

## Characterization of novel diorganotin(IV) complexes with O,N,O donor ligand derived from carbohydrazide: X-ray crystal structure of [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)]

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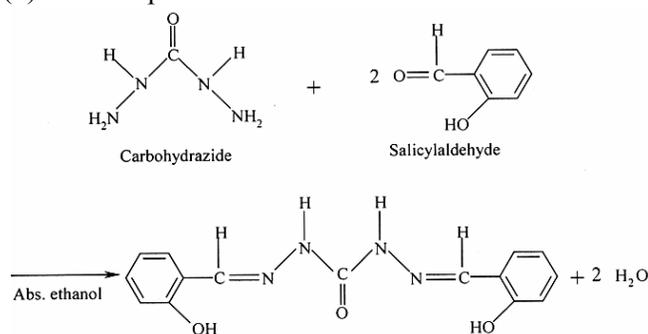
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A new series of diorganotin(IV) complexes has been synthesized by the reaction of R<sub>2</sub>SnCl<sub>2</sub> (R = Me, Bu and Ph) with O,N,O-tridentate carbohydrazone ligand derived from carbohydrazide. Three diorganotin(IV) complexes of carbohydrazone-*bis*(salicylaldehyde) ligand [H<sub>4</sub>CBS, (**1**)] with R<sub>2</sub>SnCl<sub>2</sub> have been synthesized by refluxing in the presence of base in 1:2:1 molar ratio (metal:base:ligand). All the complexes (**2-4**) have been characterized by different physico-chemical techniques like molar conductivity measurements, elemental analyses, UV-visible, IR and <sup>1</sup>H NMR spectral studies. All complexes (**2-4**) are non electrolytic in nature. Among them, diphenyltin(IV) complex (**4**) has also been characterized by X-ray crystallography diffraction analyses. In the solid state, the carbohydrazone ligand (**1**) exists as the keto tautomer. But in solution in the presence of base and organotin(IV) chloride(s), it is converted to the enol tautomer and is coordinated to the tin atom in its deprotonated enolate form. X-ray crystallographic analysis shows that the diphenyltin(IV) complex, [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (**4**), is five-coordinate and has a distorted trigonal-bipyramidal geometry with the ligand coordinated to the tin(IV) as a tridentate dinegative fashion through its phenolic-O, enolic-O and imine-N atoms. The general bond length order is: oxo < phenolato < enolato. The Sn-O (enolato) bond is longer than Sn-O (phenolato) bond by ~0.095 Å and is identical with Sn-O (carboxylate) bond. The crystal of [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (**4**) is triclinic with space group P-1 with *a* = 8.514(2)Å, *b* = 12.505(3)Å, *c* = 12.794(4)Å,  $\alpha$  = 105.169(4)°,  $\beta$  = 107.639(4)°,  $\gamma$  = 96.232(4)°, *V* = 1226.5(6) Å<sup>3</sup>, *Z* = 1 and *D*<sub>calc</sub> = 1.541 mg/m<sup>3</sup>. The IR, UV and <sup>1</sup>H NMR data are consistent with all the diorganotin(IV) derivatives having similar geometry.

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The chemistry of carbohydrazide compounds has been studied by Swamy and Siddalingaiah<sup>1</sup>. Variety of metal complexes of symmetrical dihydrazones derived from thiocarbohydrazides have been synthesized and their stereochemistry is also reported<sup>2-3</sup>. Hydrazones and their complexes with transition metals have provoked wide interest for their apparent biological and pharmaceutical activities<sup>3-5</sup>. Some carbohydrazone ligands behave as NN-chelating agents in the neutral form and an ONNO/NNO- chelating agent in deprotonated form<sup>6</sup>. Warad *et al.*<sup>4</sup> have synthesized and characterized the carbohydrazone-*bis*(salicylaldehyde) ligand and its transition metal complexes. They proposed that this ligand acted as a dinegative tetradentate (N<sub>2</sub>O<sub>2</sub>) ligand in forming the tetrahedral complexes<sup>4</sup>. Complexes of the carbohydrazide with non-transition metal ions such as organotin(IV) have not received much attention. In view of the importance of tin com-

