridine tin carboxylates are the focus of many studies due to their different coordination geometries and their structural diversity, which depends upon the reaction conditions. The 2,6-pyridine dicarboxylic acid reacts with diorganotin oxide or diorganotin diacetate, thereby generating structures with a pentagonal bipyramidal environment [32–39]. Interestingly, the presence of alkaline alkoxides favors the formation of complexes with octahedral geometry [40]. The reaction of 2,5-pyridinedicarboxylic acid with dimethyl, dibutyl or diphenyl tin oxides gives cyclotrimeric or polymeric seven coordinated tin derivatives [41]. In addition, the 2,4-, 3,4- and 3,5-pyridine dicarboxylates react with organotin-chlorides giving oligomeric structures with distorted TBP geometries [42]. Some organotin complexes derived from picolinic acid possess octahedral or five-coordinated trigonal bipyramidal structures where the carboxylate acts as a monodentated ligand [43,44]. It has been reported that seven coordinated tin complexes exhibit higher activity towards some cancer cell lines when the 2,6-pyridine carboxylate moiety is part of the molecule [45]. Other studies have focused on the structural aspects of the hypervalent species of the Schiff-based organotin complexes [46–48]. These class of compounds are important due to their biological and catalytic applications.

On the other hand, few examples of mixed ligands diorganotin complexes have been described which include the chelate ligands dithiocarbamate and quinolinates that have been used to prepare octahedral SnR_2LL' complexes [49], the mixed diorganotin(IV) complexes containing thiosemicarbazones and acetate or dithiophosphinate ligands which have shown antiproliferative activity towards different cell lines [50–51], the bis (dicyclohexylammonium)oxalate and pyridine-2,6-dicarboxylate that affords to the seven coordinated mixed-chelate diorganotin(IV) compound [52] and the octahedral mixed-complexes which obtained when two different Schiff-base ligands are used [53].

Herein, we report on the synthesis and characterization of five and seven tin coordinated complexes, using mixed ligands (Schiff bases, aminopyridine, and pyridine carboxylates) with the specific aim of evaluating the influence of the aromatic substituents on the schiff base, the stoichiometry, and the reaction conditions upon the formation of the hypervalent species.

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2. Results and discussion

The complexes **1a–1l** were obtained in one step by the reaction of dimethyl, dibutyl, or diphenyltin oxide, the corresponding 2-R-aminophenol (R = H, Me, Cl, NO_2), 2-pyridinecarboxaldehyde, and 2-pyridinecarboxylic acid and using methanol or benzene as the solvent. The reaction times were in the range of 15–40 min. The crystalline complexes **1c** and **1d** were obtained when the reaction was carried out in benzene. The **1a–1l** complexes were isolated in yields of 51–99%. The air stable products were characterized by mass spectrometry, spectroscopic methods (IR, ^{1}H, ^{13}C, and ^{119}Sn NMR), and X-ray crystallography.

The analysis of the FT-IR spectra of these complexes showed bands in the region of 1592–1598 cm^{-1} due to the ν(N=C) stretching vibrations, and similar shifts to those found for heptacoordinated tin derivatives [54], which are shifted towards lower wave number compared to the ν(N=C) stretch of the Schiff base ligand, were observed. Such shifts are a result of the displacement of the electron density from the nitrogen to the tin atom. Additionally, the spectra exhibited two different absorption bands in the ranges of 1641–1659 cm^{-1} and 1352–1364 cm^{-1}, which correspond to the $\nu_{AS}(COO^{-})$ and $\nu_{S}(COO^{-})$ modes of the coordinated carbonyl group, respectively. Deacon has proposed that $\Delta\nu$ values >200 cm^{-1} are associated with unidentated coordination [55]. The $\Delta\nu$ of the **1a–1l** derivatives are in the range of 282–303 cm^{-1}. Following the results of Deacon, we assume that the pyridinecarboxylate is coordinated to the metal center in a monodentated mode (Table 1). The **1a–1l** complexes also displayed stretching bands in the range of 417–420 cm^{-1}, which are attributed to the vibration ν(Sn–N).

The monomeric structure of complexes **1a–1l** was established by mass spectrometry, which showed the molecular ions for all complexes. Fragment ions [$M^{\cdot+}$–R], [M^{+}–PyCOO^{-}], which correspond to the base peak for the complexes **1a–1h,** and [M^{+}–PyCOO–2R] were also detected.

The evidence that newly heptacoordinated, tin heterocyclic ring species had formed was provided by ^{119}Sn, ^{1}H, and ^{13}C NMR spectroscopy. Typical signals for the heptacoordinated tin atoms were observed in the ^{119}Sn NMR spectra for the **1a–1l** complexes as a consequence of the coordination of the nitrogen atoms to the metal center, which, in connection with the simultaneous formation of Sn–O bonds, accounted for the expected geometry.

The C–Sn–C bond angles of 170.5°, for **1a** and **1b**, 170.3° and 169.8° for **1c** and **1d** were calculated by using the values of the ^{119}Sn coupling constants $^{2}J(^{1}H–^{119}Sn)$ = 115.7, 115.7, 115.6, and 115.3 Hz, respectively, whereas, for **1e** and **1f** the coupling constants $J(^{13}C–^{119}Sn)$ = 1130 Hz and 1128 Hz were used which gave angles of 175.9° and 175.7°, respectively [56].

For complexes **1e** and **1f** was also possible to measure the coupling constants $^{1}J(^{13}C–^{119/117}Sn)$, $^{2}J(^{13}C–^{119/117}Sn)$, $^{3}J(^{13}C–^{119/117}Sn)$ and $^{4}J(^{13}C–^{119/117}Sn)$ for butyl groups attached to the tin, which allowed us to corroborate the ^{13}C NMR assignation. The obtained coupling constants values were similar to those described in the literature [52].

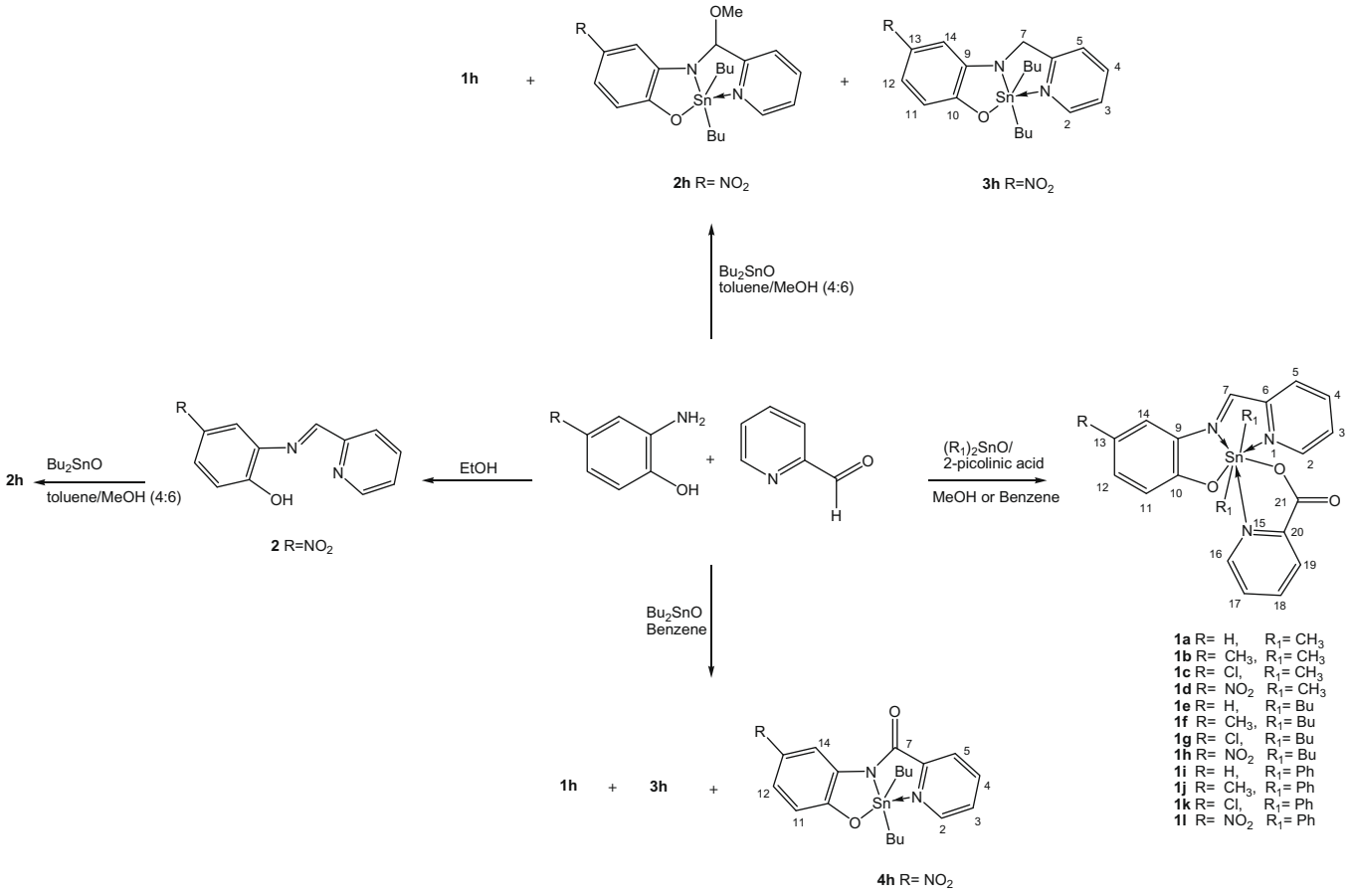
Surprisingly, when the reaction was carried out in one step with dibutyltin oxide using a toluene/methanol (4:6) mixture as solvent and 8 h of reflux in absence from 2-pyridinecarboxylic acid, a mixture of complexes, **1h, 2h,** and **3h** in a ratio of (1:12:1), was obtained. The ratios where determined by the integration of the ^{1}H NMR spectra using the proton signals of the N=CH, N–CH and N–CH_2, respectively (Scheme 1). The addition of MeOH to the reaction mixture led to the precipitation of the major compound; the ^{1}H and ^{13}C NMR data allowed us to characterize the complex, **2h**. Additional evidence supporting the formation of the three complexes could be deduced from ^{119}Sn NMR spectra, where typical signals of penta- and heptacoordinated tin atoms were detected (−83.0 ppm, −67.9 ppm, and −441.0 ppm). Although the separation of the remaining products of the mixture was not possible, the assignment of the individual signals for the **1h** and **3h** complexes was accomplished based on the comparison of the mixture's NMR spectra with the NMR spectra of the pure **1h** and **2h** complexes, which allowed us to successfully characterize the **3h** complex. The **3h** complex showed three different signals, two doublets and a singlet at 6.64 ppm, 7.68 ppm, and 7.26 ppm corresponding to H-11, H-12 and H-14, respectively. The protons of the pyridine ring showed four different signals, and there was a singlet at 4.78 ppm corresponding to the methylene resonance, H-7. Additional evidence for the formation of **3h** was obtained from the signal at 49.3 ppm in the ^{13}C NMR.

