SYNTHESIS, STRUCTURAL CHARACTERIZATION AND TOXICITY STUDIES OF NOVEL ORGANOTIN(IV) COMPLEXES DERIVED FROM BENZOYLACETONE ISONICOTINYLHYDRAZONE (H_2BAS): X-RAY CRYSTAL STRUCTURE OF [Me_2Sn(BAS)]

(Kajian Sintesis, Pencirian Struktur dan Ketoksian Kompleks Organostannum(IV) Novel yang Diterbitkan Daripada Benzoilaseton Isonikotinilhidrazon (H_2BAS): Struktur Sinar-X Hablur [Me_2Sn(BAS)])

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Abstract

Six organotin(IV) complexes, [R_mSnCl_{2-m}(BAS)], where R_m = Me_2 (**2**), *n*Bu_2 (**3**), Ph_2 (**4**), Me (**5**), *n*Bu (**6**) and Ph (**7**) have been synthesized by direct reaction of organotin(IV) halide(s) with benzoylacetone isonicotinylhydrazone ligand [(H_2BAS), (**1**)] with the presence of KOH in 1:2:1 (ligand:base:metal) mole ratio in absolute methanol. The hydrazone ligand [(H_2BAS), (**1**)] and its organotin(IV) complexes (**2-7**) have been characterized by elemental analyses, UV-Visible, IR and ^{1}H NMR spectral studies. All organotin(IV) complexes (**2-7**) are non electrolytic in nature. Among them, molecular structure of dimethyltin(IV) complex, [Me_2Sn(BAS)] (**2**) has also been studied by X-ray single crystal diffraction. Preliminary toxicity test showed that the organotin(IV) complexes (**2-7**) are more toxic against the *Artemia salina* than the free hydrazone ligand [(H_2BAS), (**1**)].

Keywords: Hydrazone ligand; organotin(IV) complexes; spectral studies; crystal structure; toxicity test

Abstrak

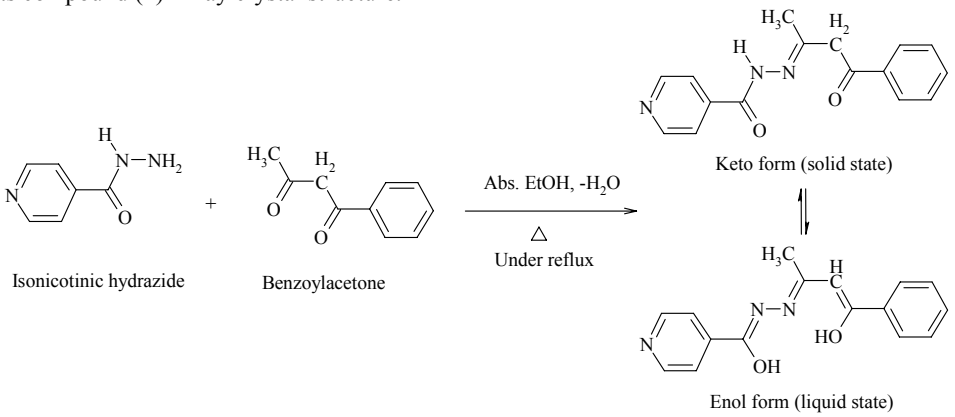
Enam kompleks organostanum(IV) [R_mSnCl_{2-m}(BAS)], where R_m = Me_2 (**2**), *n*Bu_2 (**3**), Ph_2 (**4**), Me (**5**), *n*Bu (**6**) dan Ph (**7**) telah disintesiskan melalui tindak balas terus antara halida organostanum(IV) dengan benzoilaseton isonikotinilhidrazon [(H_2BAS), (**1**)] dengan kehadiran KOH dalam nisbah mol 1:2:1 (ligan:bes:logam) dalam metanol tulen. Ligan hidrazon [(H_2BAS), (**1**)] dan kompleks organostanum(IV) (**2-7**) telah dicirikan dengan analisis unsur, UV-nampak, IR dan ^{1}H RMN. Kesemua kompleks organostanum(IV) (**2-7**) adalah bersifat bukan elektrolit. Struktur molekul kompleks [Me_2Sn(BAS)] (**2**) juga telah dicirikan dengan pembelauan hablur tunggal sinar-X. Ujian ketoksikan awal menunjukkan kompleks-kompleks organostanum(IV) nya (**2-7**) adalah lebih toksik terhadap *Artemia salina* dibandingkan dengan ligan bebas hidrazon [(H_2BAS), (**1**)].

