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Synthesis, characterization and structural studies of diorganotin(IV) complexes with Schiff base ligand salicylaldehyde isonicotinylhydrazone

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Abstract

Eight diorganotin(IV) complexes of salicylaldehyde isonicotinylhydrazone (H_2SalN) R_2Sn(SalN) R = *t*-Bu **1**, Ph **2**, $PhCH_2$ **3**, *o*-$ClC_6H_4CH_2$ **4**, *p*-$ClC_6H_4CH_2$ **5**, *m*-$ClC_6H_4CH_2$ **6**, *o*-$FPhCH_2$ **7**, *p*-$FC_6H_4CH_2$ **8** were prepared. All complexes **1**–**8** have been characterized by elemental, IR, ^{1}H, ^{13}C and ^{119}Sn NMR analyses. The crystal structures of H_2SalN and complex **1** were determined by X-ray crystallography diffraction analyses. Studies show that H_2SalN is a tridentate planar ligand. For complex **1**, the tin atom lies in this plane and forms a five- and six-membered chelate ring with the tridentate ligand. A comparison of the IR spectra of the ligand with those of the corresponding complexes, reveals that the disappearance of the bands assigned to carbonyl unambiguously confirms that the ligand coordinate with the tin in the enol form.

Keywords: Schiff base; Salicylaldehyde isonicotinylhydrazone; Diorganotin(IV) complex; Crystal structures

1. Introduction

The chemistry of organotin(IV) complexes of Schiff bases has stemmed from the reported biocidal [1,2] and anti-tumor [3,4] activities of organotin(IV) complexes and the behavior of Schiff bases as models for biological systems [5]. Moreover, some research groups also found that the Schiff base metal complexes derived from the salicylaldehyde can specially cleave the DNA [6–8]. Therefore, it is of great value for the research with salicylaldehyde to synthesize new types of Schiff base metal complexes that are characteristic of structure. To wide the scope of investigations on the coordination behavior of Schiff base ligand in biological systems towards organotins, here we report the synthesis of six diorganotin(IV) derivatives of salicylaldehyde isonicotinylhydrazone, and they have been characterized by elemental analyses, IR, ^{1}H, ^{13}C and ^{119}Sn NMR, as well as structural studies of the ligand salicylaldehyde isonicotinylhydrazone (H_2SalN) and its di-*t*-butyltin(IV) complex. Studies show that for complex **1**, the Schiff base ligand H_2SalN is a tridentate, planar ligand. The tin atom lies in this plane and forms a five-membered and a six-membered chelate ring with the ligand. Structural formula for the ligand salicylaldehyde isonicotinylhydrazone depicted in its Schiff base form is given in Scheme 1.

2. Experimental

2.1. Materials and measurements

All reagents were of analytical grade. The solvents used in this work were dried before use. The melting points were obtained with Kolfer micro melting point

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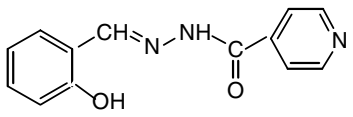

Scheme 1. Structure of the Schiff base.

apparatus and were uncorrected. IR spectra were recorded with a Nicolet-460 spectrophotometer, as KBr discs. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer in $CDCl_3$. The spectra were acquired at room temperature (298 K) 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 ^{1}H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II elemental analyzer.

2.2. Preparation of Schiff base ligand

The Schiff base H_2SalN has been prepared according to the literature for another salicylaldehyde-derived analogue salicylaldehyde salicylhydrazone [9]. An ethanol solution of salicylaldehyde (0.1 mol) was added slowly to an ethanol solution containing isonicotinyl hydrazide (0.1 mol) under stirring for 15 min, and the crude product was precipitated. Colorless crystals of H_2SalN could be taken out of the benzene–ethanol solution. Yield 88%, m.p. 249 °C. Anal. Calc. for $C_{13}H_{11}N_3O_2$: C, 64.66; H, 4.60; N, 17.41. Found: C, 64.72; H, 4.51; N, 17.38%. IR (KBr, cm^{-1}) v: 3415(s, N–H), 3255(m, O–H), 1716(s, C=O), 1620(m, C=N).