Interestingly, the reaction of the Schiff base **2** with dibutyltin oxide using the aforementioned reaction conditions led to the formation of the complex **2h** as the unique product in a yield of 94% (Scheme 1). The ^{1}H NMR spectroscopy exhibited a singlet at 6.37 ppm, corresponding to the proton of the stereogenic carbon, and an additional singlet for the methyl group was observed at 2.86 ppm. However, there was a signal at 84.0 ppm in the ^{13}C NMR, which was characteristic of a tertiary carbon. No evidence of an iminic carbon was observed. This fact supports the possibility that the C=N center reacted with a molecule of methanol, which might also explain the presence of both the methoxy and the methyne signals in the spectrum, additionally, using the Lockhart equation and the coupling constant $J(^{13}C–^{119}Sn)$ = 560.7 Hz, the bond angle C–Sn–C 125.9° was calculated. The ^{119}Sn NMR showed an intense singlet, which was indicative of a pentacoordinated tin species (δ = −83.0 ppm). The mass spectrometry showed the molecular ion [$M^{\cdot+}$] and a peak corresponding to the loss of the methoxy group, thereby confirming the addition of methanol to the iminic carbon. These results suggest that the first step of the reaction is the formation of the imine followed by the addition of (MeOH) to the C=N bond (Scheme 2). This last step could be favored by the presence of tin, which could polarize the C=N bond, thereby facilitating the nucleophile to react with the iminic carbon. This behavior has only been observed for the nitro-derivative, which suggests that the electron withdrawing effect increases the electrophilicity and reactivity of the C=N bond, thereby favoring the addition of nucleophiles. Indeed, this rationalization is part of a key step to a well-known procedure in which the use of organometallic reagents facilitates the addition of different nucleophiles [57–60].

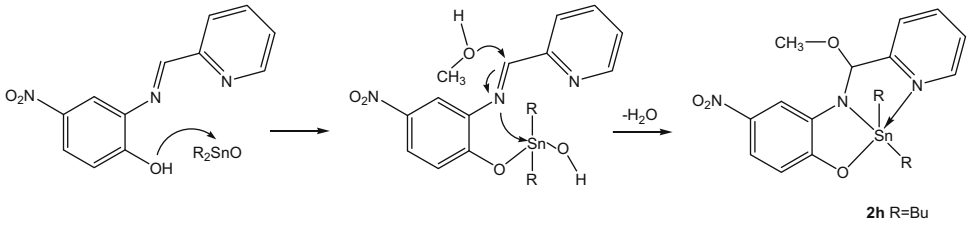
A different reactivity was also observed for the reaction of 2-amino-4-nitrophenol with 2-pyridinecarboxaldehyde and dibutyltin oxide using benzene as the solvent (Scheme 1). In this case, the NMR structural analysis indicated that the reaction gives rise to a mixture of three compounds in a ratio (1:2:1). The addition of MeOH to the crude reaction resulted in the precipitation of one compound, whose ^{1}H and ^{13}C NMR spectra exhibited signals

Table 1
FT-IR vibration (cm^{-1}) for complexes **1a–1l**.

Compound	$\nu_{as}COO^{-}$	$\nu_{s}COO^{-}$	$\Delta\nu$	N (Sn–N)
1a	1645	1364	281	421
1b	1651	1359	292	418
1c	1659	1356	303	419
1d	1649	1352	297	419
1e	1642	1360	282	418
1f	1641	1359	282	417
1g	1644	1358	286	417
1h	1648	1354	294	416
1i	1660	1359	312	421
1j	1656	1345	311	420
1k	1658	1359	299	419
1l	1649	1352	297	420

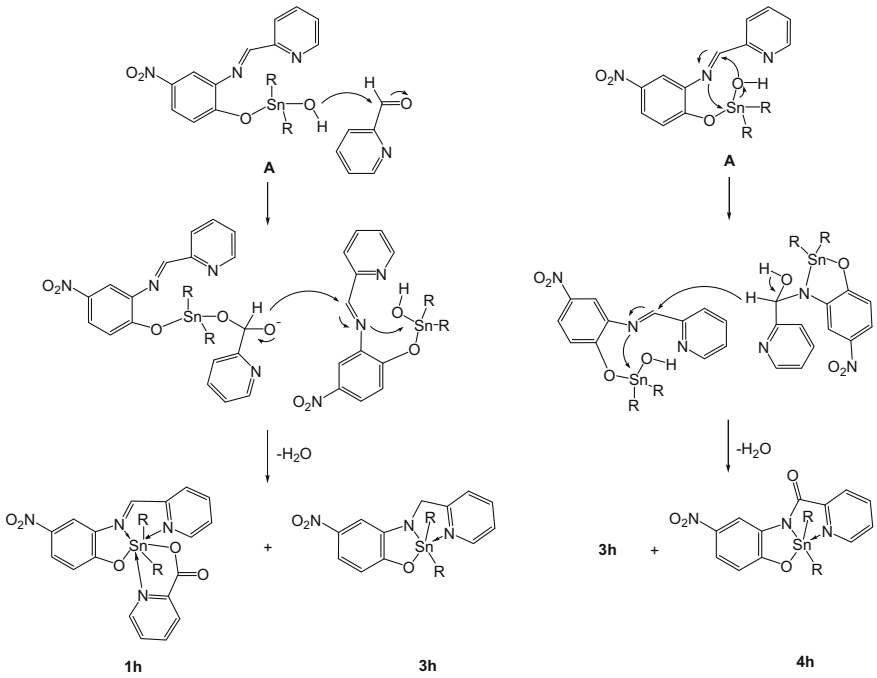


Scheme 1.



Scheme 2. Possible reaction mechanism for the formation of **2h**.

characteristic of the complex, **1h**. Eventually, the separation of the remaining products of the reaction was achieved by the addition of MeOH to the filtered solution, from which the major compound was crystallized and separated by filtration. The analysis of the ^{1}H NMR spectrum of this new compound, **4h**, showed different resonances for the aromatic protons, three doublets at 6.81 ppm, 7.95 ppm, and 9.67 ppm, which were assigned to H-11, H-12 and H-14, respectively, while the pyridine ring exhibited four different and more complex signals at 7.79 ppm, 8.24 ppm, 8.38 ppm, 8.59 ppm for the H-3, H-4, H-2, and H-5 protons, respectively. The ^{13}C NMR spectrum showed signal at 162.6 ppm corresponding to the carbonyl group. The presence of an amide carbonyl was also detected in the IR spectrum ν(CO) at 1648 cm^{-1}, which corroborated the formation of the **4h**, additionally, the coupling constant $J(^{13}C–^{119}Sn)$ = 566.4 Hz, allowed us to calculate the C–Sn–C bond angle 126.2°. Once the compound **4h** was separated**,** the remaining complex still present in the mother liquor was identified as complex **3h**, which showed the previously described chemical shifts and the coupling constant $^{1}J(^{13}C–^{119}Sn)$ = 559.6 Hz which was used to calculate the C–Sn–C bond angle 125.8°. The ^{119}Sn NMR spectra of **3h** and **4h** showed signals at −67.9 ppm and −122 ppm, which corresponded to the **3h** complex and **4h** complex, respectively, and are indicative of pentacoordinate geometries. According to the literature, the unexpected formation of the **3h** complex in the absence from a reducing agent might be taking place through a Cannizzaro reaction. This type of behavior has been observed for the reaction of 4-nitrobenzaldehyde with 2-amino-4,6-dimethylpyrimidine [61]. In this respect, the hydride shift of the hemiaminal intermediate to another molecule of the aldehyde could explain the formation of the **4h** complex; however, no evidence of the expected byproduct, 2-pyridinemethanol, was detected, indicating that the hydride was probably transferred to C=N bond, which could be polarized by the metal, thereby giving rise to complex **3h**. The nucleophilic attack of the intermediate **A** on the



Scheme 3. Possible reaction mechanism for the formation of **1h**, **3h** and **4h**.

2-pyrididinecarboxaldehyde could explain the formation of **1h** and ratio (1:2:1) of **1h**, **3h** and **4h**, respectively (Scheme 3). The reduction of coordinated Schiff bases has also been described for tungsten and aluminum complexes [62,63].

When 2 equiv. of 2-pyridine carboxaldehyde, 1 equiv. of 2-amino-4-R-phenol R = H, Me, Cl), and the corresponding diorganotin oxide were used, the reaction led to the selective formation of the **1e**–**1g** complexes as unique products, where the reaction was carried out using different solvents, such as toluene/methanol (4:6), MeOH, and benzene. However, only the heptacoordinate tin complexes were isolated irrespective of the solvent. In this case, the pyridinecarboxaldehyde was oxidized to the corresponding carboxylate, and it was coordinated to the metal center affording the heptacoordinated tin derivatives (Scheme 4).

Since the 2-amino-4-nitro-phenol showed the most versatile behavior, we performed the reaction under different conditions. Firstly, the reaction of 2-amino-4-nitrophenol with 2 equiv. of 2-pyridinecarboxaldehyde gave two complexes in a ratio of (1:1) when a mixture of toluene/methanol solvent was used. The analysis of ^{1}H NMR spectrum of the reaction mixture revealed the formation of both pentacoordinated and heptacoordinated tin complexes, the **1h** and **3h** complexes, respectively. In this case, the pyridine carboxaldehyde was oxidized to carboxylate, whereas for the pentacoordinated tin complexes, the spectroscopic data indicates that the imine had been reduced to the corresponding amine. When MeOH was used as solvent, only the complex, **2h,** was obtained. Finally, the same reaction in presence of benzene gave a mixture of products, **1h**, **3h** and **4h,** as was previously observed when 1 equiv. of aldehyde was used (Scheme 4).