pounds in medicinal chemistry and biotechnology<sup>7</sup> and as part of our on going work on tin-hydrazones/carbohydrazones<sup>8-10</sup>, we report herein the synthesis and characterization of the carbohydrazone-*bis*(salicylaldehyde) ligand (Scheme 1) and its di-organotin(IV) complexes. X-ray crystal structure of diphenyltin(IV) complex [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (**4**) is also reported here.



### Materials and Methods

All the chemicals were obtained from Fluka and Aldrich and were used without further purification. The solvents were of analytical grade and purified by standard methods<sup>11</sup>. The C, H, N elemental analyses were performed on a Carlo Erba model EA 1108 analyser. Infrared spectra were recorded as KBr disc using Shimadzu 8201 PC Fourier-Transform spectrometer. <sup>1</sup>H NMR spectra were recorded in DMSO-*d*<sub>6</sub> solution on a Bruker 300 FT-NMR spectrophotometer. Electronic spectra were recorded on a Shimadzu 2401 PC UV-Vis spectrophotometer.

#### Preparation of carbohydrazone-bis(salicylaldehyde) ligand (H<sub>4</sub>CBS) [C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>] (1)

A mixture of carbohydrazone (0.005 mole, 0.450 g) and salicylaldehyde (0.010 mole, 1.221 g) in absolute ethanol (30 mL) were heated under reflux for 3-4 h. The reaction mixture was allowed to cool to room temperature for half an hour. Then, the white precipitate was filtered off and washed several times with absolute ethanol. The crystalline white solid obtained was purified by recrystallization from hot absolute ethanol and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub> overnight. Yield = 70.05%. M.pt. = 178-180°C. Found: C, 60.33; H, 4.67; N, 18.78%. Calc. for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 60.36; H, 4.69; N, 18.79%.  $\lambda_{\max}$  (nm) (DMF): 262, 292, 328. IR ( $\nu_{\max}$ cm<sup>-1</sup> (KBr): 1681 (-C=O), 1622 (C=N)+(C=C), 1272 (C-O, phenolic), 946 (N-N). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.86 (br, 2H, OH),  $\delta$  8.44 (s, 2H, N=CH),  $\delta$  7.69 (br, 1H, CONH),  $\delta$  6.62-7.27 (m, 8H, aromatic-H).

#### Preparation of Me<sub>2</sub>Sn(H<sub>2</sub>CBS) [Me<sub>2</sub>Sn(C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>)] (2)

**1** (0.002 mole, 0.596 g) was dissolved in hot absolute methanol (20 mL) under nitrogen atmosphere with potassium hydroxide (0.0042 mole, 0.236 g) previously dissolved in methanol (10 mL). The colour of the solution changed from off-white to yellow. The resulting mixture was refluxed for an hour and a solution of Me<sub>2</sub>SnCl<sub>2</sub> (0.002 mole, 0.439 g) in methanol (10 mL) was added dropwise to the potassium salt of ligand solution till the color of the solution became darker. The resulting solution was refluxed for 4 h and allowed to cool. The precipitated potassium chloride (KCl) was removed by filtration and the filtrate was evaporated to dryness to obtain the yellow solid. The yellow micro-crystals were filtered off and washed with hexane and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub> overnight. Yield = 69.51%. M.pt. =

218-220°C. Found: C, 45.91; H, 4.03; N, 12.56%. Calc. for C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>Me<sub>2</sub>Sn: C, 45.88; H, 4.05; N, 12.59%.  $\lambda_{\max}$  (nm) (DMF): 266, 343, 398. IR ( $\nu_{\max}$ cm<sup>-1</sup> (KBr): 1604 (C=N)+(C=C), 1318 (C-O, phenolic), 962 (N-N), 608 (Sn-C), 566 (Sn-O), 470 (Sn-N). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.41 (br, 1H, OH),  $\delta$  10.89 (s, 1H, NH),  $\delta$  8.14 & 8.43 (s, 2H, N=CH),  $\delta$  6.63-7.93 (m, 8H, aromatic-H),  $\delta$  0.68 (s, 6H, Sn-CH<sub>3</sub>).