Kata kunci: Ligan hidrazon, kompleks organostannum(IV), kajian spektrum, struktur hablur, ujian ketoksikan

Introduction

The coordination behaviour of organotin(IV) complexes has been studied from the last decade due to their wide applications in several areas such as antiviral [1], antineoplastic agents [1-2], bactericides, fungicides [3], marine antifouling paints, surface disinfectants, wood preservatives [4] and many more. However, very little information is available for hydrazone ligands containing ONO-donor atoms [1] and only a few papers reports the existance of non-transition metal complexes, including silicon, lead and organotin(IV) [5-9] due to their hydrolytic instability and large lability in solution [10]. Charistos and his co-workers (2001) have prepared {methoxo[4-phenylbutane-2,4-dione(*p*-nitrobenzoyl) hydrazonato(2-)]oxovanadium(V)} [11]. Another ONO-donor atoms of hydrazone ligand is 1-naph-thoyl-hydrazone of benzoylacetone which has been synthesized by Andjelković *et al.* (2001) [12]. In 2004, Dey and his research group reported the preparation of diphenyltin(IV) and dimetyltin(IV) complexes with 4-phenyl-2,4-butanedionebenzoylhydrazone(2-) ligand derived from benzoyl acetone and benzoyl hydrazide in methanol at room temperature in the presence of triethylamine [2]. From the literature survey, the interest on the studies of hydrazone ligand containing benzoylacetone as the back bone with organotin(IV) complexes are very limited and further study is needed. In our previous work, we reported several organotin(IV) complexes with hydrazone ligands [13-16]. To the best of our knowledge, there have been no report on the organotin(IV) complexes derived from benzoylacetone isonicotinylhydrazone

ligand (H_2BAS). Therefore, it is imperative to investigate the coordination behaviour of hydrazone complex. In this paper, we report the synthesis and spectral characterization of organotin(IV) complexes (**2-7**) with benzoylacetone isonicotinylhydrazone ligand [(H_2BAS), (**1**)] containing O, N, O-donor atoms (Scheme **1**), as well as its compound (**2**) X-ray crystal structure.



Scheme 1 Synthesis pathway of hydrazone ligand [(H_2BAS), (**1**)].

Experimental

All chemicals were purchased from Fluka, Acros, Aldrich and J.T. Baker without further purification. All solvents were distilled and purified before used [17]. All reactions were carried out under dry nitrogen atmosphere using Schlenk vacuum line techniques. Melting points were obtained with a Stuart SMP3 melting point apparatus in open capillaries. Infrared spectra were recorded as KBr disc using Perkin Elmer Spectrum GX Fourier-Transform Spectrometer (4000-400 cm^{-1}). Electronic absorption spectra were recorded in methanol solution on a Perkin Elmer Lambda 25 UV-Visible spectrometer. Molar conductances were measured at room temperature using a Jenway 4510 conductivity meter. The CHN elemental analyses were performed on a FlashEA 1112 series analyzer. ^{1}H NMR spectra were recorded in DMSO-d_6 solution using TMS as the internal standard on a Jeol 500 MHz NMR spectrophotometer.

Synthesis of benzoylacetone isonicotinylhydrazone $C_{16}H_{15}N_3O_2$ (1)

The compound isonicotinic hydrazide (0.686 g, 5 mmol) compound was dissolved in absolute ethanol (20 mL) in a round bottom flask with constant stirring and heating. Then, benzoylacetone (0.811 g, 5 mmol) in absolute ethanol (20 mL) was added drop wise and the resulting mixture solution converted from colourless to light yellow colour. The mixture was heated under reflux for 4 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The white solid formed was filtered off, and washed several times using absolute ethanol. The white crystals obtained were purified by recrystallization from hot ethanol, and dried in vacuo over silica gel. Yield 1.374 g, 92 %, mp 165-167 °C; UV (MeOH) λ_{max} 238, 336 nm; IR (KBr) ν_{max} 3421 (OH/NH), 1697 (C=O), 1630 (CONH), 1602 (C=N), 981 (N–N), 675 (py-N, in-plane) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 12.27 (s, CH=C(OH)), 11.16 (s, N=C(OH)), 7.07-8.68 (m, aromatic-H/py-H), 6.02 (s, CH=C), 1.99 (s, H_3C-C=N) ppm.

Synthesis of organotin(IV) complexes (2-7)

$Me_2Sn(C_{16}H_{13}N_3O_2)$] (2)

The ligand [H_2BAS] (**1**) (0.563 g, 2 mmol) was dissolved in hot absolute methanol (10 mL) and was added drop wise by stirring with a potassium hydroxide (KOH) solution (0.236 g, 4.2 mmol) in absolute methanol (20 mL) under nitrogen atmosphere. The resulting solution colour changed from yellow to light yellow. The resulting mixture was stirred with constant stirring and heated under reflux for one and a half hour. A solution of dimethyltin(IV) dichloride (0.440 g, 2 mmol) in absolute methanol (10 mL) was added drop wise. The solution colour became darker yellow. The resulting solution was refluxed for 4 hours and allowed to cool to room temperature. The white precipitate of potassium chloride was formed and removed by filtration. The filtrate was evaporated to dryness by using a rotary apparatus under reduced pressure. The yellow crystals obtained were washed with hexane and dried in vacuo over silica gel. Single crystals for X-ray diffraction studies were prepared by slow evaporation of single solvent acetonitrile at room temperature. Yield 0.699 g, 70%, mp 179-

180 °C; Molar conductance (MeOH) Λ_M 1 Ω^{-1} cm^2 mol^{-1};UV (MeOH) λ_{max} 243, 442 nm; IR (KBr) ν_{max} 3568 (OH), 1588 (C=N–N=C), 1528 (NCO^-), 1303 (C-O), 1029 (N–N), 697 (py-N, in-plane), 516 (Sn–O), 448 (Sn–N) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.44-8.68 (m, aromatic-H/py-N), 5.89 (s, CH=C), 2.10 (s, H_3C-C=N), 0.74 (s, $(CH_3)_2$-Sn) ppm.