2.3. Synthesis of the complexes 1–8

A 100 ml three-necked flask was charged with 2.5 mmol of H_2SalN, 1 ml triethylamine and 50 ml benzene. Dialkylltin dichloride (2.5 mmol) in 10 ml benzene was added dropwise into the flask with stirring at room temperature. The solution turned yellow and a white precipitate formed. This solution was stirred for 3 h. The white deposit, which is Et_3N–HCl formed in the reaction, was filtered off, washed with 20 ml benzene, and the filtrate was concentrated to 5 ml. Yellow solid formed after 7 ml of petroleum ether (30–60 °C) had been added to the filtrate. The yellow crystals were recrystallized from CH_2Cl_2/petroleum ether. Their physical data are summarized as follows:

*(t-Bu)$_2$Sn(SalN) (**1**)* Yield 91%, m.p. 159 °C. Anal. Calc. for $C_{21}H_{27}N_3O_2Sn$: C, 53.37; H, 5.72; N, 8.89. Found: C, 53.44; H, 5.69; N, 8.93. IR (KBr, cm^{-1}) v: 1607(s, C=N), 1592(m, C=N–N=C), 572(m, Sn–O), 481(w, Sn–N).

*Ph$_2$Sn(SalN) (**2**)* Yield 86%, m.p. 176–178 °C. Anal. Calc. for $C_{25}H_{19}N_3O_2Sn$: C, 58.74; H, 3.52; N, 8.22. Found: C, 58.71; H, 3.41; N, 8.43%. IR (KBr, cm^{-1}) v: 1610(m, C=N), 1590(s, C=N–N=C), 564(w, Sn–O), 475(m, Sn–N).

*(PhCH$_2$)$_2$Sn(SalN) (**3**)* Yield 89%, m.p. 193 °C. Anal. Calc. for $C_{27}H_{23}N_3O_2Sn$: C, 60.03; H, 4.26; N, 7.78. Found: C, 60.05; H, 4.21; N, 7.81%. IR (KBr, cm^{-1}) v: 1605(s, C=N), 1585(s, C=N–N=C), 578(w, Sn–O), 470(m, Sn–N).

*(o-ClPhCH$_2$)$_2$Sn(SalN) (**4**)* Yield 92%, m.p. 251 °C. Anal. Calc. for $C_{27}H_{21}Cl_2N_3O_2Sn$: C, 53.23; H, 3.45; N, 6.89. Found: C, 53.19; H, 3.41; N, 6.92. IR (KBr, cm^{-1}) v: 1603(s, C=N), 1599(m, C=N–N=C), 570(m, Sn–O), 478(w, Sn–N).

*(p-ClPhCH$_2$)$_2$Sn(SalN) (**5**)* Yield 79%. m.p. 221 °C. Anal. Calc. for $C_{27}H_{21}Cl_2N_3O_2Sn$: C, 53.23; H, 3.45; N, 6.89. Found: C, 53.33; H, 3.49; N, 6.83. IR (KBr, cm^{-1}) v: 1605(m, C=N), 1595(s, C=N–N=C), 577(m, Sn–O), 480 (m, Sn–N).

*(m-ClPhCH$_2$)$_2$Sn(SalN) (**6**)* Yield 74%, m.p. 235–237 °C. Anal. Calc. for $C_{27}H_{21}Cl_2N_3O_2Sn$: C, 53.23; H, 3.45; N, 6.89. Found: C, 53.50; H, 3.51; N, 6.93. IR (KBr, cm^{-1}) v: 1606(m, C=N), 1591(s, C=N–N=C), 575(m, Sn–O), 479(m, Sn–N).