#### Preparation of Bu<sub>2</sub>Sn(H<sub>2</sub>CBS) [Bu<sub>2</sub>Sn(C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>)] (3)

Complex **(3)** was synthesized in a similar way as reported for **(2)**, using dibutyltin(IV) dichloride (0.002 mole, 0.608 g) instead of dimethyltin(IV) dichloride. Yield = 68.51%. M.pt. = 225-227°C. Found: C, 52.18; H, 5.69; N, 10.58%. Calc. for C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>Bu<sub>2</sub>Sn: C, 52.16; H, 5.66; N, 10.58%.  $\lambda_{\max}$  (nm) (DMF): 267, 340, 396. IR ( $\nu_{\max}$ cm<sup>-1</sup> (KBr): 1604 (C=N)+(C=C), 1323 (C-O, phenolic), 952 (N-N), 590 (Sn-C), 560 (Sn-O), 440 (Sn-N). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.45 (br, 1H, OH),  $\delta$  11.05 (s, 1H, NH),  $\delta$  8.15 & 8.41 (s, 2H, N=CH),  $\delta$  6.65-7.89 (m, 8H, aromatic-H),  $\delta$  0.79 (t, 6H, (-CH<sub>3</sub>) of butyltin),  $\delta$  1.18 (m, 4H, (-CH<sub>2</sub>) of butyltin),  $\delta$  1.26-1.45 (m, 4H, (-CH<sub>2</sub>) of butyltin),  $\delta$  1.55-1.64 (m, 4H, -CH<sub>2</sub>-Sn).

#### Preparation of Ph<sub>2</sub>Sn(H<sub>2</sub>CBS) [Ph<sub>2</sub>Sn(C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>)] (4)

Complex **(4)** was prepared similarly, as reported for **(2)**, using diphenyltin(IV) dichloride (0.002 mole, 0.688 g) instead of dimethyltin(IV) dichloride. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of dichloromethane-petroleum ether (40-60°C) solution (1:1). Yield = 64.33%. M.pt. = 208-210°C. Found: C, 56.93; H, 3.87; N, 9.27%. Calc. for C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>Ph<sub>2</sub>Sn: C, 56.95; H, 3.88; N, 9.26%.  $\lambda_{\max}$  (nm) (DMF): 266, 342, 398. IR ( $\nu_{\max}$ cm<sup>-1</sup> (KBr): 1600 (C=N)+(C=C), 1325 (C-O, phenolic), 960 (N-N), 600 (Sn-C), 520 (Sn-O), 460 (Sn-N). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.48 (br, 1H, OH),  $\delta$  11.15 (s, 1H, NH),  $\delta$  8.17 & 8.38 (s, 2H, N=CH),  $\delta$  6.70-7.62 (m, 8H, aromatic and 10H, Sn-C<sub>6</sub>H<sub>5</sub> protons).

#### X-ray Crystallography

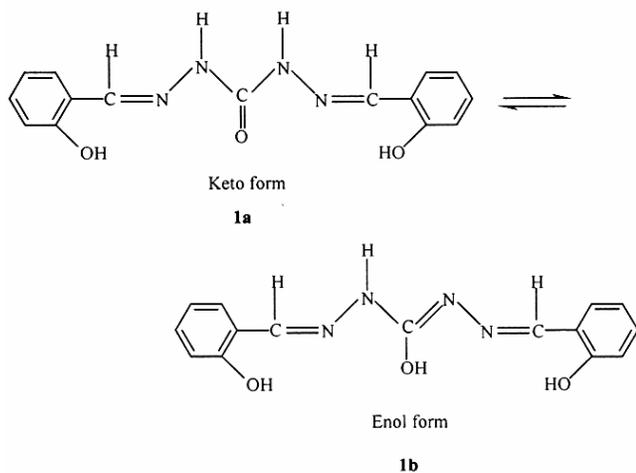
Yellow single-crystal of **(4)** (size 0.46 × 0.17 × 0.09 mm) was grown from dichloromethane-petroleum ether (40-60°C) mixture at the room temperature. The measurements were performed at 273 (2) K on Siemen SMART CCD diffraction using

graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Orientation matrix and unit cell parameters were obtained from the setting angles of 25-centered reflection. The crystals are triclinic, space group P2(1)/c with  $a = 8.514(2)$ ,  $b = 12.505(3)$ ,  $c = 12.794(4) \text{ \AA}$ ,  $\alpha = 105.169(4)^\circ$ ,  $\beta = 107.639(4)^\circ$ ,  $\gamma = 96.232(4)^\circ$ ,  $V = 1226.5(6) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_{\text{calc}} = 1.541 \text{ Mg/m}^3$ ,  $\mu = 1.078 \text{ mm}^{-1}$ . The diffraction intensities were collected by  $\omega$  scans ( $1.7$  to  $27.0^\circ$ ). A total of 13623/5308 reflections were collected ( $-10 < h < 10$ ,  $-15 < k < 15$ ,  $-16 < l < 16$ ). The structure was solved using direct methods and refined using the full-matrix least-square method on  $F^2_{\text{obs}}$  using the SHELXTL<sup>12</sup> software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located in a difference Fourier map and then were fixed geometrically and treated as riding atom on the parent C atoms, with C-H distances =  $0.97 \text{ \AA}$ .

## Results and Discussion

The carbohydrazone ligand [H<sub>4</sub>CBS, (**1**)] was synthesized by the condensation reaction of carbohydrazide with salicylaldehyde in a 1:2 ratio in absolute ethanol (Scheme 1). The carbohydrazone ligand (**1a**) has a ketoamide functional group, -NH-C=O. Therefore, in principle it can exhibit keto-enol tautomeric form. The IR spectrum of the carbohydrazone ligand, indicates that in solid state the ligand remains predominantly keto tautomer.

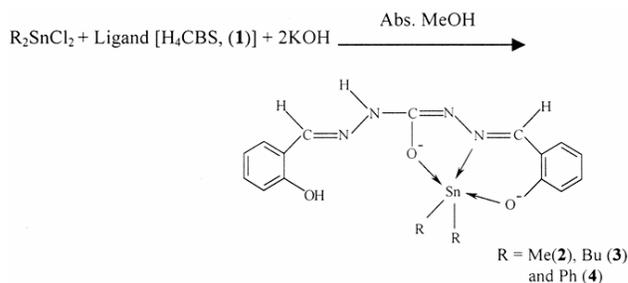
However, in solution and in the presence of base and organotin(IV) chloride(s), it was found to convert to the enol tautomeric form (**1b**), yielding organotin(IV)-carbohydrazone complexes containing the deprotonated form of the carbohydrazone ligand. Three new diorganotin(IV) complexes (**2-4**) have



been synthesized by direct reaction of the appropriate diorganotin(IV) halide(s) with **1** in the presence of a base (Scheme 2). In all the cases, a base was added to the reaction mixture in order to force the deprotonation of the ligand. The low molar conductance values,  $10\text{-}29 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (Table 1) indicate non-electrolytic nature for all the diorganotin(IV) complexes<sup>13</sup>.

