

# Synthesis and Characterization of Dimethyltin(IV) Complex with 2-Methylpyridylbenzhydrazone (AcPyBzh): Crystal Structure of [Me<sub>2</sub>SnCl (AcPyBzh)]

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**Abstract.** The reaction of dimethyltin(IV) dihalide with 2-methylpyridylbenzhydrazone (AcPyBzh) afforded the complex compound [Me<sub>2</sub>SnCl(AcPyBzh)]. The complex was characterized by IR, <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H NMR spectroscopic techniques and elemental analyses. The crystal structure of [Me<sub>2</sub>SnCl(AcPyBzh)] has been determined. The AcPyBzh anion in this complex acts as a monobasic NNO bidentate ligand, the tin(IV) lying in an elongated distorted trigonal bipyramidal environment where the azomethine nitrogen and amidate oxygen, together with the two-methyl carbons, are in the equatorial plane, whereas the chloride is the apical ligand. The crystal is monoclinic, space group P2(1)/n, with a = 12.0945 (3), b = 7.5167 (2), c = 19.9795 (4) Å, α = 90°, β = 105.85°, γ = 90°.

**Keywords:** organotin(IV) complexes; crystal structure; 2-methylpyridylbenzhydrazone ligand, dimethyltin(IV) complex

## Introduction

The chemistry of hydrazones has been intensively investigated in recent years owing to their coordination capabilities. They may coordinate to central metal ion or atom, either in the keto or in the anionic (enol) form via loss of the "amide" hydrogen. It is becoming increasingly apparent that the coordination chemistry of the organotin(IV) is of relevance in a wide variety of biological and potential pharmaceutical applications, such as anti-tumour agents (Yin *et al.*, 2004; Haiduc *et al.*, 2001; Jancso *et al.*, 2001). The coordination chemistry of tridentate acyl hydrazones derived from 2(α)-N-heterocyclic aldehydes or ketones (compound **1**; Fig. 1) has been studied extensively, and a series of transition and non-transition metal complexes have been isolated and characterized (Bacchi *et al.*, 1996; Dutta and Hossain, 1984; Domiano *et al.*, 1979). The structure of the copper(II) complex Cu(HL)(L)ClO<sub>4</sub>·C<sub>2</sub>H<sub>5</sub>OH, containing both neutral (HL) and deprotonated (L) ligands (R<sub>1</sub> = H; R<sub>2</sub> = *o*-OHC<sub>6</sub>H<sub>4</sub>), has also been described (Domiano *et al.*, 1979). The only isolated inorganic tin(IV) complex was with tridentate ligand (compound **1**; Fig. 1) (R<sub>1</sub> = R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>) and *trans*-diiodobridged dimeric structure (SnI<sub>2</sub>L)<sub>2</sub> has been proposed for this complex (Dutta and Hossain, 1984). Khalil *et al.* (1994)

described the mode of complexation of monoorganotin(IV) chloride and diorganotin(IV) dichloride with N(2-pyridinylmethylene)benzhydrazone (R<sub>1</sub> = H, R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>) and proposed a six-coordinated complex. However, owing to the insolubility of this diorganotin(IV) complex in common polar and non-polar organic solvents, its structural characterization by X-ray crystallography could not be carried out. The related hydrazone ligand (**2**) (R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>; Fig. 1), is expected to yield organotin(IV) complexes with increased solubility in organic solvents. Therefore, it was thought that it might be possible to grow single crystals of some of these complexes and study them by X-ray diffraction. The present report is a systematic study of organotin(IV) complexes of the hydrazone ligand formed by the condensation of 2-acetylpyridine with benzhydrazide. As a part of the investigation is reported the synthesis and characterization of this hydrazone ligand and its dimethyltin(IV) (complex **3**; Fig. 1), together with the X-ray single-crystal structure determination of the [Me<sub>2</sub>SnCl (AcPyBzh)] complex (**3**).