*(o-FPhCH$_2$)$_2$Sn(SalN) (**7**)* Yield 85%, m.p. 196 °C. Anal. Calc. for $C_{27}H_{21}F_2N_3O_2Sn$: C, 58.21; H, 3.71; N, 7.41. Found: C, 58.24; H, 3.62; N, 7.33%. IR (KBr, cm^{-1}) v: 1608(m, C=N), 1589(s, C=N–N=C), 575(w, Sn–O), 471(w, Sn–N).

*(p-FPhCH$_2$)$_2$Sn(SalN) (**8**)* Yield 83%, m.p. 124 °C. Anal. Calc. for $C_{27}H_{21}F_2N_3O_2Sn$: C, 58.21; H, 3.71; N, 7.41. Found: C, 58.02; H, 3.65; N, 7.44%. IR (KBr, cm^{-1}) v: 1611(m, C=N), 1592(s, C=N–N=C), 577(w, Sn–O), 475(w, Sn–N).

2.4. X-ray crystallographic studies of H_2SalN and complex 1

All measurements were made on a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo Kα(λ = 0.71073 Å) radiation at 298(2) K. The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on F^2. All non hydrogen atoms were included in the model at their calculated positions. The position of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. Crystal data and structure refinement parameters are listed in Table 1.

3. Results and discussion

3.1. IR spectroscopic studies

In the IR spectra of ligand, the stretching vibration bands of N–H, O–H and C=O appear at 3415, 3255

Table 1
Crystal data and structure refinement parameters for H_2SalN and complex **1**

	H_2SalN	Complex **1**
Empirical formula	$C_{13}H_{11}N_3O_2$	$C_{21}H_{27}N_3O_2Sn$
Molecular weight	241.25	472.15
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a (Å)	8.135(4)	8.5593(12)
b (Å)	15.499(7)	20.898(3)
c (Å)	9.521(4)	12.5465(18)
β (°)	105.768(7)	105.314(2)
Crystal size (mm)	$0.39 \times 0.35 \times 0.31$	$0.46 \times 0.39 \times 0.31$
Volume (Å^3)	1155.2(9)	2164.6(5)
Z	4	4
Density (calc.) (Mg m^{-3})	1.387	1.449
Absorption coefficient (mm^{-1})	0.097	1.200
θ Range (°)	2.58–25.03	1.97–25.03
Reflections collected	5937	11185
Independent reflections	2048 (R_{int} = 0.0490)	3811 (R_{int} = 0.0217)
Goodness-of-fit	1.046	1.000
Final R indices ($I > 2\sigma$ (I)) (all data)	R_1 = 0.0522, wR_2 = 0.1348	R_1 = 0.0305, wR_2 = 0.0822
R indices (all data)	R_1 = 0.0912, wR_2 = 0.1646	R_1 = 0.0352, wR_2 = 0.864
Largest difference peak and hole (e A^{-3})	0.252 and −0.207	0.445 and −1.431

and 1716 cm^{-1}, respectively [9], which disappear from the spectra of the complexes **1**–**8**. The disappearance of ν_{O-H} shows the deprotonation of the –OH and its subsequent coordination to the center tin atom. The disappearance of $\nu_{C=O}$ unambiguously confirms that the ligand coordinates with the tin in enol form. The $\nu_{C=N}$ band of the ligand at 1620 cm^{-1} shifts to 1611–1603 cm^{-1} in the spectra of the complexes **1**–**8**, suggesting coordination of the imine nitrogen to the moiety [10,11]. The characteristic absorptions at 1599–1585 cm^{-1} in the spectra of these complexes indicate the presence of C=N–N=C group [12,13]. Two new bands at 578–564 and 470–481 cm^{-1} are characteristic of Sn–O and Sn–N absorption, respectively [14].