## Electronic absorption spectra

The UV-Vis electronic spectra (**1**) and the complexes (**2-4**) measured at room temperature in DMF ( $10^{-4} \text{ M}$ ) solutions over  $200 - 800 \text{ nm}$  range are given in Table 2. Carbohydrazone ligand (**1**) exhibited three main bands at  $262$ ,  $292$  and  $328 \text{ nm}$ . The first and second bands were attributed to benzene  $\pi - \pi^*$  and imino ( $\text{C}=\text{N}$ )  $\pi - \pi^*$  transition, which were not affected by the chelation. The third band is assigned to  $n - \pi^*$  transition. In the UV spectra of the complexes (**2-4**), the first band at  $266\text{-}267 \text{ nm}$  region is attributed to  $\pi - \pi^*$  transition of the free imino ( $\text{C}=\text{N}$ ) group of the ligand in the complexes. The appearance of two new bands at  $340\text{-}343 \text{ nm}$  and at  $396\text{-}398 \text{ nm}$  regions showed the metal-ligand



Scheme 2

Table 1—Molar conductance values for di-organotin(IV) complexes (**2-4**) of ligand (**1**)

Compound	Molar conductance, $\Lambda_m$ ( $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
[Me <sub>2</sub> Sn(H <sub>2</sub> CBS)] ( <b>2</b> )	10
[Bu <sub>2</sub> Sn(H <sub>2</sub> CBS)] ( <b>3</b> )	23
[Ph <sub>2</sub> Sn(H <sub>2</sub> CBS)] ( <b>4</b> )	29

Table 2—The  $\lambda_{\text{max}}$  (nm) peaks of ligand (**1**) and its diorganotin(IV) complexes (**2-4**).

Compounds	$\lambda_{\text{max}}$ (nm)
( <b>1</b> ) H <sub>4</sub> CBS	328, 292, 262
( <b>2</b> ) [Me <sub>2</sub> Sn(H <sub>2</sub> CBS)]	398, 343, 266
( <b>3</b> ) [Bu <sub>2</sub> Sn(H <sub>2</sub> CBS)]	396, 340, 267
( <b>4</b> ) [Ph <sub>2</sub> Sn(H <sub>2</sub> CBS)]	398, 342, 266

coordination in all the complexes (**2-4**). The longer wavelength bands in the region 396-398 nm can be attributed to a charge transfer transition involving the tin atom<sup>14</sup>.

#### Infrared spectra

The IR data for the ligand (**1**) and the complexes (**2-4**) have been described already. The free carbohydrazone ligand, [(H<sub>4</sub>CBS) (**1**)] exists in the keto form, exhibiting characteristic  $\nu(\text{NH})$ ,  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{C}-\text{O})$  and  $\nu(\text{N}-\text{N})$  bands at 3360, 1681, 1622, 1272 and 946 cm<sup>-1</sup>, respectively. A weak broad band absorption 3250-3340 cm<sup>-1</sup> in all the complexes of ligand is assigned to the stretching vibration of OH group. This indicates that one phenolic oxygen is not coordinated with tin(IV), as supported by <sup>1</sup>H NMR and single crystal X-ray crystallography of [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (**4**). The IR spectra of the organotin(IV) complexes (**2-4**) do not display the characteristic bands associated with the  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{O})$  bands of the amide functionality present in the free ligand. Thus, in each complex the amide group is deprotonated and exists in the enolate form<sup>15</sup>. A medium to strong band observed in the 1600-1604 cm<sup>-1</sup> is most likely associated with the conjugated >C=N-N=C< fragment of the ligand [(H<sub>4</sub>CBS) (**1**)]. Owing to the overlapping of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{N}-\text{N}=\text{C})$  bands in the complexes (**2-4**), it is hard to identify the free >C=N group in the IR spectra analyses. The hydrazinic stretching  $\nu(\text{N}-\text{N})$  band observed at 946 cm<sup>-1</sup> for the ligand (**1**) is shifted to the higher region at 952-962 cm<sup>-1</sup> in the complexes (**2-4**) further supporting that azomethine nitrogen is coordinated to Sn(IV) ion. This is also apparent from the  $\nu(\text{Sn}-\text{N})$  band at 440-470 cm<sup>-1</sup> in the IR spectra<sup>15</sup> of **2-4**. The high intensity band observed at 1272 cm<sup>-1</sup> in the ligand (**1**) attributed due to phenolic  $\nu(\text{C}-\text{O})$ , appears as a medium band at 1318-1325 cm<sup>-1</sup> in the IR spectra of **2-4**. These observations favour the formation of Sn-O bond via deprotonation. The medium and weak bands observed at 590-608, 520-566 and 440-470 cm<sup>-1</sup> in the IR spectra of **2-4** are attributable to the  $\nu(\text{Sn}-\text{C})$ ,  $\nu(\text{Sn}-\text{O})$  and  $\nu(\text{Sn}-\text{N})$  vibration bands, respectively indicating coordination of the free ligand to the central Sn(IV) atom via deprotonated enolic oxygen and azomethine nitrogen in the complexes **2-4**.

#### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR data for the ligand (**1**) and its complexes (**2-4**) are described already. The <sup>1</sup>H NMR

spectrum of ligand (**1**) is characterized by four signals at 10.86, 8.44, 7.69 and 6.62-7.27 ppm, which are assigned to the protons associated with -OH, -N=CH, -CONH and aromatic ring protons, respectively. In <sup>1</sup>H NMR spectra of (**2-4**), azomethine N=CH signal is splitted into two signals at 8.14-8.17 and 8.38-8.43 ppm due to unsymmetrical in the ligand structure after complexation reaction. This indicates that only one of the azomethine nitrogen in ligand (**1**) could be bonded to the Sn(IV) ion in (**2-4**), and another one HC=N group could be free. This is confirmed from X-ray crystallographic analyses. The disappearance of the signal due to -CONH proton in (**2-4**) indicated the enolization of the form of the ligand (**1**) in the complexes<sup>8</sup> (**2-4**). The new signal at 10.89-11.15 ppm in (**2-4**) is due to the free NH group of ligand (**1**), which is not involved in the coordination to tin(IV) in the complexes (**2-4**). A signal appeared at 11.41-11.48 ppm, indicating that phenolic proton is present in (**2-4**). 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<sup>16</sup>. The sharp signal attributed to methyl group attached to tin atom appeared as a singlet at 0.68 ppm in the dimethyltin(IV) complex (**2**) and the <sup>2</sup>J(<sup>119</sup>Sn-H) and <sup>2</sup>J(<sup>117</sup>Sn-H) coupling constant values are 84 Hz and 80 Hz, which are almost similar with the coupling constant previously reported for five-coordinated tin complex<sup>17</sup>. In the complex (**3**), a multiplet in the region 0.79-1.64 ppm is assigned to the butyl group attached to the tin(IV) atom. Complex (**4**) showed a multiplet in the region 6.70-7.62 ppm, which may be assigned to aromatic ring protons and Sn-Ph protons, respectively. The signals could not properly assign due to overlap of corresponding signals of Ph-Sn and aromatic ring protons.

#### Crystal structure of [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (**4**)

The X-ray structural investigation of [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (**4**) (Fig. 1) revealed that the carbohydrazone-*bis*(salicylaldehyde) ligand [H<sub>4</sub>CBS, (**1**)] is O,N,O-coordinated in complex (**4**). The crystal data and structure refinement for compound [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (**4**) are summarized in Table 3 and the selected bond distances and angles are given in Table 4. The crystal structure of (**4**) reveals that tin(IV) atom has a five coordination geometry in a distorted trigonal-bipyramidal arrangement. The Sn(1) atom lies in the ligand plane and form five membered