[$nBu_2Sn(C_{16}H_{13}N_3O_2)$] (3)

The synthesis of [$n$$Bu_2$Sn(BAS)] (**3**) was prepared from the same procedures as the preparation for [Me_2Sn(BAS)] (**2**), with dibutyltin(IV) dichloride (0.608 g, 2 mmol) being used instead of dimethyltin(IV) dichloride. The di-*n*-butyltin(IV) complex (**3**) obtained as a reddish orange precipitate by recrystallization from methanol. Yield 0.595 g, 51 %, mp 132-134 °C; Molar conductance (MeOH) Λ_M 6 Ω^{-1} cm^2 mol^{-1}; UV (MeOH) λ_{max} 242, 420 nm; IR (KBr) ν_{max} 3439 (OH), 1588 (C=N–N=C), 1524 (NCO^-), 1304 (C-O), 1031 (N–N), 697 (py-N, in-plane), 524 (Sn–O), 447 (Sn–N) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.45-8.68 (m, aromatic-H/py-N), 5.89 (s, CH=C), 2.36 (s, H_3C-C=N), 0.74-1.65 (m, (nBu)$_2$-Sn) ppm.

[$Ph_2Sn(C_{16}H_{13}N_3O_2)$] (4)

The complex [Ph_2Sn(BAS)] (**4**) was synthesized similarly to [Me_2Sn(BAS)] (**2**), diphenyltin(IV) dichloride (0.688 g, 2 mmol) was used instead of dimethyltin(IV) dichloride. The diphenyltin(IV) complex (**4**) was obtained as a yellow precipitate by recrystallization from methanol. Yield 0.797 g, 64 %, mp 237-239 °C; Molar conductance (MeOH) Λ_M 2 Ω^{-1} cm^2 mol^{-1}; UV (MeOH) λ_{max} 232, 424 nm; IR (KBr) ν_{max} 3446 (OH), 1589 (C=N–N=C), 1529 (NCO^-), 1303 (C-O), 1031 (N–N), 698 (py-N, in-plane), 531 (Sn–O), 450 (Sn–N) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.38-8.70 (m, aromatic-H/py-N/Sn-C_6H_5 protons), 6.05 (s, CH=C), 2.07 (s, H_3C-C=N) ppm.

[$MeSnCl(C_{16}H_{13}N_3O_2)$] (5)

The procedure described above for [Me_2Sn(BAS)] (**2**) was followed for the synthesis of [MeSnCl(BAS)] (**5**), with methyltin(IV) trichloride (0.482 g, 2 mmol) was used instead of dimethyltin(IV) dichloride. The methyltin(IV) complex (**5**) was obtained as a reddish orange precipitate by recrystallization from methanol. Yield 0.710 g, 68 %, mp 307-309 °C; Molar conductance (MeOH) Λ_M 6 Ω^{-1} cm^2 mol^{-1}; UV (MeOH) λ_{max} 246, 449 nm; IR (KBr) ν_{max} 3463 (OH), 1591 (C=N–N=C), 1523 (NCO^-), 1304 (C-O), 1031 (N–N), 695 (py-N, in-plane), 512 (Sn–O), 454 (Sn–N) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.42-8.67 (m, aromatic-H/py-N), 6.10 (s, CH=C), 2.38 (s, H_3C-C=N), 1.01 (s, CH_3-Sn) ppm.

[$nBuSnCl(C_{16}H_{13}N_3O_2)$] (6)

The procedure for the synthesis of [Me_2Sn(BAS)] (**2**) was followed for the preparation of [nBuSnCl(BAS)] (**6**), with butyltin(IV) trichloride (0.564 g, 2 mmol) used instead of dimethyltin(IV) dichloride. The *n*-butyltin(IV) complex (**6**) was obtained as a red precipitate and was further purified from methanol. Yield 0.560 g, 50 %, mp 261-263 °C; Molar conductance (MeOH) Λ_M 4 Ω^{-1} cm^2 mol^{-1}; UV (MeOH) λ_{max} 244, 434 nm; IR (KBr) ν_{max} 3470 (OH), 1591 (C=N–N=C), 1527 (NCO^-), 1305 (C-O), 1034 (N–N), 695 (py-N, in-plane), 513 (Sn–O), 451 (Sn–N) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.45-8.68 (m, aromatic-H/py-N), 6.10 (s, CH=C), 2.37 (s, H_3C-C=N), 0.81-1.86 (m, nBu-Sn) ppm.