3.2. NMR spectra

Further evidence for the coordination of the ligand to the tin atom is provided by the NMR spectra for organotin complexes of the Schiff base ligand. The spectra data are given in Table 2. In the ^{1}H NMR spectra of the ligand H_2SalN, the chemical shifts of the proton on phenolic hydroxy are around δ 11.25. The signals at δ 8.32 can be assigned to the azomethine protons. In ^{1}H NMR of complexes **1**–**8**, the –OH signals are absent and the signals of azomethine protons occur at δ 8.86–8.98. All these data are similar to those cases appear in literature [15–17]. The absence of –OH signals confirms the deprotonation of salicylaldehyde –OH group and its involvement in coordination. In addition, the signals of azomethine protons shifted to downfield about 0.5. The reason is that the coordination of N with tin atoms leads to large deshielding effect.

The ^{1}H NMR of complexes **3**–**8** show that the chemical shifts of the protons of methylene on the benzyl group exhibit signals about 3.13–3.33 ppm as single with 119-Sn satellites, the coupling constant J_{Sn-H} is equal 79–89 Hz. The signals at 7.35–8.13 ppm as multiplicity for all the eight complexes are assigned to the protons of pyridinyl group of ligand, which is shifting slightly to the high field compared with the free ligand.

The ^{13}C NMR spectra of all six show a significant downfield shift of all carbon resonances compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor, which is consistent with that reported in the literature [18]. The $^1J(^{119}Sn-^{13}C)$ value for **1**–**8** are 589–655 Hz, similar to those previously reported for analogous five-coordinate organotin(IV) compounds [19].

The ^{119}Sn chemical shift values in compounds (**1**–**8**) are found to be in the range of −262.4 to −323.2 ppm. The appearance of chemical shift values in this region indicates five-coordination environment [20] around the central tin atoms in these complexes.

3.3. Crystal structures

Selected bond distances and angles for H_2SalN and complex **1** are collected in Table 3. Perspective views for the asymmetric units of H_2SalN and **1** can be seen in Figs. 1(a) and (b).

As expected, the bond distances in H_2SalN (see Table 3) are very similar to those determined before for 2-benzoylpyridine *N*(4)-phenylthiosemicarbazone (H2Bz4Ph), in which the phenyl ring is attached to the C7 position [18]. Significant differences were found for the angles between the plane of the acylhydrazone (or thiosemicar-

Table 2
^{1}H, ^{13}C and ^{119}Sn NMR signals for salicylaldehyde isonicotinylhydrazone (H_2SalN) and its tin(IV) complexes in $CDCl_3$