## Materials and Methods

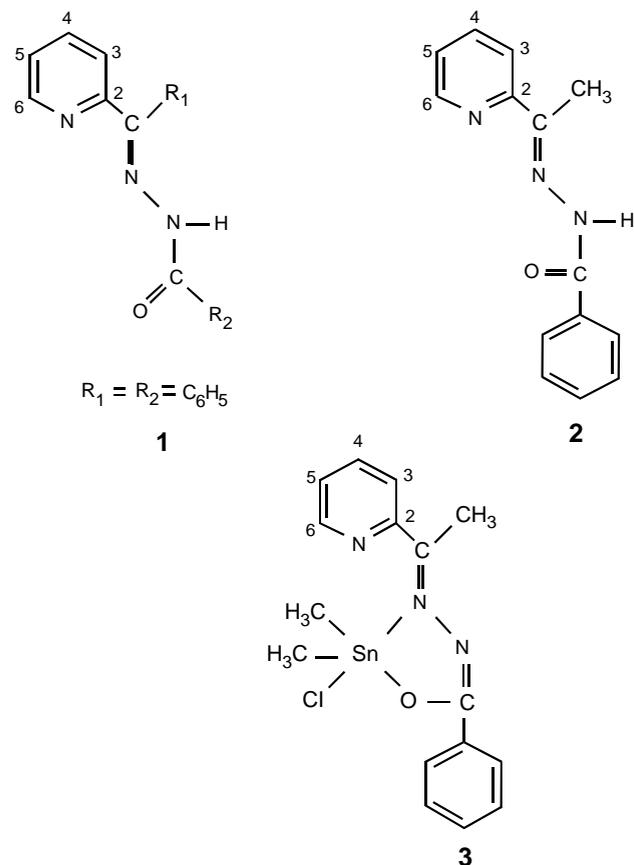
**Reagents.** All chemicals were procured from Fluka (Fluka Chemie GmbH, Industriestrasse 35, CH-9471 Buchs, Switzerland) and were used without further purification. Metha-

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nol and ethanol were purified and dried before use by standard methods. All procedures were performed under dry argon or nitrogen atmosphere.

**Physical measurements and elemental analyses.** Infrared spectra were recorded as KBr disc using Perkin Elmer 1600 fourier-transform spectrometer at the wavelength range between 4000 and 400  $\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectra were recorded in DMSO- $d_6$  solution on a Varian YH 400 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR chemical shifts are relative to tetramethylsilane. Microanalyses were carried out using CHNOS-Fisons model EA 1108 elemental analyzer.

**Preparation of 2-methylpyridylbenzhydrazone (ACPyBzh hydrazone) ligand [ $\text{C}_5\text{H}_4\text{N}(\text{CH}_3)\text{C}=\text{NNHCOC}_6\text{H}_5$ ]; compound 2 (Fig. 1).** A mixture of 2-acetylpyridine (1.15 ml, 0.01 mol,  $d = 1.0880$ ) and benzhydrazide (1.36 g, 0.01 mol) in dry ethanol (25 ml) were heated under reflux for 6 h. The colourless reaction mixture obtained was concentrated and cooled in ice bath for 1 h. The white crystalline solid thus formed was filtered off, recrystallized from hot ethanol and dried *in vacuo*



**Fig. 1.** Tridentate ligand (1), 2-methylpyridylbenzhydrazone ligand (2), dimethyltin(IV) complex with 2-methylpyridylbenzhydrazone ligand (3).

over  $\text{P}_2\text{O}_5$ ; yield: 1.70 g, 70%; m. p. 148-152  $^\circ\text{C}$ . Calculated values for  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$ : C = 70.13, H = 5.47, N = 17.56%; found values: C = 70.10, H = 5.47, N = 17.55%. IR ( $\nu_{\text{max}}$   $\text{cm}^{-1}$ ; KBr): 3177 (–NH), 1579 and 1616 (C=N) + (C=C); 1654 (C=O, amide I); 1543 (amide II); 1282 (amide III); 990 (N–N).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  2.45 (s, 3H,  $\text{CH}_3\text{C}=\text{N}$ );  $\delta$  10.86 (br, 1H, CONH);  $\delta$  7.87 (br, 1H, pyridine- $\text{H}_3$ );  $\delta$  8.10 (br, 1H, pyridine- $\text{H}_4$ );  $\delta$  7.41 (d, 1H, pyridine- $\text{H}_5$ );  $\delta$  8.60 (d, 1H, pyridine- $\text{H}_6$ );  $\delta$  7.41-7.57 (m, aromatic-H).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  164.35 (s, CO);  $\delta$  12.70 ( $\text{CH}_3\text{C}=\text{N}$ );  $\delta$  152.96 (s,  $\text{CH}_3\text{C}=\text{N}$ );  $\delta$  155.12 (s, pyridine- $\text{C}_2$ );  $\delta$  124.52 (s, pyridine- $\text{C}_3$ );  $\delta$  136.67 (s, pyridine- $\text{C}_4$ );  $\delta$  124.27 (s, pyridine- $\text{C}_5$ );  $\delta$  148.66 (s, pyridine- $\text{C}_6$ );  $\delta$  124.20-133.80 (s, phenyl ring carbons).