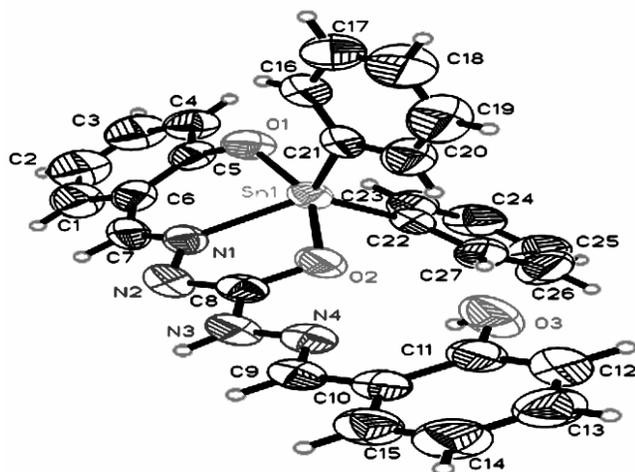


Fig. 1—Molecular structure of  $[\text{Ph}_2\text{Sn}(\text{H}_2\text{CBS})]$  (**4**) (Thermal ellipsoids at the 50% level).

and six membered chelate ring with the ligand. Thus, the two phenyl groups and an imine nitrogen take the equatorial position, while the oxygen atoms, O(1) and O(2), take up the axial sites around the Sn(1) atom.

The distorted trigonal-bipyramidal arrangement is a result of the strain imposed by the tridentate ligand, and from the constraints imposed by the six membered ring, Sn(1)-N(1)-C(7)-C(6)-C(5)-O(1) and five membered ring Sn(1)-N(1)-N(2)-C(8)-O(2). The trigonal-bipyramidal geometry in (**4**) is distorted as indicated by the bond angles of  $157.08(8)^\circ$  for O(1)-Sn(1)-O(2) and the deviation from  $90^\circ$  of the

Table 3—Crystal data and the structure refinement for the complex  $[\text{Ph}_2\text{Sn}(\text{H}_2\text{CBS})]$  (**4**)

Formula	$\text{C}_{27}\text{H}_{22}\text{N}_4\text{O}_3\text{Sn}$
Formula weight	569.18
Crystal system	Triclinic
Space group	P-1
Z	1
<i>a</i> (Å)	8.514(2)
<i>b</i> (Å)	12.505(3)
<i>c</i> (Å)	12.794(4)
$\alpha$ ( $^\circ$ )	105.169(4)
$\beta$ ( $^\circ$ )	107.639(4)
$\gamma$ ( $^\circ$ )	96.232(4)
<i>V</i> (Å <sup>3</sup> )	1226.5(6)
<i>D</i> <sub>calc</sub> (mg m <sup>-3</sup> )	1.541
Absorption coefficient (mm <sup>-1</sup> )	1.078
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0337, <i>wR</i> <sub>2</sub> = 0.0805
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0380, <i>wR</i> <sub>2</sub> = 0.0829
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.135

angles O(1)-Sn(1)-N(1) ( $84.96(8)^\circ$ ) and O(2)-Sn(1)-N(1) ( $72.89(8)^\circ$ ). The sum of the angles O(1)-Sn(1)-N(1),  $84.96(8)^\circ$  and O(2)-Sn(1)-N(1),  $72.89(8)^\circ$  is  $157.85^\circ$ , and it is almost the same with the angle O(1)-Sn(1)-O(2),  $157.08(8)^\circ$ , so that the atoms Sn(1), N(1), O(1) and O(2) are co-planar. The sum of the angles C(21)-Sn(1)-N(1), C(22)-Sn(1)-N(1) and C(21)-Sn(1)-C(22) is  $358.62^\circ$ , thus the atoms Sn(1), N(1), C(21) and C(22) are almost in the same plane.

The asymmetry of H<sub>4</sub>CBS ligand is strongly reflected in the Sn-O distances. In (**4**), the Sn(1)-O(2) bond,  $2.1430(19)\text{Å}$ , is longer than the Sn(1)-O(1)

Table 4—Selected bond lengths (Å) and angles ( $^\circ$ ) of diphenyltin(IV) complex  $[\text{Ph}_2\text{Sn}(\text{H}_2\text{CBS})]$  (**4**)