	^{1}H NMR (δ)	^{13}C NMR (δ)	^{119}Sn NMR (δ)
H_2SalN	11.25 (1H, s, OH), 8.32 (1H, s, N=CH), 8.73 (2H, d, J = 5 Hz, 2,6-pyridine-H), 7.79 (2H, d, J = 6 Hz, 3,5-pyridine-H), 7.41–6.87 (4H, m, $H_{aromatic}$), 3.71–3.74 (1H, m, NH)	150.3, 143.5, 126.2 ($C_{pyridine}$), 149.9, 135.9, 128.7, 121.0, 115.9, 112.0 ($C_{aromatic}$), 164.6 (C=O), 155.2 (C=N)	
1	8.86 (1H, m, N=CH), 7.93 (2H, d, J = 6 Hz, 2,6-pyridine-H), 7.35 (2H, d, J = 7 Hz, 3,5-pyridine-H), 7.26–6.70 (4H, m, $H_{aromatic}$), 1.34 (18H, s, $-C(CH_3)_3$)	159.0, 143.7, 129.0 ($C_{pyridine}$), 142.3, 137.6, 129.7, 121.2, 115.3, 112.0 ($C_{aromatic}$), 172.1 (C–O), 159.1 (C=N), 40.7, 29.9 (C–Bu^t, $^{1}J_{SnC}$ = 650 Hz)	−262.4
2	8.88 (1H, m, N=CH), 8.13 (2H, d, J = 6 Hz, 2,6-pyridine-H), 7.65 (2H, d, J = 6 Hz, 3,5-pyridine-H), 7.78–7.04 (14H, m, $H_{aromatic}$)	160.3, 144.1, 122.3 ($C_{pyridine}$), 150.5, 143.2, 138.3, 136.9, 134.6, 130.5, 129.1, 127.3, 125.3, 114.4 ($C_{aromatic}$, $^{1}J_{SnC}$ = 589 Hz), 171.3 (C–O), 163.9 (C=N)	−323.2
3	8.89 (1H, m, N=CH), 8.06 (2H, d, J = 4 Hz, 2,6-pyridine-H), 7.52 (2H, d, J = 6 Hz, 3,5-pyridine-H), 7.84–6.34 (14H, m, $H_{aromatic}$), 3.13 (4H, t, J_{Sn-H} = 79 Hz, $PhCH_2Sn$)	161.2, 145.2, 127.7 ($C_{pyridine}$), 152.3, 148.5, 139.3, 137.4, 134.7, 131.3, 129.5, 127.4, 125.3, 111.5 ($C_{aromatic}$), 169.4 (C–O), 157.8 (C=N), 38.3 (Sn–CH_2, $^{1}J_{SnC}$ = 624 Hz)	−305.4
4	8.95 (1H, m, N=CH), 7.99 (2H, d, J = 6 Hz, 2,6-pyridine-H), 7.75 (2H, d, J = 5 Hz, 3,5-pyridine-H), 7.64–6.63 (12H, m, $H_{aromatic}$), 3.26 (4H, s, J_{Sn-H} = 86 Hz, $ArCH_2Sn$)	152.3, 146.3, 123.4 ($C_{pyridine}$), 151.8, 146.5, 140.2, 138.3, 136.5, 135.4, 133.6, 131.4, 129.2, 128.5, 127.3, 109.9 ($C_{aromatic}$), 172.3 (C–O), 156.9 (C=N), 34.5 (Sn–CH_2, $^{1}J_{SnC}$ = 655 Hz)	−310.5
5	8.86 (1H, m, N=CH), 8.10 (2H, d, J = 6 Hz, 2,6-pyridine-H), 7.68 (2H, d, J = 6 Hz, 3,5-pyridine-H), 7.81–6.89 (12H, m, $H_{aromatic}$), 3.33 (4H, s, J_{Sn-H} = 89 Hz, $ArCH_2Sn$)	158.5, 142.4, 121.4 ($C_{pyridine}$), 152.0, 144.6, 136.5, 135.6, 132.6, 128.5, 127.6, 121.3, 115.6, 109.9 ($C_{aromatic}$), 169.4 (C–O), 159.9 (C=N), 32.6 (Sn–CH_2, $^{1}J_{SnC}$ = 623 Hz)	−322.8
6	8.88 (1H, m, N = CH), 8.13 (2H, d, J = 6 Hz, 2,6-pyridine-H), 7.65 (2H, d, J = 6 Hz, 3,5-pyridine-H), 7.65–6.88 (12H, m, $H_{aromatic}$), 3.31 (4H, s, J_{Sn-H} = 80 Hz, $ArCH_2Sn$)	155.1, 147.2, 123.7 ($C_{pyridine}$), 153.1, 147.5, 141.4, 138.1, 137.1, 135.2, 134.1, 131.8, 129.5, 128.5, 127.3, 107.4 ($C_{aromatic}$), 172.8 (C–O), 157.3 (C=N), 34.9 (Sn–CH_2, $^{1}J_{SnC}$ = 635 Hz)	−297.9
7	8.98 (1H, m, N=CH), 8.04 (2H, d, J = 6 Hz, 2,6-pyridine-H), 7.58 (2H, d, J = 4 Hz, 3,5-pyridine-H), 7.98–7.21 (12H, m, $H_{aromatic}$), 3.12 (4H, s, J_{Sn-H} = 79 Hz, $ArCH_2Sn$)	161.4, 147.4, 126.5 ($C_{pyridine}$), 154.3, 145.4, 139.5, 135.9, 134.4, 132.0, 127.6, 125.4, 124.7, 122.4, 112.6, 109.2 ($C_{aromatic}$), 170.2 (C–O), 161.4 (C=N), 34.7 (Sn–CH_2, $^{1}J_{SnC}$ = 642 Hz)	−304.9
8	8.89 (1H, m, N=CH), 8.21 (2H, d, J = 6 Hz, 2,6-pyridine-H), 7.72 (2H, d, J = 6 Hz, 3,5-pyridine-H), 7.76–7.13 (12H, m, $H_{aromatic}$), 3.28 (4H, s, J_{Sn-H} = 85 Hz, $ArCH_2Sn$)	160.1, 143.1, 121.6 ($C_{pyridine}$), 152.6, 145.1, 136.7, 135.4, 133.1, 128.2, 127.7, 121.6, 117.4, 110.2 ($C_{aromatic}$), 170.2 (C–O), 159.6 (C=N), 32.7 (Sn–CH_2, $^{1}J_{SnC}$ = 619 Hz)	−317.6