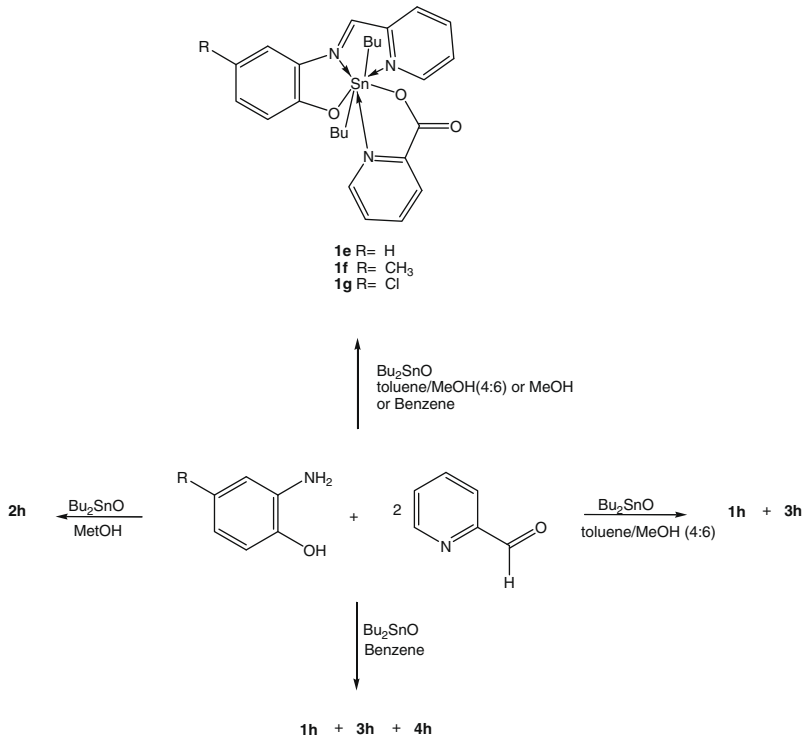
3. X-ray diffraction

The molecular structures for the complexes **1e**–**1h**, **2h, 4h** were established by X-ray diffraction. For the series **1e**–**1h,** the **1e** and **1h** complexes were selected as representatives for the analysis. Details of the crystal data and a summary of the data collection parameters for the complexes are given in Table 2. Selected bond lengths and bond angles are listed in Table 3.

The examination of the molecular structure of the **1e** and **1h** complexes revealed that their structural geometry is pentagonal–bipyramidal (PBP) (see Fig. 1). The equatorial plane is constituted of two oxygen atoms and three nitrogen atoms, the azomethine and the nitrogen atoms of the pyridine rings, whereas the axial positions are occupied by the two butyl groups, which exhibit disorder in the two positions and form angles of 169.2(1)° and 170.8(1)° for **1e** and **1h** complexes, respectively, which are in agreement with the values for C–Sn–C bond angles performed from the NMR data solution. The Sn(1)–N(1) bond length of 2.538(2) Å and the Sn(1)–N(3) bond length of 2.423(2) Å for the **1e** complex are slightly longer than Sn(1)–N(2) bond length of 2.303(2) Å. However, the shortest tin-nitrogen bond length for the **1h** complex is Sn(1)–N(3) bond length of 2.436(3) Å. For the **1e** and **1h** complexes, the 2-pyridinecarboxylate is bonded to the tin atom in a monodentated manner, as evidenced by the spectral data. The Sn(1)–O(2) bond lengths of 2.304(2) Å and 2.242 (3) Å are slightly shorter than those found for the 2,6-pyridine carboxylate dibutylstannate derivatives [45].

Fig. 1 depicts the molecular structure of compound **2h**, which contains two five-membered ring heterocycles. The tin atom has a pentagonal coordination environment, and the geometry could be interpreted as distorted trigonal bipyramidal, with the oxygen and the nitrogen of the pyridine ring occupying the axial positions and the nitrogen and the carbons of the butyl groups occupying the equatorial positions. The distortion of the geometry is evident from the N(1)–Sn–O(1) bond angle of 150.4(3)°; meanwhile, the atoms in the equatorial plane exhibit bond angles in the range of 115.7(2)–124.4(2)°. The five-membered rings are not completely planar since the Sn atom deviates by 0.109(7) Å and 0.086(7) Å from the mean plane formed by the pyridine and the six-membered rings, respectively. Meanwhile, the C-7 is coplanar to the pyridine and aromatic rings. The N → Sn bond length of 2.394(4) Å is slightly longer than that found for pentacoordinated tin complexes [64], where the pyridine nitrogen forms a coordinative bond, the Sn–N and Sn–O distances are in the range of 2.062(3) Å and 2.114 (3) Å, respectively.

The unit cell of the **3h** complex consists of two chemically equivalent, but crystallographically independent, molecules. Similar to



Scheme 4.

Table 2
Crystallographic data for compounds **1e**, **1h**, **2h** and **4h**.

Complex	1e	1h	2h	3h	4h
Formula	$C_{26}H_{31}N_3O_3Sn{\cdot}0.5CH\ Cl_3$	$C_{27}H_{32}Cl_2N_4O_5Sn$	$C_{21}H_{29}N_3O_4Sn$	$C_{20}H_{27}N_3O_3Sn$	$C_{20}H_{25}N_3O_4Sn$
Formula weight (g mol^{-1})	1223.82	682.16	506.16	476.14	490.12
Crystal size (mm)	0.40 × 0.20 × 0.08	0.42 × 0.26 × 0.16	0.26 × 0.15 × 0.10	0.32 × 0.12 × 0.11	0.24 × 0.16 × 0.10
Color	Red	Red	Orange	Red	Red
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
a (Å)	26.777(2)	14.517(2)	10.501 (1)	11.350(1)	17.158(2)
b (Å)	12.937 (1)	9.838(1)	10.792(1)	12.165(2)	16.566(2)
c (Å)	16.426(1)	20.984(2)	11.501(2)	16.728(2)	16.262(2)
α (°)	90	90	82.468(2)	70.251(2)	90
β (°)	102.202 (1)	91.807(2)	81.355(2)	78.666(2)	113.587(2)
γ (°)	90	90	61.566(2)	86.249(2)	90
V (Å^3)	5561.6(6)	2995.1(6)	1130.5(3)	2131.5(5)	4236.3(9)
Z	4	4	2	4	8
$D_{calc.}$ (g/cm^3)	1.462	1.513	1.487	1.484	1.537
No. of collected reflections	22 352	23 732	9403	7782	17 221
No. of independent reflections (R_{int})	4901 (0.0498)	5256 (0.0439)	4121 (0.0360)	7782 (0.0519)	3867 (0.0498)
No. of observed reflections	4901	5256	4121	7782	3867
No. of parameters	399	358	292	599	310
R^a	0.0311	0.0407	0.0437	0.0437	0.0513
$R_w{}^b$	0.0546	0.1063	0.1023	0.0942	0.1423
GOF	0.850	0.968	1.031	0.876	1.001

[a] $R = ||F_o| - |F_c||/|F_o|$.
[b] $R_w(F_o)^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

complex **2h,** the molecular structure of the **3h** and **4h** complexes contain two five-membered ring heterocycles. For both complexes, the geometry around the tin atom is distorted trigonal bipyramidal, where the amine or amide nitrogen and the butyl groups occupy the equatorial positions and the pyridinic nitrogen and the oxygen occupy the axial ones. The butyl group of the **3h** complex and the carbonyl group of **4h** exhibit disorder in two positions. The two Sn–N bonds of the **3h**/**4h** complexes show significant differences, in which the Sn(1)–N(2) bond length of 2.059(2)/2.086(4) Å is shorter than Sn(1)–N(1) bond length of 2.319(4)/2.323(5) Å (Table 3) and that found for the bond length of tyrosinylphenylalaninate-*O*,*N*,*N*-(2)-dimethyltin(IV), 2.103(7) Å [65]. In this geometry, the C(14)–Sn(1)–C(18) bond angles of 122.5(2)/116.9(4)° and O(1)–Sn(1)–N(1) 151.2(1)/150.9(2)° represent a high degree of

Table 3
Bond lengths (Å) and angles (°) for complexes **1e**, **1h**, **2h**, **3h** and **4h**.

	1e	**1h**	**2h**	**4h**	**3h** molecule A		**3h** molecule B
Bond lengths							
Sn(1)– O(1)	2.177(2)	2.243(3)	2.114(3)	2.104(5)	2.108(3)	Sn(2)–O(4)	2.118(3)
Sn(1)– O(2)	2.304(2)	2.242(3)					
Sn(1)– N(1)	2.538(2)	2.538(3)	2.349(4)	2.323(5)	2.319(4)	Sn(2)–N(4)	2.357(4)
Sn(1)– N(2)	2.383(2)	2.436(3)	2.062(3)	2.086(4)	2.059(2)	Sn(2)–N(5)	2.053(4)
Sn(1)– N(3)	2.423(2)	2.382(3)					
Sn(1)–C(14)			2.114(5)	2.120(9)	2.132(5)	Sn(2)–C(38)	2.130(5)
Sn(1)– C(18)			2.123(5)	2.113(9)	2.125(5)	Sn(2)–C(34)	2.108(6)
Sn(1)– C(19)	2.119(3)						
Sn(1)– C(20)		2.128(4)					
Sn(1)– C(23)	2.115(3)						
Sn(1)– C(24)		2.137(4)					
N(2)– C(6)	1.275(3)						
N(2)– C(7)		1.274(4)	1.413(5)	1.368(7)	1.434(5)	N(5)–C(27)	1.444(5)
C(7)–O(2)			1.420(5)				
C(7)–O(4)				1.178(8)			