[$PhSnCl(C_{16}H_{13}N_3O_2)$] (7)

The synthesis procedure for [Me_2Sn(BAS)] (**2**) was followed for the preparation of [PhSnCl(BAS)] (**7**), with phenyltin(IV) trichloride (0.606 g, 2 mmol) was used instead of dimethyltin(IV) dichloride. The phenyltin(IV) complex (**7**) formed orange solid by recrystallization from methanol. Yield 0.873 g, 75 %, mp 344-346 °C; Molar conductance (MeOH) Λ_M 8 Ω^{-1} cm^2 mol^{-1}; UV (MeOH) λ_{max} 234, 426 nm; IR (KBr) ν_{max} 3447 (OH), 1599 (C=N–N=C), 1508 (NCO^-), 1302 (C-O), 1033 (N–N), 692 (py-N, in-plane), 506 (Sn–O), 452 (Sn–N) cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.36-8.74 (m, aromatic-H/py-N/Sn-C_6H_5 protons), 6.14 (s, CH=C), 2.39 (s, H_3C-C=N) ppm.

X-ray Crystallography of [Me_2Sn(BAS)] (2)

[Me_2Sn(BAS)] (**2**) is brownish yellow single-crystals which have empirical formula, $C_{18}H_{19}N_3O_2Sn$ with the size of 0.30 x 0.29 x 0.15 mm. It was measured on a Siemen SMART CCD diffraction at 100(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Orientation matrix and unit cell dimensions were obtained from the setting angles of 25-centered reflection. The crystals are monoclinic, space group P2(1)/n with a = 10.9363(6) Å, b = 8.4429(4) Å, c = 19.6553(11) Å, α = 90˚, β = 103.452(2)˚ and γ = 90˚, V = 1765.06(16) A^3, Z = 4, D_{calc} = 1.611 Mg/m^3, μ = 1.462 mm^{-1}. The diffraction intensities were collected by ω

scans (2.13 to 27.50°). A total of 12078 / 3934 reflections were collected ($-14 \leq h \leq 14$, $-10 \leq k \leq 10$, $-25 \leq l \leq 25$). The structure was solved using direct method and refined by full-matrix least-square method on F^2 using the SHELXTL [18] 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 Å.

Toxicity assay

Toxicity was assessed by Brine Shrimp Lethality Bioassay [19]. The procedures were followed with some minor modifications.

Brine shrimp hatching

Brine shrimp (*Artemia salina*) eggs were purchased from Hong Da, Hai Xing Country Li Da Brine Shrimp Eggs Processing Factory, China. The eggs (2.5 g) were hatched in artificial sea water (1 L) using a beaker under constant aeration by incubation under a lamp, providing direct light and warmth (24-26 °C). The artificial sea water was prepared by dissolving 35 g commercial sea salt in 1 L of water and then filtered. The salinity measured is 2.0 psu for optimum hatching. After 24 hours, the phototrophic nauplii were collected by pipette.

Sample preparation

Samples were prepared by dissolving 3.5 mg of the compounds (**1**-**7**) in 3.5 mL of DMSO (Solution A). Mycotoxin solutions (Solution B) were prepared with different concentrations/dose levels: 1, 10, 25, 50, 75, 100, 125 and 150 µg/mL (ppm) by transferring 2, 20, 50, 100, 150, 200, 250 and 300 µL of Solution A into multiwell plates and air-dried over night. After 24 hours, the samples in each well were added with 1 mL artificial sea water. Another 1 mL of the artificial sea water containing 20 nauplii was pipetted into each well, resulting final well volume of 2 mL. Then, the multiwall plates were incubated for 24 hours under direct light at 24-26 °C.

For each sample, eight different dose levels and three replicates per dose levels were preformed. However, only one assay was managed to be carried out because of the limited amount of compounds.

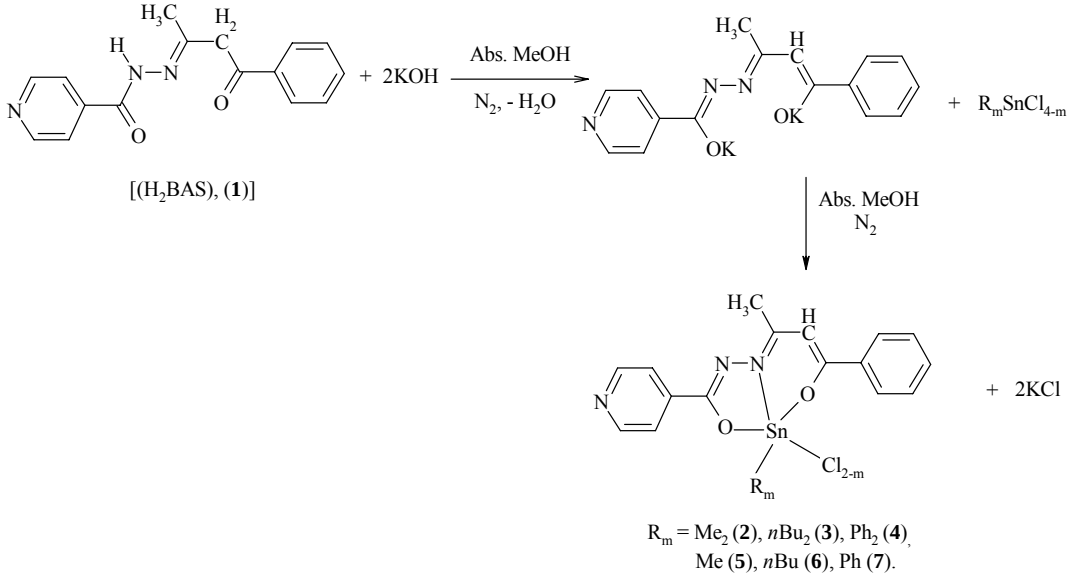
LC_{50} determination

After 24 hours of incubation, the number of dead (i.e. non-motile) nauplii in each well were counted and recorded. The percentage of death for each dose levels and controls (DMSO and artificial sea water without samples) were determined. In cases where control death occurred, the data were corrected using Abbott's formula [19]: Percentage of death = {[(test death-control death)/control survivors] x100 %}. The LC_{50} was then determined for each samples from a plot of log samples concentrations/dose levels versus percentage of death.