**Synthesis of  $\text{Me}_2\text{SnClAcPyBzh}$  [ $\text{Me}_2\text{SnCl}(\text{C}_5\text{H}_4\text{N}(\text{Me})\text{C}=\text{NNCOPh})$ ]; compound 3 (Fig.1).** An anhydrous methanolic solution (10 ml) of ligand AcPyBzh (0.4790 g, 0.002 mol) was added with stirring to a freshly prepared solution of sodium methoxide (2.40 ml, 0.002 mol) under nitrogen atmosphere. The colour of the solution changed from off-white to yellow. The resulting mixture was stirred for 1 h and a solution of  $\text{MeSnCl}_2$  (0.440 g, 0.002 mol) in methanol (10 ml) was added dropwise. The clear solution was refluxed for 4 h and allowed to cool. The precipitated sodium chloride was removed by filtration and the filtrate evaporated to dryness *in vacuo*. The required tin(IV) complex (compound 3; Fig.1) was obtained as yellow microcrystals after recrystallizing the residue with chloroform-methanol; yield: 0.5 g, 65%; m. p. 235-237  $^\circ\text{C}$ . Calculated values for  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{OSnCl}$ : C = 45.48; H = 4.29, N = 9.94%; found values: C = 45.40, H = 4.29, N = 9.84%. IR ( $\nu_{\text{max}}$   $\text{cm}^{-1}$ ; KBr): 1587 (C = N–N = C); 1562 (amide II); 1295 (amide (III)); 1005 (N–N); 576 (Sn–C); 508 (Sn–O); 472 (Sn–N).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  2.78 (s, 3H,  $\text{CH}_3\text{C}=\text{N}$ );  $\delta$  8.15 (d, 1H, pyridine- $\text{H}_3$ );  $\delta$  8.24 (t, 1H, pyridine- $\text{H}_4$ );  $\delta$  7.74 (t, 1H, pyridine- $\text{H}_5$ ),  $\delta$  9.21 (d, 1H, pyridine- $\text{H}_6$ ); 7.45-7.60 (m, aromatic-H),  $\delta$  0.69 (s, Sn– $\text{CH}_3$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  169.69 (s, CO);  $\delta$  14.30 ( $\text{CH}_3\text{C}=\text{N}$ );  $\delta$  155.10 ( $\text{CH}_3\text{C}=\text{N}$ );  $\delta$  156.20 (s, pyridine- $\text{C}_2$ );  $\delta$  121.70 (s, pyridine- $\text{C}_3$ );  $\delta$  140.49 (s, pyridine- $\text{C}_4$ );  $\delta$  125.30 (s, pyridine- $\text{C}_5$ );  $\delta$  148.72 (s, pyridine- $\text{C}_6$ );  $\delta$  125.29-134.20 (s, phenyl ring carbons).

**X-ray crystallography.** Yellow single-crystals of (compound 3), size 0.36 x 0.32 x 0.22 mm, were grown from chloroform methanol mixture which had been kept at 0-5  $^\circ\text{C}$  for 7 days. The measurements were performed at 293 K on Siemens SMART CCD diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Orientation matrix and unit cell parameters were obtained from the setting angles of 25

centered reflections. The crystals were monoclinic, space group P2(1)/n, with  $a = 12.0945$  (3),  $b = 7.5167$  (2),  $c = 19.9795$  (4) Å,  $\alpha = 90^\circ$ ,  $\beta = 105.85^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1747.23$ (7) Å<sup>3</sup>,  $d = 1.606$  mg/m<sup>3</sup>,  $\mu = 1.620$  mm<sup>-1</sup>. The diffraction intensities were collected by  $\omega$  scans ( $2.91 < \theta < 27.50^\circ$ ). A total of 10799 reflections were collected ( $-11 < = h < 18$ ,  $-11 < = k < 11$ ,  $-30 < = l < 27$ ). The structure was solved using direct methods, and refined using the full-matrix least-square method on  $F^2$ , using the SHELXTL software package (Sheldrick, 1997). All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference syntheses and refined isotropically. The molecular graphics were created using SHELXTL.