	1e		**1h**		**2h**	**4h**	**3h** molecule A		**3h** molecule B
Bond angles									
O(1)–Sn(1)–N(2)	71.7(1)	O(1)–Sn(1)–N(2)	69.8(1)	O(1)–Sn(1)– N(2)	77.7(1)	77.7(2)	77.8(1)	O(4)–Sn(2)– N(5)	77.4(1)
O(1)–Sn(1)–N(3)	77.4(1)	O(1)–Sn(1)–N(3)	78.1(1)	O(1)–Sn(1)–C(14)	96.0(2)	97.3(3)	98.9(2)	O(4)–Sn(2)– C(34)	102.3(2)
O(2)–Sn(1)–N(1)	76.5(1)	O(2)–Sn(1)–N(1)	76.2(1)	O(1)–Sn(1)–C(18)	104.2(2)	104.3(3)	97.8(2)	O(4)–Sn(2)–C(38)	97.0(2)
O(2)–Sn(1)–N(3)	68.9(1)	O(2)–Sn(1)–N(3)	70.6(1)	N(1)–Sn(1)–O(1)	150.4(1)	150.9(2)	151.2(1)	N(4)–Sn(2)–O(4)	150.2(2)
N(2)–Sn(1)–N(1)	65.9(1)	N(2)–Sn(1)–N(1)	65.5(1)	N(2)–Sn(1)–N(1)	72.7(1)	73.2(2)	73.4(1)	N(5)–Sn(2)–N(4)	72.9(2)
C(19)–Sn(1)–C(23)	169.2(1	C(20)–Sn(1)–C(24)	170.8(1)	C(14)–Sn(1)–N(1)	90.4(2)	97.2(3)	95.7(2)	C(34)–Sn(2)–N(4)	93.5(2)
C(19)–Sn(1)–O(1)	93.4(1)	C(20)–Sn(1)–O(1)	89.1(2)	C(18)–Sn(1)–N(1)	96.7(2)	91.3(3)	95.0(2)	C(38)–Sn(2)–N(4)	94.3(2)
C(19)–Sn(1)–N(2)	90.0(1)	C(20)–Sn(1)–N(2)	86.8(1)	C(18)–Sn(1)–C(14)	124.4(2)	116.9(4)	122.5(2)	C(38)–Sn(2)–C(34)	125.0(3)
C(19)–Sn(1)–N(1)	84.0(1)	C(20)–Sn(1)–N(1)	86.7(2)	C(7)–N(2)–Sn(1)	125.0(3)	122.1(4)	123.7(3)	C(27)–N(5)–Sn(2)	124.5(3)
C(19)–Sn(1)–O(2)	85.8(1)	C(20)–Sn(1)–O(2)	93.6(2)	C(8)–N(2)–Sn(1)	115.7(3)	114.9(3)	116.1(3)	C(28)–N(5)–Sn(2)	116.7(3)
C(19)–Sn(1)–N(3)	96.5(1)	C(20)–Sn(1)–N(3)	93.1(2)	N(2)–Sn(1)–C(18)	115.7(2)	120.9(4)	118.6(2)	N(5)–Sn(2)–C(38)	117.3(2)
C(23)–Sn(1)–O(1)	97.2(1)	C(24)–Sn(1)–O(1)	92.1(2)	N(2)–Sn(1)–C(14)	119.1(2)	121.4(3)	118.6(2)	N(5)–Sn(2)–C(34)	117.1(3)
C(23)–Sn(1)–N(2)	91.2(1)	C(24)–Sn(1)–N(2)	85.1(1)	N(2)–C(7)–C(6)	110.0(3)	114.3(5)	111.0(3)	N(5)–C(27)–C(26)	109.9(4)
C(23)–Sn(1)–N(1)	86.7(1)	C(24)–Sn(1)–N(1)	86.0(2)	C(8)–N(2)–C(7)	119.3(3)	122.8(4)	120.2(3)	C(28)–N(5)–C(27)	118.4(4)
C(23)–Sn(1)–O(2)	86.7(1)	C(24)–Sn(1)–O(2)	90.1(1)	N(2)–C(7)–O(4)		123.0(2)			
C(23)–Sn(1)–N(3)	87.9(1)	C(24)–Sn(1)–N(3)	96.1(2)	N(2)–C(7)–O(2)	115.3(4)				

distortion in the molecule. The N(2)–C(7) bond length of 1.434(5) Å and the N(2)–C(7)–C(6) bond angle of 111.0(3)° corroborate the formation of the reduced complex, **3h**.

4. Conclusions

This contribution reveals that heptacoordinated complexes, **1a**–**1l,** and pentacoordinated complexes, **2h**, **3h**, **4h**, can be isolated depending upon the stoichiometry and the reaction conditions. The electronic effect of the nitro-phenols favors the formation of products where the original imine bond (C=N) acts as an electrophilic center for both the reduction and the oxidation reactions, thereby generating the corresponding amine or amide **3h** and **4h** complexes, most probably via a Cannizzaro reaction.

5. Experimental

2-Aminophenol, 2-amino-4-methylphenol, 2-amino-4-chlorophenol, 2-amino-4-nitrophenol, 2-pyridinecarboxaldehyde, 2-picolinic acid, dimethyl, diphenyl and dibutyltin oxide, were obtained from the Aldrich Chemical Co. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a JEOL Eclipse +300. Chemical shifts (ppm) are relative to $(CH_3)_4Si$, and coupling constants are quoted in Hz. Melting points were measured on a Fisher Johns apparatus and are uncorrected. Mass spectra were obtained with a JEOL JMS-AX505 HA mass spectrometer. The elemental analysis was obtained on an Exeter Analytical CE-440. The IR spectra were recorded on a Bruker Tensor 27. The X-Ray crystallographic studies were done on a Bruker Smart Apex CCD diffractometer with a $\lambda_{(Mo\ K\alpha)} = 0.71073$ Å, graphite monochromator, at $T = 293$ K. All structures were solved by direct methods; all nonhydrogen atoms were refined anisotropically, using full-matrix, least squares techniques. All hydrogen atoms were placed on idealized positions based on the hybridization with thermal parameters fixed at 1.2 times (for –CH) and 1.5 times (for $-CH_3$) the value of the attached atom. Structure solutions and refinements were performed using SHELXTL v 6.10.

5.1. Complex *1a*

To a solution of 0.1143 g (1.048 mmol) de 2-aminophenol in 20 mL of benzene, 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1732 g (1.051 mmol) of dimethyltin oxide and 0.1290 g (1.048 mmol) of 2-picolinic acid was added. The reaction mixture was refluxed for 20 min, then 15 mL of solvent was removed under reduced pressure giving a precipitate, which was filtered to leave 0.4493 g (91.6% yield) of a dark red solid, m.p. 234–237 °C; IR (KBr cm^{-1}): 1645 (s, $\nu_{asym}CO_2$), 1364 (s, $\nu_{sym}CO_2$), 1593 (s, νC=N), 421 (w, νSn–N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.50 (6H, s, $^{2}J(^{1}H-^{119/117}Sn) = 115.7$, 110.7 Hz, Sn-$CH_3$), 6.65 (1H, ddd, $J = 8.2$, 7.1, 1.1 Hz, H-13), 7.05 (1H, dd, $J = 8.4$, 1.1 Hz, H-11), 7.31 (1H, ddd, $J = 8.4$, 7.1, 1.4 Hz, H-12), 7.56 (1H, dd, $J = 8.2$, 1.4 Hz, H-14), 7.60 (1H, ddd, $J = 7.6$, 5.1, 1.0 Hz, H-3), 7.69 (1H, ddd, $J = 7.6$, 5.3, 1.2 Hz, H-17), 7.74 (1H, d, $J = 7.8$ Hz, H-5), 8.00 (1H, ddd, $J = 7.8$, 7.6, 1.5 Hz, H-4), 8.07 (1H, ddd, $J = 7.8$, 7.6, 1.5 Hz, H-18), 8.52 (1H, d, $J = 7.8$ Hz, H-19), 8.75 (s, 1H, H-7), 9.77 (1H, d, $J = 5.3$ Hz, H-16) 9.88 (1H, d, $J = 5.1$ Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.8 (Sn-CH_3), 115.4 (C-14), 116.5 (C-11), 122.0 (C-13), 125.7 (C-19), 126.3 (C-17, C-3), 126.4 (C-5), 129.9 (C-9), 133.4 (C-12), 139.0 (C-4), 140.0 (C-18), 142.2 (C-7), 148.0 (C-16), 149.9 (C-6), 151.2 (C-2), 155.6 (C-20), 164.1 (C-10), 166.6 (C-21); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −428.1; MS (FAB$^+$) [m/z] (%): [(M^+, 469]