Results and discussion

Ligand [(H_2BAS), (**1**)] was synthesized by the condensation reaction of benzoylacetone and isonicotinic hydrazide in absolute ethanol (Scheme **1**) with constant stirring and refluxing. Organotin(IV) complexes (**2**-**7**) have also been synthesized by the direct reaction of the ligand, KOH and organotin(IV) chloride(s) in 1:2:1 (ligand:KOH:metal) mole ratio in absolute methanol using Schlenk vacuum line technique under nitrogen atmosphere (Scheme **2**). In this case, the KOH played a role to force the deprotonation CH=C-OH and N=C-OH groups and then contributed to the coordination.

The physical and analytical data of ligand [(H_2BAS), (**1**)] and its organotin(IV) complexes (**2**-**7**) are listed in Table 1. All the compounds (**2**-**7**) have quite sharp melting points with the differences is only 1-2 °C. Therefore, the compounds (**2**-**7**) show high purity. The found/experimental C, H, N values of compounds (**20**-**26**) are nearly agreed with the calculated values, suggested that the proposed structures of the compounds (**2**-**7**) are acceptable. All organotin(IV) complexes (**2**-**7**) showed the low molar conductance values (1-8 $ohm^{-1}\,cm^2\,mol^{-1}$) indicating non-electrolytic nature [20]. These values support that the anion is coordinated to the central tin(IV) atom [21].



Scheme 2 Synthesis pathway of organotin(IV) complexes (**2-7**).

Table 1: The physical properties and elemental analyses of hydrazone ligand (**1**) and its organotin(IV) complexes (**2-7**).

Compounds	Colour	Yield (%)	Melting point (°C)	Found (Calcd.) %		
				C	H	N
[H_2BAS] (**1**)	Colourless	92	165-167	60.08 (60.31)	5.34 (5.37)	14.90 (14.94)
[Me_2Sn(BAS)] (**2**)	Brownish yellow	70	179-180	50.36 (50.50)	4.38 (4.47)	9.75 (9.82)
[*n*Bu_2Sn(BAS)] (**3**)	Reddish orange	51	132-134	55.98 (56.27)	5.07 (6.10)	7.98 (8.20)
[Ph_2Sn(BAS)] (**4**)	Yellow	64	237-239	60.58 (60.90)	4.05 (4.20)	7.58 (7.61)
[MeSnCl(BAS)] (**5**)	Reddish orange	68	307-309	45.26 (45.53)	3.59 (3.60)	9.31 (9.37)
[*n*BuSnCl(BAS)] (**6**)	Red	50	261-263	48.88 (48.97)	4.44 (4.52)	8.51 (8.57)
[PhSnCl(BAS)] (**7**)	Orange	75	344-346	51.647 (51.75)	3.39 (3.55)	8.19 (8.23)

Electronic absorption spectra

The UV-Visible electronic spectra of [H_2BAS] (**1**) and its organotin(IV) complexes (**2-7**) were measured at room temperature in methanol (10^{-4} M) solution in the range of 200-600 nm. [H_2BAS] (**1**) showed two bands

238 nm and 336 nm which are attributed to benzene π-π* and imino (>C=N) n-π* transitions, respectively [22]. Organotin(IV) complexes (**2-7**) showed two major peaks. The first peak at 232-246 nm region is attributed to n-π* transition which has hyperchromic (blue) shift suggested the free imino (>C=N) group of [H_2BAS] (**1**) is coordinated to the tin(IV) atoms [23]. Another new peak in the range 420-449 nm indicated the complexation occurred via ligand-to-metal charge transfer (LMCT) transition [24].