## Results and Discussion

Treatment of the hydrazone ligand AcPyBzh (**2**) with one mole equivalent of dimethyltin dichloride ( $\text{Me}_2\text{SnCl}_2$ ) in anhydrous methanol in the presence of equimolar sodium methoxide gave yellow solid (**3**), which was found soluble in common organic solvents. This solid complex (**3**) was characterized by elemental analyses, IR, <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR spectroscopic and single-crystal X-ray analyses.

The important bands observed in the IR spectra of the ligand AcPyBzh (**2**), as well as in its dimethyltin(IV) complex are given above (Materials and Method). The band observed at 1579 cm<sup>-1</sup> is attributable to a  $\nu(\text{C}=\text{N})$  of an azomethine group. A strong absorption band at 1654 cm<sup>-1</sup> has been assigned to a  $\nu(\text{C}=\text{O})$  stretching band, while bands at 1543, 1282 and 990 cm<sup>-1</sup> are attributable to amide II, amide III and  $\nu(\text{N}-\text{N})$  stretching modes, respectively.

The amide I, II and III bands completely disappeared in the IR spectrum of the tin(IV) complex (**3**). However, a sharp strong band, diagnostic of a  $>\text{C}=\text{N}-\text{N}=\text{C}<$  group appeared at 1587 cm<sup>-1</sup>. This band indicated the transformation of the carbonyl group to C–OH through the amide imidol tautomerism and subsequent coordination of the imidol oxygen (Khalil *et al.*, 1994). The appearance of  $\nu(\text{C}-\text{O})$  band at 1295 cm<sup>-1</sup> in the complex, and its positive shift of 13 cm<sup>-1</sup>, as compared to its position at 1282 cm<sup>-1</sup> in the free ligand AcPyBzh (**2**), further supported that the imidol oxygen atom was coordinated to tin(IV) and the deprotonation of imidol hydrogen. The  $\nu(\text{N}-\text{N})$  stretching mode underwent a higher shift of 16 cm<sup>-1</sup> in the complex, which supported the coordination of the azomethine nitrogen to Sn(IV) (Khalil *et al.*, 1994). The medium band observed at 1465 cm<sup>-1</sup>, attributable to a pyridine ring  $\nu(\text{C}=\text{C})$  vibration, appeared almost at the same frequency as that in the complex, indicating that pyridine ring nitrogen was not involved in bond formation with the tin(IV) complex. Two weak bands