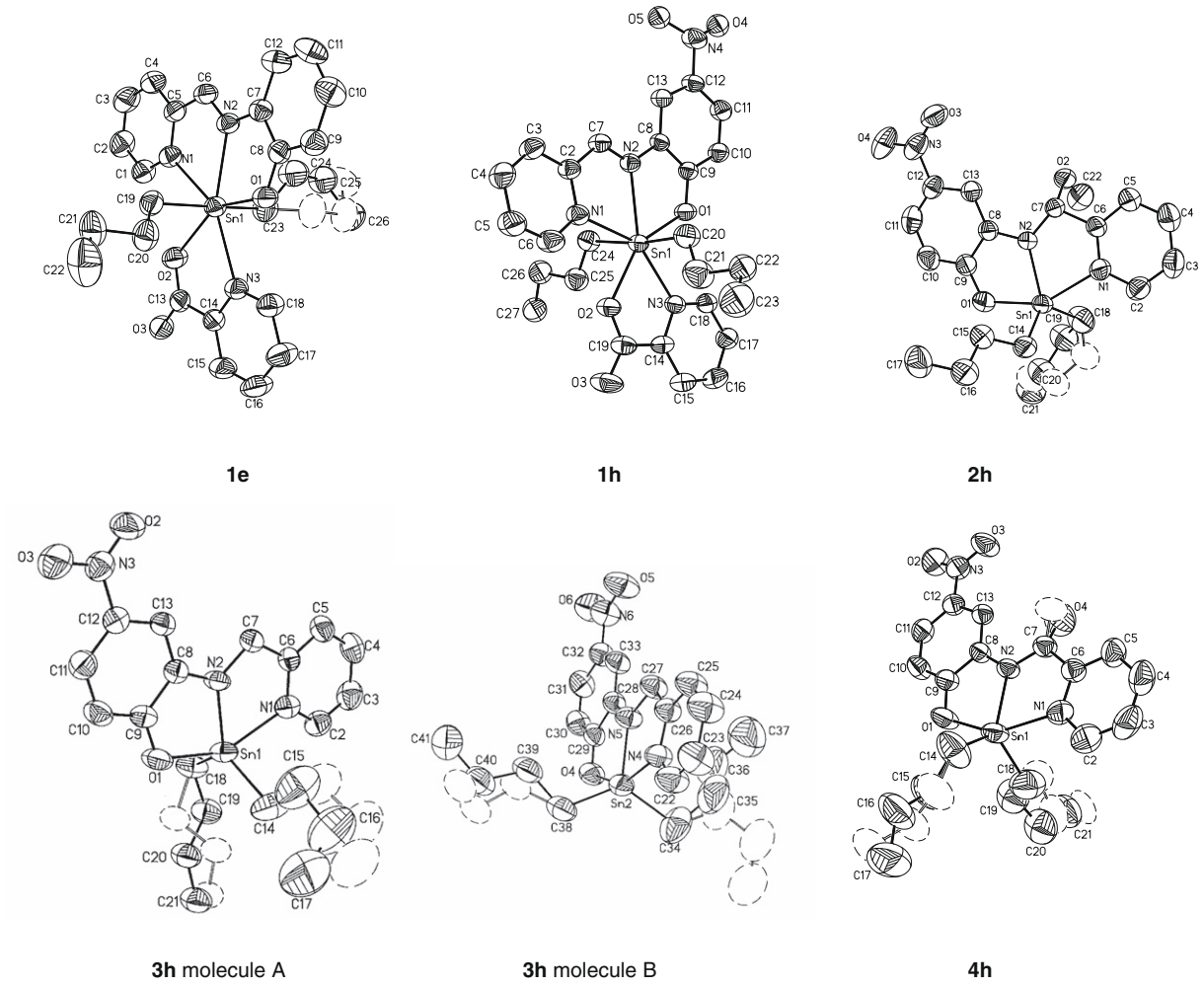


Fig. 1. Perspective view of molecular structures of complexes **1e**, **1h**, **2h**, **3h** and **4h** ORTEP (Thermal ellipsoids at 30% of probability level minor component of disordered side chain drawn using open ellipsoids and broken lines).

(5); [(M−Me)$^+$, 454] (20), [(M−PyCOO)$^+$, 347] (100), [(M−PyCOO −2Me)$^+$, 317] (20);HR-MS (FAB$^+$) *m*/*z*: 454.0214 (Calcd. for the fragment ion $C_{19}H_{16}O_3N_3Sn$), Observed: 454.0200. Anal. Calc. for $C_{20}H_{19}N_3O_3Sn$: C, 51.32; H, 4.09; N, 8.98. Found: C, 51.37; H, 4.17; N, 9.02%.

5.2. Complex ***1b***

Following the procedure described for complex **1a,** complex **1b** was prepared from 0.1289 g (1.048 mmol) of 2-amino-4-methylphenol, 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1727 g (1.048 mmol) dimethyltin oxide, and 0.1291 g (1.048 mmol) of 2-picolinic acid in 30 mL of methanol. The reaction mixture was refluxed for 20 min, giving 0.4875 g (96.5% yield) of dark red solid, m.p. 236–239 °C; IR (KBr cm^{-1}): 1659 (s, $\nu_{asym}CO_2$), 1356 (s, $\nu_{sym}CO_2$), 1596 (s, νC=N), 419 (w, νSn–N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.49 (6H, s, $^2J(^1H–^{119/117}Sn)$ = 115.7, 110.8 Hz, Sn-*CH*$_3$), 2.32 (1H, s, CH_3), 6.97 (1H, d, *J* = 8.5 Hz, H-11), 7.15 (1H, dd, *J* = 8.5, 2.1 Hz, H-12), 7.36 (1H, d, *J* = 2.1 Hz, H-14), 7.58 (1H, ddd, *J* = 7.6, 5.2, 1.0 Hz, H-3) 7.69 (1H, ddd, *J* = 7.6, 5.4, 1.2 Hz, H-17), 7.72 (1H, d, *J* = 7.4 Hz, H-5), 7.99 (1H, ddd, *J* = 7.6, 7.4, 1.6 Hz, H-4), 8.07 (1H, ddd, *J* = 7.7, 7.6, 1.6 Hz, H-18), 8.52 (1H, d, *J* = 7.7 Hz, H-19), 8.72 (1H, s, H-7), 9.76 (1H, d, *J* = 5.4 Hz, H-16), 9.87 (1H, d, *J* = 5.2 Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.8 (Sn-CH_3), 20.8 (Ar-CH_3), 116.1 (C-14), 121.7 (C-11), 124.7 (C-13), 125.7 (C-19), 126.4 (C-17), 126.2 (C-3), 125.7(C-5), 129.3 (C-9), 134.9 (C-12), 139.0 (C-4), 139.9 (C-18), 141.6 (C-7), 148.0 (C-16), 148.1 (C-6), 151.2 (C-2), 149.9 (C-20), 162.1 (C-10); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −426.2; MS (FAB$^+$) [*m*/*z*] (%): [M$^{\cdot+}$, 483] (2); [(M−Me)$^+$, 468] (5), [(M−PyCOO)$^+$, 361] (40), [(M−PyCOO−2Me)$^+$, 331] (10); HR-MS (FAB$^+$) *m*/*z*: 468.0370 (Calcd. for the fragment ion $C_{20}H_{18}O_3N_3Sn$), Observed 468.0376. Anal. Calc. for $C_{21}H_{21}N_3O_3Sn$: C, 52.32; H, 4.39; N, 8.72. Found: C, 51.03; H, 4.57; N, 8.49%.

5.3. Complex ***1c***

Following the procedure described for complex **1a,** complex **1c** was prepared following from 0.1505 g (1.048 mmol) of 2-amino-4-chlorophenol, 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1728 g (1.049 mmol) dimethyltin oxide and 0.1290 g (1.048 mmol) of 2-picolinic acid in 30 mL of benzene. The reaction mixture was refluxed for 40 min, yielding 0.2673 g (50.8% yield) of dark red crystals, m.p. 246–250 °C**;** IR (KBr cm^{-1}): 1651 (s, $\nu_{asym}CO_2$), 1359 (s, $\nu_{sym}CO_2$), 1594 (s, νC=N), 418 (w, νSn–N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.49 (6H, s, $^2J(^1H–^{119/117}Sn)$ = 115.6, 110.5 Hz, Sn-*CH*$_3$), 6.98 (1H, d, *J* = 8.9 Hz, H-11), 7.24 (1H, dd, *J* = 8.9, 2.6 Hz, H-12), 7.54 (1H, d, *J* = 2.6 Hz, H-14), 7.63 (1H, ddd, *J* = 7.6, 5.1, 1.1 Hz, H-3), 7.71 (1H, ddd, *J* = 7.6, 5.4, 1.4 Hz, H-17), 7.77 (1H, d, *J* = 7.7 Hz, H-5), 8.03 (1H, ddd, *J* = 7.7, 7.6, 1.7 Hz, H-4), 8.09 (1H, ddd, *J* = 7.7, 7.6, 1.5 Hz, H-18), 8.53 (1H, d, *J* = 7.7 Hz, H-19), 8.71 (1H, s, H-7), 9.72 (1H, d, *J* = 5.4 Hz, H-16), 9.88 (1H, d, *J* = 5.1 Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.8 (($^1J(^{13}C–^{119/117}Sn)$ = 1190, 1130 Hz, Sn-CH_3), 116.3 (C-14), 123.0 (C-11), 120.0 (C-13), 125.7 (C-19), 126.7 (C-3,C-17), 126.5 (C-5), 130.2 (C-9),

132.2 (C-12), 139.2 (C-4), 140.2 (C-18), 143.0 (C-7), 147.9 (C-16), 148.1 (C-6), 149.7 (C-20), 151.3 (C-2), 162.7 (C-10), 166.5 (C-21); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −425.7; MS (FAB^+) [m/z] (%): [$M^{\cdot+}$, 503] (5); [(M−Me)$^+$, 488] (20), [(M−PyCOO)$^+$, 381] (100); HR-MS (FAB^+) m/z: 487.9824 (Calcd. for the fragment ion $C_{20}H_{18}O_3N_3Sn$), Observed 487.9821. Anal. Calc. for $C_{20}H_{18}N_3O_3ClSn$: C, 47.80; H, 3.61; N, 8.36. Found: C, 48.23; H, 3.74; N, 8.30%.

5.4. Complex **1d**

Following the procedure described for complex **1a,** complex **1d** was prepared from 0.1618 g (1.048 mmol) of 2-amino-4-nitrophenol, 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1730 g (1.050 mmol) dimethyltin oxide and 0.1290 g (1.048 mmol) of 2-picolinic acid. The reaction mixture was refluxed for 40 min giving 0.3718 g (69% yield) of orange crystals, m.p. 267–270 °C**;** IR (KBr cm^{-1}): 1649 (s, $\nu_{asym}CO_2$), 1351 (s, $\nu_{sym}CO_2$), 1592 (s, νC=N), 419 (w, νSn–N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.52 (6H, s, ^2J (^{1}H–$^{119/117}$Sn) = 115.30, 110.35 Hz, Sn-*CH*$_3$), 7.00 (1H, d, J = 9.4 Hz, H-11), 7.71 (1H, ddd, J = 7.7, 5.1, 1.2 Hz, H-3), 7.75 (1H, ddd, J = 7.6, 5.4, 1.4 Hz, H-17), 7.94 (1H, d, J = 7.6 Hz, H-5), 8.12 (1H, ddd, J = 7.7, 7.6, 1.7 Hz, H-4), 8.13 (1H, ddd, J = 7.7, 7.6, 1.7 Hz, H-18), 8.22 (1H, dd, J = 9.4, 2.8 Hz, H-12), 8.55 (1H, d, J = 7.7 Hz, H-19), 8.62 (1H, d, J = 2.8 Hz, H-14), 9.01 (1H, s, H-7), 9.70 (1H, d, J = 5.4 Hz, H-16), 9.92 (1H, d, J = 5.1 Hz, H-2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 13.8 (Sn-CH_3), 114.3 (C-11), 121.3 (C-12), 125.9 (C-5), 127.1 (C-3), 127.8 (C-17), 128.1 (C-19), 128.4 (C-14), 129.6 (C-9), 136.1 (C-13), 140.0 (C-4), 140.7 (C-18), 146.9 (C-7), 147.6 (C-6), 147.9 (C-16), 149.7 (C-20), 151.2 (C-2), 166.0 (C-10), 170.0 (C-21); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −427.9; MS (FAB^+) [m/z] (%): [(M+1)$^+$, 515] (5); [(M−Me)$^+$, 499] (15), [(M−PyCOO)$^+$, 392] (60); [(M−PyCOO−2Me)$^+$, 362] (10); HR-MS (FAB^+) m/z: 499.0064 (Calcd. for the fragment ion $C_{20}H_{18}O_3N_3Sn$), Observed 499.0064. Anal. Calc. for $C_{20}H_{18}N_4O_5Sn$: C, 46.82; H, 3.54; N, 10.92. Found: C, 46.63; H, 3.74; N, 10.60%.