Infrared spectra

The characteristic IR bands of [H_2BAS] (**1**) and its organotin(IV) complexes (**2-7**) derivatives assigned with the help from the related paper as references and the molecular structures have been proposed. The infrared spectrum of [H_2BAS] (**1**) showed ν(OH/NH), ν(CONH), ν(C=N), ν(N-N) and ν(pyridyl-N, in-plane) bands at 3421, 1689, 1592, 981 and 675 cm^{-1}, respectively. In the spectra of organotin(IV) complexes (**2-7**), the disappearance of ν(CONH) band at 1630 cm^{-1} indicated the coordination via deprotonation of enolic oxygen through tautomerism process [2,13,25]. This is further supported by the formation of new band ν(NCO^-) in organotin(IV) complexes (**2-7**) at 1508-1529 cm^{-1}. The disappearance of ν(C=O) band at 1697 cm^{-1} in organotin(IV) complexes (**2-7**) indicated the coordination of both enolic oxygen atoms in ligand (**1**) to the central tin(IV) atom. A strong to medium band at 1302-1305 cm^{-1} in all organotin(IV) complexes (**2-7**) is assigned to ν(C-O) [2] which further supported the coordination of both of the enolic oxygen atoms to the tin(IV) atom via deprotonation of OH group and finally formation of Sn-O bond in the range 506-531 cm^{-1} in all organotin(IV) complexes (**2-7**) spectra [26]. The presence of strong intensity ν(C=N-N=C) band between 1588-1599 cm^{-1} has lower frequencies shift [10,27] with respect to the free ligand [H_2BAS] (**1**) at 1602 cm^{-1}, confirming the azomethine nitrogen atom is coordinated to organotin(IV) moiety [2,28]. This is also apparent from the new ν(Sn-N) band at 447-454 cm^{-1} in the infrared spectra of all organotin(IV) complexes (**2-7**) [13,16]. A ligand hydrazinic ν(N-N) stretching band at 981 cm^{-1} underwent to higher wave number at 1029-1034 cm^{-1}, further supporting the coordination of azomethine nitrogen to the central tin(IV) atom. The shift is because of the repulsion between the lone pairs of adjacent nitrogen atoms is reduced after complexation [10,29]. A very strong and sharp band at 675 cm^{-1} in the free ligand [H_2BAS] (**1**) is attributed to the ν(pyridyl-N, in-plane), shifted to higher frequency between 692-698 cm^{-1} in all organotin(IV) complexes (**2-7**) [28]. This shift may be due to the electron density reduction after complexation. The overlapped strong and typical board bands which present at 3421-3568 cm^{-1} are due to either the carboxylic ν(O-H) or ν(NH) stretching vibration [28] in the ligand [H_2BAS] (**1**) and lattice water (H_2O) in all organotin(IV) complexes (**2-7**) [29], respectively, could not be identified properly.

^{1}H NMR spectra

The ^{1}H NMR data of the [H_2BAS] (**1**) and its all organotin(IV) complexes (**2-7**) were recorded in DMSO-d_6 solution using TMS as internal standard at room temperature. The ligand [H_2BAS] (**1**) showed the resonance signals at 12.27, 11.16, 7.07-8.68, 6.02 and 1.99 ppm are due to CH=C(OH), N=C(OH), aromatic-H/py-H/Sn-C_6H_5 protons, CH=C and H_3C-C=N protons, respectively. The disappearance of CH=C(OH) and N=C(OH) singlet signals in the ^{1}H NMR spectra of organotin(IV) complexes (**2-7**) indicating both of the enolic oxygen atoms are coordinated to the central tin(IV) atom via deprotonation [27,30-31] and is further supported by the IR data. In general, the aromatic-H/Py-H multiplet signals range shifted down field from 7.07-8.68 ppm to 7.36-8.74 ppm after the complex formation [29,32]. This down field shift observation may be assigned to the deshielding of these protons as a result of the reduction of electron density after coordination [33]. The CH=C resonance signal appeared between 5.89-6.14 ppm in all organotin(IV) complexes (**2-7**) showed a up field shift compared to the free ligand [H_2BAS] (**1**) at 6.02 ppm. The azomethine (H_3C-C=N) resonance signal is appeared at 2.07-2.39 ppm in all organotin(IV) complexes (**2-7**) [29,31,34]. This down field chemical shift observation showed the coordination of the azomethine nitrogen to central tin(IV) atom [27]. All of these statements are further confirmed by the X-ray crystallographic analysis of [$Me_2Sn(BAS)$] (**2**).

X-ray crystal structure of [$Me_2Sn(BAS)$] (2)

Molecular structure of [$Me_2Sn(BAS)$] (**2**) is showed in Figure 1. The crystallographic data and refinement details for [$Me_2Sn(BAS)$] (**2**) are given in Table 2 and the selected bond lengths and bond angles are listed in Table 3. The central tin(IV) atom is coordinated with N(1), C(17), C(18), O(1) and O(2) atoms. N(1), from the hydrazone ligand; C(17) and C(18) atoms from the methyl groups are in the equatorial positions. One axial position is occupied by enolic oxygen of -C(O)NH group, O(1), forming Sn-O(1) with bond length of 2.079(6) Å while the other site is occupied by another enolic oxygen of -C(O)CH_2 group, O(2) atom with a bond length of Sn-O(2) 2.165(7) Å. Both of the Sn-O bond lengths are very much less than the sum of the van der Waals radii for Sn-O (2.8 Å), indicating the strong coordination exist in Sn-O via deprotonation of both enolic oxygen