bazone) moiety and the plane of the phenyl (or pyridine) ring, which are 3.9° and 10.58(10)° in H_2SalN and H2Bz4Ph, respectively, and the angles between the acylhydrazone (or thiosemicarbazone) chain and the pyridine (or N(4)-phenyl) ring, which are 9.9° and 15.95(8)°, respectively. Such dissimilarities are probably responsible for the differences in the angles in the acylhydrazone (or thiosemicarbazone) moiety of

Table 3
Selected bond lengths (Å) and angles (°) for H_2SalN and complex **1**

H_2SalN	
N1–C7	1.270(3)
N1–N2	1.366(3)
N2–C1	1.351(3)
O1–C1	1.215(3)
O2–C9	1.347(3)
C1–C2	1.492(3)
C7–N1–N2	118.0(2)
C1–N2–N1	118.2(2)
O1–C1–N2	123.3(2)
O1–C1–C2	121.4(2)
N2–C1–C2	115.3(2)
N1–C7–C8	120.7(2)
O2–C9–C10	118.8(2)
O2–C9–C8	122.1(2)
Complex ***1***	
Sn1–O2	2.089(2)
Sn1–C18	2.159(3)
Sn1–N1	2.181(2)
N1–N2	1.411(3)
O1–C1	1.300(3)
C1–C2	1.484(4)
Sn1–O1	2.163(2)
Sn1–C14	2.168(3)
N1–C7	1.299(4)
N2–C1	1.301(4)
O2–C9	1.318(4)
C7–C8	1.427(4)
O2–Sn1–C18	93.64(12)
O1–Sn1–C18	95.81(11)
C18–Sn1–C14	130.58(14)
O2–Sn1–N1	83.08(8)
O1–Sn1–N1	72.37(8)
C7–N1–N2	114.7(2)
N1–C7–C8	127.3(3)
O1–C1–C2	116.8(2)
O2–Sn1–O1	155.35(8)
O2–Sn1–C14	95.59(12)
O1–Sn1–C14	95.42(11)
C18–Sn1–N1	117.86(11)
C14–Sn1–N1	111.43(11)
C1–N2–N1	110.6(2)
N2–C1–C2	117.7(2)
O1–C1–N2	125.5(3)

the two ligands. For example, the C1–N2–N1 (or C8–N3–N2) angles are 118.2(2)° and 120.5(2)° and the O1–C1–C2 (or N4–C8–S) angles are 121.4(2)° and 128.01(14)° for H_2SalN and H2Bz4Ph, respectively. Furthermore, crystals of H_2SalN are stabilized by a hydrogen bond between salicylaldehyde –OH and the acylhydrazone moiety nitrogen N1.