5.5. Complex **1e**

Following the procedure described for complex **1a,** complex **1e** was prepared from 0.1144 g (1.048 mmol) of 2-aminophenol, 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.2609 g (1.048 mmol) dibutyltin oxide and 0.1290 g (1.048 mmol) of 2-picolinic acid. The reaction mixture was refluxed for 40 min, then 80% of the solvent was evaporated under vacuum. The resulting precipitate was filtered thereby giving 0.4541 g (78.5% yield) of a dark red solid, m.p. 218–221 °C; IR (KBr cm^{-1}): 1642 (s, $\nu_{asym}CO_2$), 1360 (s, $\nu_{sym}CO_2$), 1594 (s, νC=N), 416 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.47 (6H, t, J = 6.85 Hz, Sn(CH_2)$_3$*CH*$_3$), 0.80–1.16 (12H, m, Sn-(*CH*$_2$)$_3$CH$_3$), 6.63 (1H, ddd, J = 8.1, 7.0, 1.0 Hz, H-13), 7.05 (1H, dd, J = 8.4, 1.0 Hz, H-11), 7.31 (1H, t, J = ddd, 8.4, 7.0, 1.3 Hz, H-12), 7.56 (1H, dd, J = 8.1, 1.3 Hz, H-14), 7.57 (1H, ddd, J = 7.7, 5.2, 1.0 Hz, H-3), 7.69 (1H, ddd, J = 7.6, 5.6, 1.2 Hz, H-17), 7.75 (1H, d, J = 7.7 Hz, H-5), 8.00 (1H, ddd, J = 7.7, 7.7, 1.4 Hz, H-4), 8.07 (1H, ddd, J = 7.6, 7.6, 1.5 Hz, H-18), 8.51 (1H, d, J = 7.6 Hz, H-19), 8.80 (1H, s, H-7), 9.74 (1H, d, J = 5.6 Hz, H-16), 9.84 (1H, d, J = 5.2 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 13.5 (^4J(^{13}C–^{119}Sn) = 13.9 Hz, C_δ), 26.3 (^3J(^{13}C–^{119}Sn) = 182.3 Hz, C_γ), 27.8 (^2J(^{13}C–$^{119/117}$Sn) = 60.0, 45.0 Hz, C_β), 32.6 (^1J(^{13}C–$^{119/117}$Sn) = 1130, 1080 Hz, C_α), 115.1 (C-14), 116.3 (C-11), 121.9 (C-13), 125.7 (C-19), 126.1 (C-17), 126.2 (C-3), 126.3 (C-5), 130.5 (C-9), 133.3 (C-12), 139.0 (C-4), 139.9 (C-18), 142.3 (C-7), 148.2 (C-16), 148.5 (C-6), 150.4 (C-20), 151.4 (C-2), 162.9 (C-10), 167.0 (C-21); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −443.6; MS (FAB^+) [m/z] (%): [$M^{\cdot+}$, 553] (2); [(M−Bu)$^+$, 496] (53), [(M−PyCOO)$^+$, 431] (100), [(M−PyCOO−2Bu)$^+$, 317] (55); HR-MS (FAB^+) m/z: 496.0683 (Calcd. for $C_{22}H_{22}N_3O_3Sn$), Observed 496.0694. Anal. Calc. for $C_{20}H_{18}N_4O_5Sn$: C, 56.55; H, 5.55; N, 7.61. Found: C, 57.56; H, 5.98; N, 7.37%.

5.6. Complex **1f**

Following the procedure described for complex **1a,** complex **1f** was prepared from 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1290 g (1.048 mmol) of 2-amino-4-methylphenol, 0.2609 g (1.048 mmol) of dibutyltin oxide and 0.1290 g (1.048 mmol) of 2-picolinic acid in 25 mL of methanol. This yielded 0.4701 g (79.3% yield) of a dark red solid, m.p. 224–227 °C; IR (KBr cm^{-1}): 1644 (s, $\nu_{asym}CO_2$), 1358 (s, $\nu_{sym}CO_2$), 1597 (s, νC=N), 416 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.49 (6H, t, J = 7.02 Hz, Sn(CH_2)$_3$*CH*$_3$), 0.79–1.15 (12H, m, Sn-(*CH*$_2$)$_3$CH$_3$), 2.30 (3H, s, Ar-CH_3), 6.97 (1H, d, J = 8.5 Hz, H-11), 7.14 (1H, dd, J = 8.5, 1.8 Hz, H-12), 7.36 (1H, d, J = 1.8 Hz, H-14), 7.57 (1H, ddd, J = 7.6, 5.1, 1.0 Hz, H-3), 7.68 (1H, ddd, J = 7.5, 5.4, 1.2 Hz, H-17), 7.72 (1H, d, J = 7.7 Hz, H-5), 7.99 (1H, ddd, J = 7.7, 7.6, 1.7 Hz, H-4), 8.06 (1H, ddd, J = 7.6, 7.5, 1.7 Hz, H-18), 8.52 (1H, d, J = 7.6 Hz, H-19), 8.76 (1H, s, H-7), 9.73 (1H, d, J = 5.4 Hz, H-16), 9.83 (1H, d, J = 5.1 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 13.5 (^4J(^{13}C–^{119}Sn) = 12.7 Hz, C_δ), 20.8 (Ar-CH_3), 26.3 (^3J(^{13}C–^{119}Sn) = 183.5 Hz, C_γ), 27.8 (^2J(^{13}C–^{119}Sn) = 46.2 Hz, C_β), 32.5 (^1J(^{13}C–$^{119/117}$Sn) = 1128, 1080 Hz, C_α), 116.1 (C-14), 121.6 (C-11), 124.3 (C-13), 125.6 (C-19), 125.9 (C-5), 126.0 (C-3), 126.2 (C-17), 129.9 (C-9), 134.7 (C-12), 138.9 (C-4), 139.8 (C-18), 141.6 (C-7), 148.3 (C-16), 148.6 (C-6), 150.4 (C-20), 151.4 (C-2), 162.3 (C-10), 167.0 (C-21); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −441.3; MS (FAB^+) [m/z] (%): [$M^{\cdot+}$, 567] (3); [(M−Bu)$^+$, 510] (75), [(M−PyCOO)$^+$, 445] (100), [(M−PyCOO-2Bu)$^+$, 331] (95); HR-MS (FAB^+) m/z: 510.0840 (Calcd. for the fragment ion $C_{23}H_{24}N_3O_3Sn$), Observed 510.0851. Anal. Calc. for $C_{27}H_{33}N_3O_3Sn$: C, 57.27; H, 5.87; N, 7.42. Found: C, 57.01; H, 5.88; N, 7.31%.

5.7. Complex **1g**

For complex **1g** 0.2609 g (1.048 mmol) of dibutyltin oxide was added to a solution of 0.1 mL (1.048 mmol) 2-pyridinecarboxaldehyde and 0.1501 g (1.046 mmol) of 2-amino-4-chlorophenol in 20 mL methanol. After 5 min, the solution turned dark red, and 0.1290 g (1.048 mmol) of 2-picolinic acid was added. The reaction mixture was refluxed for 20 min after which time the solvent was removed under vacuum. The solution was filtered, affording 0.4310 g (70.2% yield) of a dark red solid, m.p. = 217–220 °C; IR (KBr cm^{-1}): 1641 (s, $\nu_{asym}CO_2$), 1359 (s, $\nu_{sym}CO_2$), 1594 (s, νC=N), 417 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.50 (6H, t, J = 7.0 Hz, Sn-(CH$_2$)$_3$*CH*$_3$), 0.80–1.15 (12H, m, Sn-(*CH*$_2$)$_3$CH$_3$), 6.98 (1H, d, J = 8.9 Hz, H-11), 7.23 (1H, dd, J = 8.9, 2.5 Hz, H-12), 7.53 (1H, d, J = 2.5 Hz, H-14), 7.62 (1H, ddd, J = 7.6, 5.0, 1.0 Hz, H-3), 7.70 (1H, ddd, J = 7.5, 5.4, 1.2 Hz, H-17), 7.76 (1H, d, J = 7.7 Hz, H-5), 8.03 (1H, ddd, J = 7.7, 7.6, 1.7 Hz, H-4), 8.09 (1H, ddd, J = 7.6, 7.5, 1.7 Hz, H-18), 8.53 (1H, d, J = 7.6 Hz, H-19), 8.74 (1H, s, H-7), 9.68 (1H, d, J = 5.4 Hz, H-16), 9.86 (1H, d, J = 5.1 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 13.5 (C_δ), 26.2 (C_γ), 27.8 (C_β), 32.6 (C_α), 116.1(C-14), 119.7 (C-13), 122.9 (C-11), 125.8 (C-19), 126.4 (C-17), 126.5 (C-3), 126.6 (C-5), 130.7 (C-9), 133.1 (C-12), 139.1 (C-4), 140.1 (C-18), 143.2 (C-7), 148.1 (C-16), 148.3 (C-6), 150.2 (C-20), 151.5 (C-2), 157.2 (C-10), 163.4 (C-21), ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −441.4; MS (FAB^+) [m/z] (%): [$M^{\cdot+}$, 587] (2); [(M−Bu)$^+$, 530] (50), [(M−PyCOO)$^+$, 465] (100), [(M−PyCOO−2Bu)$^+$, 351] (55); HR-MS (FAB^+) m/z: 530.0293 (Calcd. for the fragment ion $C_{22}H_{21}N_3O_3ClSn$), Observed 530.0298. Anal. Calc. for $C_{26}H_{30}N_3O_3ClSn$: C, 53.23; H, 5.15; N, 7.16. Found: C, 53.90; H, 5.24; N, 7.11%.