atoms [36]. The more electronegative atoms lying axially, just like in the case of dimethyltin(IV) of 4-phenyl-2,4-butanedionebenzoylhydrazone(2-) [2], dimethyltin(IV) of *N*-[(2-pyrroyl)methylidene]-*N'*-tosylbenzene-1,2-diamine [39],[*N*-(3-hydroxypyridine-2-yl)-5-chlorosalicylideneiminato]dimethyltin(IV) [30] and dimethyltin(IV) complex of *N'*-(5-bromo-2-hydroxybenzylidene)benzoylhydrazone [11]. Benzoylacetone-isonicotinylhydrazone ligand forms a five-membered and a six-membered chelate rings [2]. [Me_2Sn(BAS)] is distorted trigonal-bipyramidal configuration as the angle of O(1)-Sn-O(2) is compressed to 156.3(3); which is considered deviated significantly from linearity, 180° [10] while the sum of equatorial angles is 359.4° is closed to the ideal values, 360° [38], thus the atoms Sn, C(17), N(1) and C(18) are almost coplanar. The sum angles of the five-membered and six- membered chelate rings are 540° and 719.1°, respectively, which means Sn, O(2), C(11), N(2) and N(1) are in the same planar whereas C(9), C(8), C(7) and O(1) are deviated slightly from the planarity [10,37]. The pyridine ring and benzene ring have the sum angles of 719.9° and 720.1°, respectively; thus all the atoms in the pyridyl ring and benzene ring are almost in the same planar, respectively. The Sn(1)-N(1) bond length is 2.175 Å, which is longer than the sum of the covalent radii of Sn-N (2.15 Å), but is considerably very much less than the sum of the van der Waals radii (3.75 Å), indicating the significant bonding of the central Sn(IV) atom with N(1) [39]. The bond length of Sn-C(17) [2.105(7) Å] and Sn-C(18) [2.105(6) Å] are the same and comparable with the other reported dimethyltin(IV) complexes: [Me_2Sn{5-Br-(2-OC_6H_4CH=N–N=C(O)Ph)}] [10]; Me_2SnL^1 (L^1 = *N*-(3-hydroxypyridine-2-yl)-5-chlorosalicylideneimine) [30]; Me_2SnL^2 (L^2 = *N*-[(2-hydroxyphenyl)metylidene]-*N'*-tosylbenzene-1,2-diamine) [37].

Table 2: Crystallographic data and refinement details for [Me_2Sn(BAS)] (**2**).

Empirical formula	$C_{18}H_{19}N_3O_2Sn$
Formula weight	428.05
Temperature (K)	100(2)
Colour	Brownish yellow
Crystal size (mm)	0.30 x 0.29 x 0.15
Crystal system	Monoclinic
Space group	P2(1)/n
Θ limit (°)	2.13-27.50
Unit cell dimensions	
a (Å)	10.9363(6)
b (Å)	8.4429(4)
c (Å)	19.6553(11)
α (°)	90
β (°)	103.452(2)
γ (°)	90
Volume ($Å^3$)	1765.06(16)
Z	4
Calculated density (Mg m^{-3})	1.611
Absorption coefficient (mm^{-1})	1.462
Final R indices [*I*>2sigma(*I*)]	R_1 = 0.0684, wR_2 = 0.2762
R indices (all data)	R_1 = 0.0704, wR_2 = 0.2796
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3934/0/217
Goodness-of-fit on F^2	2.365

Table 3: Selected bond lengths (Å) and bond angles (˚) for [Me_2Sn(BAS)] (**2**).

Bond lengths			
Sn-O(1)	2.079(6)	C(1)-C(7)	1.527(10)
Sn-C(18)	2.105(6)	C(2)-C(3)	1.387(13)
Sn-C(17)	2.105(7)	C(3)-C(4)	1.367(12)
Sn-O(2)	2.165(7)	C(4)-C(5)	1.335(11)
Sn-N(1)	2.175(6)	C(5)-C(6)	1.422(10)
N(1)-C(9)	1.241(9)	C(7)-C(8)	1.359(12)
N(1)-N(2)	1.425(8)	C(8)-C(9)	1.534(10)
N(2)-C(11)	1.273(11)	C(9)-C(10)	1.476(9)
N(3)-C(14)	1.338(11)	C(11)-C(12)	1.476(8)
N(3)-C(15)	1.356(10)	C(12)-C(13)	1.362(11)
O(1)-C(7)	1.292(8)	C(12)-C(16)	1.412(9)
O(2)-C(11)	1.272(9)	C(13)-C(14)	1.392(13)
C(1)-C(6)	1.374(9)	C(15)-C(16)	1.345(10)
C(1)-C(2)	1.387(11)		
Bond angles			
O(1)-Sn-C(18)	96.6(2)	C(4)-C(3)-C(2)	121.4(7)
O(1)-Sn-C(17)	95.1(3)	C(5)-C(4)-C(3)	119.6(7)
C(18)-Sn-C(17)	122.0(2)	C(4)-C(5)-C(6)	120.9(7)
O(1)-Sn-O(2)	156.3(3)	C(1)-C(6)-C(5)	119.4(7)
C(18)-Sn-O(2)	97.4(3)	O(1)-C(7)-C(8)	122.9(7)
C(17)-Sn-O(2)	93.6(3)	O(1)-C(7)-C(1)	114.6(8)
O(1)-Sn-N(1)	85.6(2)	C(8)-C(7)-C(1)	122.4(6)
C(18)-Sn-N(1)	113.0(2)	C(7)-C(8)-C(9)	130.7(6)
C(17)-Sn-N(1)	124.4(2)	N(1)-C(9)-C(10)	129.6(8)
O(2)-Sn-N(1)	71.3(3)	N(1)-C(9)-C(8)	118.1(6)
C(9)-N(1)-N(2)	111.1(7)	C(10)-C(9)-C(8)	112.4(7)
C(9)-N(1)-Sn	131.5(5)	O(2)-C(11)-N(2)	126.9(7)
N(2)-N(1)-Sn	117.3(5)	O(2)-C(11)-C(12)	118.0(7)
C(11)-N(2)-N(1)	109.4(6)	N(2)-C(11)-C(12)	115.2(6)
C(14)-N(3)-C(15)	116.4(7)	C(13)-C(12)-C(16)	117.8(7)
C(7)-O(1)-Sn	130.8(6)	C(13)-C(12)-C(11)	118.7(6)
C(11)-O(2)-Sn	115.1(6)	C(16)-C(12)-C(11)	123.5(7)
C(6)-C(1)-C(2)	119.3(7)	C(12)-C(13)-C(14)	120.3(7)
C(6)-C(1)-C(7)	120.6(7)	N(3)-C(14)-C(13)	122.2(8)
C(2)-C(1)-C(7)	120.1(6)	C(16)-C(15)-N(3)	124.9(7)
C(1)-C(2)-C(3)	119.5(7)	C(15)-C(16)-C(12)	118.3(7)