Bond lengths			
Sn(1)-O(1)	2.0482(19)	Sn(1)-N(1)	2.162(2)
Sn(1)-O(2)	2.1430(19)	Sn(1)-C(21)	2.112(3)
Sn(1)-C(22)	2.117(3)	O(1)-C(5)	1.340(3)
O(2)-C(8)	1.282(3)	N(1)-C(7)	1.301(3)
N(1)-N(2)	1.376(3)	N(2)-C(8)	1.310(4)
N(3)-N(4)	1.362(3)	N(3)-C(8)	1.361(3)
C(6)-C(7)	1.424(4)	N(4)-C(9)	1.272(4)
C(9)-C(10)	1.456(4)		
Bond angles			
O(1)-Sn(1)-C(21)	97.52(9)	O(1)-Sn(1)-C(22)	99.19(10)
C(21)-Sn(1)-C(22)	120.45(9)	O(1)-Sn(1)-O(2)	157.08(8)
C(21)-Sn(1)-O(2)	91.16(9)	C(22)-Sn(1)-O(2)	94.52(9)
O(1)-Sn(1)-N(1)	84.96(8)	C(21)-Sn(1)-N(1)	126.43(9)
C(22)-Sn(1)-N(1)	111.74(9)	O(2)-Sn(1)-N(1)	72.89(8)
C(5)-O(1)-Sn(1)	127.47(18)	C(8)-O(2)-Sn(1)	112.67(17)
C(7)-N(1)-Sn(1)	125.69(19)	N(2)-N(1)-Sn(1)	116.73(16)
C(7)-N(1)-N(2)	117.4(2)	C(9)-N(4)-N(3)	119.4(2)
O(1)-C(5)-C(6)	122.7(2)	C(5)-C(6)-C(7)	125.2(2)
N(1)-C(7)-C(6)	117.0(3)	O(2)-C(8)-N(2)	126.4(2)

bond, 2.0482(19)Å. This is a consequence of O(2) being a carbonyl and O(1) being bound to a benzene ring. In Ph<sub>2</sub>SnSalAp (where SalAp/salicylideneamino-o-hydroxybenzene), the Sn-C bonds are 2.118(5) Å and 2.111(5) Å<sup>18</sup>, is almost similar with the Sn-C bonds found in complex (4), 2.112(3) Å and 2.117(3) Å. The Sn-N, 2.162(2) Å bond of the compound (4) is a little longer than that of the compound {[Ph<sub>2</sub>Sn(2-OC<sub>10</sub>H<sub>6</sub>CHNCH<sub>2</sub>COO)]SnPh<sub>2</sub>Cl<sub>2</sub>} 2.136 Å<sup>19</sup> and Ph<sub>2</sub>Sn[Ph(O)C=CH-C(Me)=N-N=C(O)Ph] 2.145(3) Å<sup>20</sup> but shorter than that of [Me<sub>2</sub>Sn(2-OC<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>COO)] 2.221(3) Å<sup>21</sup> and {Ph<sub>2</sub>Sn[4-NC<sub>5</sub>H<sub>4</sub>-(O)N<sub>2</sub>C(CH<sub>3</sub>)CO<sub>2</sub>](H<sub>2</sub>O)}<sub>2</sub>.CH<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O, 2.288(7) Å and 2.282(7) Å<sup>22</sup>, and it is considerably less than the sum of the van der Waals radii of tin and nitrogen, 3.75 Å<sup>23</sup>. Due to the involvement of N(1) atom in tin binding, the bond length of N(1)-C(7) is significantly increased to 1.301(3) Å as compared with the imine function N(4)-C(9) (1.272(4) Å) which is having a double bond character.

### Conclusions

The synthesis and physical properties of a new series of di-organotin(IV) compounds with carbohydrazone ligand (1) are described. The ligand behaved as a tridentate dinegative fashion towards to tin(IV). The complexes (2-4) are monometallic. The coordination around the tin(IV) ion is established by means of single crystal X-ray diffraction analysis on [Ph<sub>2</sub>Sn(H<sub>2</sub>CBS)] (4).

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