5.8. Complex **1h**

Following the procedure described for complex **1g**, complex **1h** was prepared from 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1615 g (1.048 mmol) of 2-amino-4-nitrophenol, 0.2609 g (1.048 mmol) of dibutyltin oxide, and 0.1290 g (1.048 mmol) of 2-picolinic acid thereby giving 0.5247 g (83.7% yield) of a brown-orange solid, m.p. = 211–216 °C; IR (KBr cm^{-1}): 1648 (s, $\nu_{asym}CO_2$), 1354 (s, $\nu_{sym}CO_2$), 1593 (s, νC=N), 416 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.50 (6H, t, J = 7.3 Hz, Sn-$(CH_2)_3CH_3$), 0.77–1.17 (12H, m, Sn-$(CH_2)_3CH_3$), 7.01 (1H, d, J = 9.4 Hz, H-11), 7.68 (1H, ddd, J = 7.6, 5.3, 1.1 Hz, H-3), 7.75 (1H, ddd, J = 7.6, 5.4, 1.2 Hz, H-17), 7.91 (1H, d, J = 7.6 Hz, H-5), 8.12 (1H, ddd, J = 7.6, 7.6, 1.7 Hz, H-4), 8.14 (1H, ddd, J = 7.7, 7.6, 1.7 Hz, H-18), 8.22 (1H, dd, J = 9.4, 2.5 Hz, H-12), 8.55 (1H, d, J = 7.7 Hz, H-19), 8.65 (1H, d, J = 2.5 Hz, H-14), 9.00 (1H, s, H-7), 9.65 (1H, d, J = 4.5 Hz, H-16), 9.87 (1H, d, J = 5.0 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 13.4 (C_δ), 26.2 (C_γ), 27.8 (C_β), 32.9 (C_α), 113.8 (C-11), 121.3 (C-12), 125.9 (C-19), 126.7 (C-5), 127.3 (C-3), 127.5 (C-17), 128.4 (C-14), 129.7 (C-9), 135.8 (C-13), 139.6 (C-4), 139.6 (C-18), 146.2 (C-7), 147.7 (C-6), 147.9 (C-16), 149.9 (C-20), 151.7 (C-2), 166.7 (C-10), 170.4 (C-21), ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −441.1; MS (FAB^+) [m/z] (%): [$M^{\cdot+}$, 598] (2); [(M−PyCOO)$^+$, 476] (100), [(M−PyCOO−2Bu)$^+$, 362] (35), [(M−PyCOO−NO_2)$^+$, 430] (10); HR-MS (FAB^+) m/z: 476.0996 (Calcd. for the fragment ion $C_{20}H_{26}N_3O_3Sn$), Observed 476.0996. Anal. Calc. for $C_{26}H_{30}N_4O_5Sn$: C, 52.29; H, 5.06; N, 9.38. Found: C, 51.78; H, 5.11; N, 9.10%.

5.9. Complex **1i**

0.3030 g (1.049 mmol) diphenyltin oxide and 0.1290 g (1.048 mmol) of 2-picolinic acid in 30 mL benzene was added to a solution of 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1144 g (1.048 mmol) of 2-aminophenol. The combined solution was refluxed for 40 min. After evaporating 20 mL of solvent to vacuum, a precipitate formed which was then filtered to give 0.6175 g (99.5%) of a dark red solid, m.p. 295 °C; IR (KBr cm^{-1}): 1657 (s, $\nu_{asym}CO_2$), 1343 (s, $\nu_{sym}CO_2$), 1594 (s, νC=N), 421 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.67 (1H, ddd, J = 8.6, 7.0, 1.4 Hz, H-13), 6.97–7.02 (6H, m, H-*m*, H-*p*), 7.28 (1H, dd, J = 9.1, 1.4 Hz, H-11), 7.39–7.44 (2H, m, H-12, H-14), 7.51 (1H, d, J = 8.1 Hz, H-5), 7.56 (1H, ddd, J = 7.4, 5.5, 1.3 Hz, H-3), 7.60–7.63 (4H, m, H-*o*), 7.64 (1H, ddd, J = 7.6, 5.2, 1.2 Hz, H-17), 7.89 (2H, ddd, J = 7.8, 7.6, 1.5 Hz, H-4, H-18), 8.33 (1H, d, J = 7.8. Hz, H-19), 8.49 (1H, s, H-7), 9.87 (1H, d, J = 5.2. Hz, H-16), 10.31 (1H, d, J = 5.5 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 115.9 (C-14), 116.5 (C-11), 121.1 (C-13), 125.5 (C-19), 126.4 (C-17), 126.6 (C-3), 127.2 (C-5), 128.0 (C-*p*), 128.1 (C-*m*), 133.6 (C-12), 134.3 (^2J(^{13}C–^{119}Sn) = 66.9 Hz, C-*o*), 139.1 (C-4), 139.9 (C-18), 142.5 (C-7), 148.1 (C-16), 148.3 (C-6), 151.6 (C-2); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −583.8; MS (FAB^+) [m/z] (%): [$M^{\cdot+}$, 593] (5); [(M−Ph)$^+$, 516] (10), [(M−PyCOO)$^+$, 471] (40), [(M−PyCOO−Ph)$^+$, 394] (20), [(M−PyCOO−2Ph)$^+$, 317] (10); HR-MS (FAB^+) m/z: 516.0370; (Calcd. for the fragment ion $C_{24}H_{18}N_3O_3Sn$), Observed 516.0372. Anal. Calc. for $C_{30}H_{23}N_3O_3Sn$: C, 60.84; H, 3.91; N, 7.10. Found: C, 58.81; H, 4.34; N, 6.61%.

5.10. Complex **1j**

Following the procedure described for complex **1i,** complex **1j** was formed from 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde, 0.1290 g (1.048 mmol) of 2-amino-4-methylphenol, 0.3031 g (1.049 mmol) diphenyltin oxide and 0.1289 g (1.048 mmol) of 2-picolinic acid, thereby producing 0.6030 g (94.9%) of a dark red solid, m.p. 250 °C (dec); IR (KBr cm^{-1}): 1657 (s, ν_{asym} CO_2), 1345 (s, $\nu_{sym}CO_2$), 1598 (s, νC=N), 420 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.30 (3H, s, Ar-CH_3), 6.90–7.09 (6H, m, H-*m*, H-*p*), 7.18 (1H, d, J = 1.7 Hz, H-14), 7.19 (1H, d, J = 8.4 Hz, H-11), 7.24 (1H, dd, J = 8.4, 1.7 Hz, H-12), 7.42 (1H, d, J = 7.6 Hz, H-5), 7.53 (1H, ddd, J = 7.6, 5.4, 1.4 Hz, H-3), 7.58–7.63 (5H, m, H-17, H-*o*), 7.83 (1H, ddd, J = 7.6, 7.6, 1.7 Hz, H-4), 7.86 (1H, ddd, J = 7.7, 7.7, 1.7 Hz, H-18), 8.29 (1H, d, J = 7.7 Hz, H-19), 8.39 (1H, s, H-7), 9.84 (1H, d, J = 4.7 Hz, H-16), 10.27 (1H, d, J = 5.4 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 20.8 (Ar-CH_3), 116.4 (C-14), 120.7 (C-11), 125.2 (C-13), 125.4 (C-19), 126.1 (C-3), 126.6 (C-5), 127.0 (C-17), 128.0 (C-*m*, C-*p*), 130.2 (C-9), 134.4 (C-*p*), 135.0 (C-12), 139.0 (C-4), 139.9 (C-18), 141.9 (C-7), 147.6 (C-*ipso*), 148.2 (C-16), 149.1 (C-20), 151.4 (C-2), 151.9 (C-6), 162.6 (C-10), 166.0 (C-21), ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −582.7; MS (FAB^+) [m/z] (%): [$M^{\cdot+}$, 607], (2), [(M−Ph)$^+$, 530] (1), [(M−PyCOO)$^+$, 485] (15), [(M−PyCOO−2Ph)$^+$, 331] (3); HR-MS (FAB^+) m/z: 485.0676; (Calcd. for the fragment ion $C_{25}H_{21}ON_2Sn$), Observed 485.0686. Anal. Calc. for $C_{31}H_{25}N_3O_3Sn$: C, 61.42; H, 4.16; N, 6.93. Found: C, 61.23; H, 4.23; N, 6.88%.

5.11. Complex **1k**

Following the procedure described for **1i,** complex **1k** was formed from 0.1 mL of 2-pyridinecarboxaldehyde, 0.1509 g (1.051 mmol) of 2-amino-4-chlorophenol, 0.3031 g diphenyltin oxide and 0.1291 g (1.048 mmol) 2-picolinic acid, which was refluxed for 20 min and which lead to 0.5445 g (83% yield) of a red solid, m.p. 280–285 °C; IR (KBr cm^{-1}): 1659 (s, $\nu_{asym}CO_2$), 1359 (s, $\nu_{sym}CO_2$), 1594 (s, νC=N), 419 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.91–7.11 (6H, m, H-*m*, H-*p*), 7.23 (1H, d, J = 9.4 Hz, H-11), 7.35 (1H, dd, J = 9.4, 2.5 Hz, H-12), 7.36 (1H, s, H-14), 7.50 (1H, d, J = 7.6 Hz, H-5), 7.54–7.52 (5H, m, H-3, H-*o*), 7.67 (1H, ddd, J = 7.5, 5.2, 1.1, H-17), 7.89 (2H, ddd, J = 7.7, 7.5, 1.1 Hz, H-4, H-18), 8.33 (1H, d, J = 7.7 Hz, H-19), 8.38 (s, 1H, H-7), 9.82 (1H, d, J = 5.2 Hz, H-16), 10.29 (1H, d, J = 5.2 Hz, H-2); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 116.7 (C-14), 120.6 (C-13), 122.4 (C-11), 125.6 (C-19), 127.1 (C-3), 127.3 (C-17), 128.2 (C-5), 128.4 (C-*m, p*), 131.3 (C-9), 133.5 (C-12), 134.3 (C-*o*), 139.8 (C-4), 140.5 (C-18), 144.5 (C-7), 147.3 (C-*ipso*), 148.3 (C-16), 149.5 (C-6), 151.8 (C-20), 151.9 (C-2), 163.3 (C-10), 166.2 (C-21); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −580.6; MS(FAB^+) [m/z] (%): [$M^{\cdot+}$, 627] (5); [(M−Ph)$^+$, 550] (5), [(M−PyCOO)$^+$, 505] (20), [(M−PyCOO−2Ph)$^+$, 351] (5); HR-MS (FAB^+) m/z: 549.9980 (Calcd. for the fragment ion $C_{24}H_{17}O_3N_3ClSn$), Observed 549.9989. Anal. Calc. for $C_{30}H_{22}N_3O_3ClSn$: C, 57.50; H, 3.54; N, 6.71. Found: C, 56.30; H, 3.60; N, 6.32%.