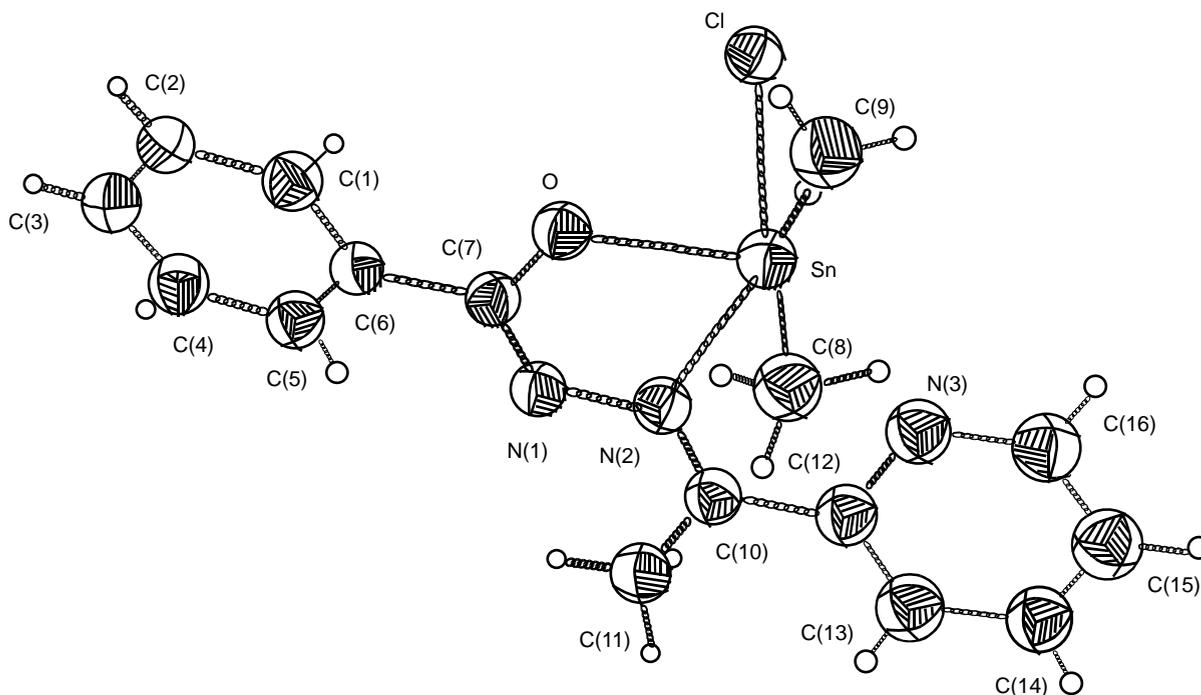
that appeared at 427–490 cm<sup>-1</sup> in the IR spectrum of the tin(IV) complex, which were absent in the IR spectrum of the free ligand AcPyBzh (**2**), are consistent with the values of  $\nu(\text{Sn}-\text{O})$  and  $\nu(\text{Sn}-\text{N})$  vibrations, respectively, as reported in literature (Jankovics *et al.*, 2003; Sandhu *et al.*, 1991). This mode of chelation was confirmed by the X-ray structural analysis of  $[\text{Me}_2\text{SnCl}(\text{AcPyBzh})]$  complex (**3**).

The <sup>1</sup>H-NMR spectra were recorded in DMSO-*d*<sub>6</sub> at room temperature. The <sup>1</sup>H NMR data of AcPyBzh (**2**) and tin(IV) complex (**3**) have been given above (Materials and Methods). The disappearance of the signal due to  $>\text{CONH}$  proton further indicated that the removal of proton through enolization of the group  $>\text{CONH}$  had occurred.

From the NMR data given above (Materials and Methods), it is apparent that in tin(IV) complex (**3**) the azomethine ( $\text{C}=\text{NMe}$ ) and the pyridyl protons of the anionic ligand  $\text{AcPyBzh}^-$  were deshielded relative to those of the neutral ligand AcPyBzh (**2**) due to the deprotonation of hydrazinic N–H. The signal at  $\delta$  2.78 ppm of  $\text{C}=\text{N}-\text{Me}$  methyl protons was observed in tin(IV) complex (**3**), which was downfield as compared to the signal of the free ligand AcPyBzh at  $\delta$  2.45 ppm. This observation indicated again that the coordination to tin(IV) had occurred via azomethine nitrogen.

The magnitude of <sup>2</sup>J (<sup>119</sup>Sn–H) for five to six or seven coordinated dimethyltin(IV) complex has been reported in the range of 71–116 Hz, depending on the stereochemistry of tin and the nature of the ligand (Jain *et al.*, 1985). For complex (**3**), a sharp signal attributable to methyl groups attached to tin appeared as a singlet at  $\delta$  0.96 ppm, and the magnitude of <sup>2</sup>J  $\delta$  (<sup>119</sup>Sn–H) = 111 Hz was greater than the coupling constant previously reported for five coordinated tin compounds (Iskander *et al.*, 1989). This might reflect that the Sn(IV) complex (**3**) had a six coordinate geometry in DMSO solution by the expansion of the coordination number of tin(IV) and the formation of a solvated species. A similar phenomena was previously reported for  $[\text{Sn}(\text{Me})(\text{FPT})\text{Cl}_2]$ , where FPT = deprotonated 2-formylpyridine thiosemicarbazone (Labib *et al.*, 1996). This inference was not supported by the results of an X-ray diffraction study in the present case, however.