From Fig. 1(b) it can be seen that for complex **1**, salicylaldehyde isonicotinylhydrazone (H_2SalN) is a tridentate planar ligand. The tin atom lies in this plane and forms a five- and six-membered chelate ring with the tridentate ligand. The tin atom has a distorted trigonal bipyramidal coordination with two oxygen atoms occupying the axial positions and two carbon atoms and one nitrogen atom occupying the equatorial positions. The tin atom

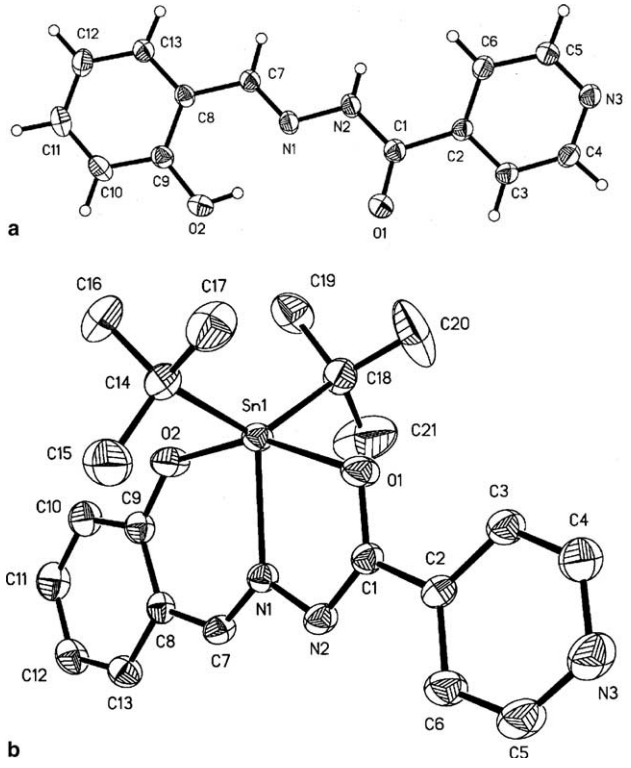

Fig. 1. (a) Perspective view of the molecular structure of salicylaldehyde isonicotinylhydrazone (H_2SalN); (b) perspective view of the molecular structure of $(t\text{-Bu})_2Sn(SalN)$.

is displaced by 0.0171 Å from the equatorial plane in the direction of the phenolic-oxygen atom. This arrangement is in accord with that in which more electronegative ligands occupy the axial positions preferentially in the complexes containing five coordinated tin atom [21].

Upon complexation the C1–N2 bond length goes from 1.351(3) Å in H_2SalN to 1.301(4) Å and the C1–O1 bond distance varies from 1.215(3) Å in H_2SalN to 1.300(3) Å in complex **1** (see Table 3), as a consequence of deprotonation at N2 and formation of extensively conjugated system involving the acylhydrazone moiety, the phenyl ring and the pyridine ring. Therefore, C–O goes from a carbonyl bond in the ligand to a enolate bond in the complex and C1–N2 from a single bond in H_2SalN to a predominantly double bond in the complex **1**. The N1–N2 distance goes from 1.366(3) Å in the ligand to 1.411(3) Å in complex **1** and N1–C7 goes from 1.270(3) Å in H_2SalN to 1.299(4) Å in complex **1**.

As expected, the angles in the acylhydrazone moiety undergo modifications on coordination (see Table 3). For example, the C1–N2–N1 angle goes from 118.2(2)° in the ligand to 110.6(2)° in complex **1**; the O1–C1–N2 angle goes from 123.3(3)° in H_2SalN to 125.5(3)° in complex **1** and the N2–C1–C2 angle from 115.3(2)° to 117.7(2)°.

In the previously prepared complex $Ph_2Sn[NH_2\text{-}C_6H_4C(O)N_2CHC_6H_4O]$ [17], the C–O bond distance, 2.119(7) Å, is comparable to the C1–O1 distance ob-

tained for complex **1**, 2.163(2) Å, in accordance with deprotonation upon complexation in both cases. All metal-to-ligand bond distances are bigger in complex **1**, as a consequence of the bulkiness of H_2SalN, as well as of the two *t*-butyl groups, which do not allow a closer interaction of the ligand with the tin center.

4. Supplementary material

Crystallographic data for H_2SalN and complex **1** have been deposited at the Cambridge Crystallographic Data Center as Supplementary Publication Numbers CCDC 267048 and 267049, respectively. Copies of available material may be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax, +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.

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