5.12. Complex **1l**

Following the procedure described for **1i,** complex **1l** was formed from 0.1 mL of pyridinecarboxaldehyde, 0.1614 g (1.047 mmol) of 2-amino-4-nitrophenol, 0.3031 g (1.049 mmol) of diphenyltin oxide and 0.1289 g (1.048 mmol) of 2-picolinic acid, refluxed 20 min to give 0.6069 g (90.9% yield) of an orange solid, m.p. 290 °C (dec); IR (KBr cm^{-1}): 1648 (s, $\nu_{asym}CO_2$), 1362 (s, ν_{sym}-CO_2), 1592 (s, νC=N), 420 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.95–7.09 (6H, m, H-*m*, H-*p*), 7.50 (4H, dd, J = 7.7, 1.8 Hz, H-*o*), 7.29 (1H, d, J = 9.5 Hz, H-11), 7.63 (1H, ddd, J = 7.5, 5.4, 1.4 Hz, H-3), 7.71 (1H, d, J = 7.4 Hz, H-5), 7.78 (1H, ddd, J = 7.7, 5.1, 1.2 Hz, H-17), 7.97 (1H, ddd, J = 7.5, 7.4, 1.65 Hz, H-4), 8.03 (1H, ddd, J = 7.7, 7.7, 1.7 Hz, H-18), 8.34 (1H, dd, J = 9.5, 2.8 Hz, H-12), 8.37 (1H, d, J = 7.7. Hz, H-19), 8.48 (1H, d, J = 2.8 Hz, H-14), 8.72 (s, 1H, H-7), 9.79 (1H, d, J = 5.1 Hz, H-16), 10.32 (1H, d, J = 5.4 Hz, H-2); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 114.1 (C-11), 120.9 (C-12), 125.8 (C-5), 127.3 (C-3), 128.1 (C-17), 128.6 (^2J(^{13}C–^{119}Sn) 119.42 Hz, C-*m*), 128.7 (C-*p*), 128.7 (C-14), 128.9 (C-19), 130.2 (C-9), 134.0 (C-*o*), 137.0 (C-13), 140.2 (C-4), 140.8 (C-18), 147.1 (C-*ipso*), 147.4 (C-7), 148.1 (C-16), 149.3 (C-6), 151.1 (C-20), 152.0 (C-2), 166.1 (C-10), 170.0 (C-21); ^{119}Sn NMR (112 MHz, CD_2Cl_2) δ: −580.5; MS

(FAB$^+$) [m/z] (%): [M$^{\cdot+}$, 638] (4), [(M−Ph)$^+$, 561] (10), [(M−PyCOO)$^+$, 516] (50), [(M−PyCOO−2Ph)$^+$, 362] (5); HR-MS (FAB$^+$) m/z: 561.0221 (Calcd. for the fragment ion $C_{24}H_{17}O_5N_4Sn$), Observed 561.0236. Anal. Calc. for $C_{30}H_{22}N_4O_5Sn$: C, 55.55; H, 3.48; N, 8.79. Found: C, 55.70; H, 3.67; N, 8.52%.

5.13. Complex **2h**

For complex **2h** 0.2609 g (1.048 mmol) of the dibutyltin oxide was added to a solution of 0.2547 g (1.048 mmol) of the Schiff base **2** in 30 mL of toluene/methanol (4:6) mixture. The reaction mixture was refluxed for 8 h, then the solvent was evaporated under reduced pressure, thereby giving 0.4864 g (94.5% yield), of an orange solid which was crystallized from methanol; m.p. 122 °C, IR (KBr cm^{-1}): 3071, 3036, 2950, 2928, 2859, 395, 419, 467, 532, 575, 649, 671; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.76 (3H, t, J = 7.3 Hz, Sn-$(CH_2)_3CH_3$), 0.88 (3H, t, J = 7.3 Hz, Sn-$(CH_2)_3CH_3$), 1.14–1.71 (12H, m, Sn-$(CH_2)_3CH_3$), 2.86 (3H, s, –O–CH_3), 6.37 (1H, s, H-7), 6.69 (1H, d, J = 8.7 Hz, H-11), 7.65 (1H, ddd, J = 7.6, 5.4, 1.1 Hz, H-3), 7.74 (1H, dd, J = 8.7, 2.8 Hz, H-12), 7.89 (1H, d, J = 2.8 Hz, H-14), 7.97 (1H, d, J = 7.8, H-5), 8.17 (1H, ddd, J = 7.8, 7.6, 1.5 Hz, H-4), 8.35 (1H, d, J = 5.4 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.5 (C_δ), 13.6 (C_δ), 19.9, 20.7 ($^1J(^{13}C–^{119/117}Sn)$ = 559.6, 535.4 C_α), 26.4, 26.8 (C_β) 27.2 27.5 (C_γ), 84.0 (C-7), 47.7 (–O–CH_3), 112.5 (C-14), 117.1 (C-12), 106.3 (C-11), 125.4 (C-5), 125.7 (C-3), 138.2 (C-9), 139.4 (C-13), 141.4 (C-4), 143.9 (C-2), 157.1 (C-6), 162.0 (C-10); ^{119}Sn NMR 112 MHz, ($CDCl_3$) δ: −83.0; MS(ESI): [M$^{\cdot+}$] 507 (1), [(M+Na)$^+$, 530], (5), [(M−MeO)$^+$, 476] (100). Anal. Calc. for $C_{21}H_{29}N_3O_4Sn$: C, 49.83; H, 5.77; N, 8.30. Found: C, 50.00; H, 5.78; N, 8.37%.

5.14. Complex **3h**

For complex **3h** 0.5229 g (2.1 mmol) of dibutyltin oxide was added to a solution of 0.4 mL (4.19 mmol) of 2-pyridinecarboxaldehyde and 0.3233 g (2.1 mmol) of 2-amino-4-nitrophenol in 30 mL of a toluene/methanol (4:6) mixture. The reaction mixture was refluxed for 17 h under nitrogen atmosphere. After a week, a precipitate was observed which was filtered, thereby providing 0.3324 g (33.3% yield) or a red solid, mp. 173–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.79 (6H, t, J = 7.2 Hz, Sn-$(CH_2)_3CH_3$), 1.19–1.58 (12H, m, Sn-$(CH_2)_3CH_3$), 4.78 (2H, s, H-7), 6.64 (1H, d, J = 8.7, H-11), 7.26 (1H, d, J = 2.9 Hz, H-14), 7.54 (1H, ddd, J = 7.6, 5.5, 1.0 Hz, H-3), 7.65 (1H, d, J = 7.9 Hz, H-5), 7.68 (1H, dd, J = 8.7, 2.9 Hz, H-12), 8.05 (1H, ddd, J = 7.9, 7.6, 1.6 Hz, H-4), 8.35 (1H, d, J = 5.5 Hz, H-2); 13C NMR (75 MHz, $CDCl_3$) δ: 13.6 (C_δ), 20.3 (($^1J(^{13}C–^{119/117}Sn)$ = 559.9, 535.4 Hz, C_α), 26.2 (C_β), 27.3 (C_γ), 49.3 (C-7) 102.2 (C-11), 111.5 (C-14), 116.0 (C-12), 124.2 (C-3), 124.2 (C-5), 138.1 (C-9), 140.2 (C-4), 141.9 (C-13), 144.2 (C-2), 157.6 (C-6), 162.3 (C-10); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −67.9; MS (FAB+): [M$^{\cdot+}$, 475] (100), [(M−Bu)$^+$, 418] (7). Anal. Calc. for $C_{20}H_{27}N_3O_3Sn$: C, 50.45; H, 5.72; N, 8.82. Found: C, 50.40; H, 5.71; N, 8.85%.

5.15. Complex **4h**

For complex **4h** 0.2611 g (1.049 mmol) of dibutyltin oxide was added to a solution of 0.1 mL (1.048 mmol) of 2-pyridinecarboxaldehyde and 0.1616 g (1.048 mmol) of 2-amino-4-nitrophenol in 30 mL of benzene. The reaction mixture was refluxed for 8 h under nitrogen atmosphere, after which time the solvent was removed under reduced pressure to give 0.4148 g of an orange solid, which was washed with methanol and filtered which contained complexes **3h** and **4h** in a 2:1 ratio. The mixture was treated with warm methanol, and after 3 days, red crystals of **4h** were formed, m.p. 196–197 °C; IR (KBr cm^{-1}): 1648 (s, νCO), 415 (w, νSn–N); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.82 (6H, t, J = 7.2 Hz, Sn-$(CH_2)_3CH_3$), 1.15–1.62 (12H, m, Sn-$(CH_2)_3CH_3$), 6.81 (1H, d, J = 8.9, H-11), 7.79 (1H, ddd, J = 7.7, 5.5, 1.2 Hz, H-3), 7.96 (1H, dd, J = 8.9, 2.8 Hz, H-12), 8.25 (1H, ddd, J = 7.8, 7.7, 1.2 Hz, H-4), 8.38 (1H, d, J = 5.4 Hz, H-2), 8.62 (1H, d, J = 7.8 Hz, H-5), 9.70 (1H, d, J = 2.8 Hz, H-14); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.5 (C_δ), 20.6 ($^1J(^{13}C–^{119/117}Sn)$ = 566.4, 538.8 Hz, (C_α), 26.5 (C_β), 27.1 (C_γ), 116.0 (C-14), 121.8 (C-12), 114.8 (C-11), 124.9 (C-5), 127.6 (C-3), 132.2 (C-9), 137.5 (C-13), 142.3 (C-4), 143.6 (C-2) 149.7 (C-6), 161.8 (C-10), 162.6 (C-7); ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −122.3; MS (EI): [M$^{\cdot+}$, 491] (100), [(M−Bu)$^+$, 434] (10), [M−2Bu)$^+$, 377] (50). Anal. Calc. for $C_{20}H_{25}N_3O_4Sn$: C, 49.01; H, 5.14; N, 8.57. Found: C, 49.51; H, 5.40; N, 8.63%.

6. Supplementary material

CCDC 719552, 719553, 719554, 719555, 719556, 719557, 719558 and 719559 contain the supplementary crystallographic data for **1h**, **1c**, **1e**, **3h**, **2h**, **1f**, **1g** and **4h**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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