The <sup>13</sup>C-{<sup>1</sup>H}NMR spectra of AcPyBzh (**2**) and  $[\text{Me}_2\text{SnCl}(\text{AcPyBzh})]$  complex (**3**) were also recorded in DMSO-*d*<sub>6</sub>, and the data so obtained has been summarized (Materials and Methods). The considerable shifts observed in the position of carbon atoms, adjacent to atoms involved in the complex formation, clearly indicated the bonding of the azomethine nitrogen and enolic oxygen to tin(IV). A singlet peak attributable to azomethine methyl carbon at  $\delta$  14.30 ppm, which shifted downfield, supports the coordination of azomethine nitrogen to the tin(IV) complex. The shifting of the  $\delta$  (C–O) value of the ligand AcPyBzh (**2**) downfield by



**Fig. 2.** Molecular structure of  $[\text{Me}_2\text{SnCl}(\text{AcPyBzh})]$  (compound **3**); thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are represented by arbitrarily small spheres.

**Table 1.** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for compound (**3**)

Sn–C(8)	2.109(3)	C(8)–Sn–C(9)	157.43(14)
Sn–C(9)	2.110(3)	C(8)–Sn–O	102.14(10)
Sn–O	2.1404(14)	C(9)–Sn–O	100.29(11)
Sn–N(2)	2.343(2)	C(8)–Sn–N(2)	96.51(10)
Sn–Cl	2.622(6)	C(9)–Sn–N(2)	93.39(12)
O–C(7)	1.294(2)	O–Sn–N(2)	69.99(6)
N(1)–C(7)	1.320(3)	C(8)–Sn–Cl	90.17(9)
N(1)–N(2)	1.396(3)	C(9)–Sn–Cl	91.65(11)
N(2)–C(10)	1.296(3)	N(2)–Sn–Cl	149.19(4)
C(1)–C(2)	1.393(3)	C(7)–O–Sn	118.44(12)
C(1)–C(6)	1.398(3)	C(2)–C(1)–C(6)	120.0(2)
C(2)–C(3)	1.379(4)	C(4)–C(5)–C(6)	120.3(2)

$\delta$  5.3 ppm, upon complex formation, is again characteristic of the coordination of the enolic oxygen atom to the tin(IV) complex.

Based on the elemental analyses, IR,  $^1\text{H}$  and  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectra analyses, a five coordinate tin(IV) geometry has been suggested for complex (**3**) in the solid state, which however appeared six coordinate in DMSO solution. Five coordinate geometry was confirmed by the single crystal X-ray analysis done on complex (**3**).

The X-ray crystallographic study of complex (**3**) was undertaken in order to correlate the proposed solution-state structure with the solid-state structure. The structure of complex (**3**), together with the numbering scheme used, is proposed in Fig. 1. In the structure of complex (**3**), the ligand AcPyBzh (**2**) was found coordinated in a bidentate fashion to a central tin atom, which is present in distorted trigonal bipyramidal geometry. In this geometry, the deprotonated amidate oxygen and the two methyl carbons C(8) and C(9) occupy the equatorial positions, while the azomethine N(2) and the chlorine atom Cl are located at the axial positions. The important bond lengths and angles are presented in Table 1. The structure is distorted from an ideal geometry. Furthermore, the Cl–Sn–N(2) angle is smaller than  $180^\circ$ , most probably due to the involvement of the N(2) atom in the five membered chelate ring, as well as the large covalent radius of tin. The Sn–Cl bond distance [2.622(6) $\text{\AA}$ ] is one of the longest such bond yet observed. It is longer than the corresponding bond distance reported for  $[\text{SnMeCl}_2(\text{PyBzh})]$  by Khalil *et al.* (1994). It is, however, comparable with the values reported for  $[\text{PyH}]_2[\text{SnMe}_2\text{Cl}_4]$  by Smart and Webster (1976). The pronounced lengthening of Sn–Cl could be attributed to the large non-bonded Cl–CH repulsions, as well as to a decrease in the Sn–Cl bond 5s-electron character (Einstein and Penfold, 1968). The Sn–O bond distance is slightly longer than that found in dimethyltin(IV) complex

[Sn (MeCl<sub>2</sub> (PyBzh)] with O-donor ligands system (Khalil *et al.*, 1994), but is comparable with those reported for other organotin(IV) complexes (Mancilla *et al.*, 2001). Both Sn–N(2) and Sn–C distances are within the normal range observed for other dimethyltin(IV) complexes (Labib *et al.*, 1996).

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