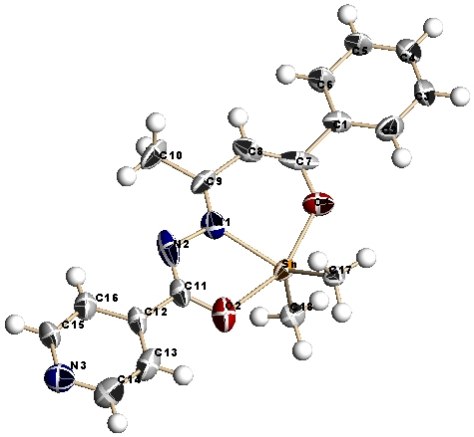


Figure 1: Molecular structure of [Me_2Sn(BAS)] (**2**) with displacement ellipsoid drawn at the 50% probability level.

Toxicity Test

The synthesized [H_2BAS] (**1**) and its organotin(IV) complexes (**2-7**) were screened against brine shrimp (*Artemia salina*) for the preliminary determination of their toxicity level. The percentage of death (%) at log concentrations as well as the LC_{50} (µg/mL) of each compounds are listed in Table 4. The percentage of death (%) at particular log concentrations/dose levels (µg/mL) for the [H_2BAS] (**1**) and its organotin(IV) complexes (**2-7**) are shown in Figure 2a-2g accordingly.

Table 4: Percentage of death (%) at different log concentrations and LC_{50} of hydrazone ligand (**1**) and its organotin(IV) complexes (**2-7**).

Compounds	Log Concentrations (µg/mL)											LC_{50}
	1.00	2.00	5.00	10.00	15.00	25.00	50.00	75.00	100.00	125.00	150.00	(µg/mL)
(**1**)	0.00	0.00	0.00	0.00	0.00	10.00	35.00	73.68	100.00	100.00	100.00	57.39
	0.00	0.00	0.00	0.00	0.00	15.00	40.00	73.68	100.00	100.00	100.00	
	0.00	0.00	0.00	0.00	0.00	10.00	40.00	73.68	100.00	100.00	100.00	
(**2**)	0.00	0.00	0.00	15.00	25.00	40.00	73.68	94.74	100.00	100.00	100.00	27.21
	0.00	0.00	0.00	10.00	25.00	45.00	84.21	100.00	100.00	100.00	100.00	
	0.00	0.00	0.00	10.00	30.00	45.00	84.21	100.00	100.00	100.00	100.00	
(**3**)	0.00	0.00	0.00	0.00	15.00	70.00	89.47	100.00	100.00	100.00	100.00	21.65
	0.00	0.00	0.00	5.00	15.00	65.00	89.47	100.00	100.00	100.00	100.00	
	0.00	0.00	0.00	0.00	10.00	65.00	89.47	100.00	100.00	100.00	100.00	
(**4**)	0.00	0.00	0.00	25.00	50.00	78.95	100.00	100.00	100.00	100.00	100.00	15.31
	0.00	0.00	0.00	20.00	45.00	78.95	95.00	100.00	100.00	100.00	100.00	
	0.00	0.00	0.00	20.00	50.00	84.21	100.00	100.00	100.00	100.00	100.00	
(**5**)	0.00	0.00	0.00	5.00	15.00	30.00	52.63	78.95	100.00	100.00	100.00	45.29
	0.00	0.00	0.00	5.00	10.00	30.00	57.89	84.21	100.00	100.00	100.00	
	0.00	0.00	0.00	0.00	10.00	30.00	52.63	78.95	100.00	100.00	100.00	
(**6**)	0.00	0.00	0.00	0.00	15.00	25.00	57.89	89.47	100.00	100.00	100.00	41.48
	0.00	0.00	0.00	5.00	15.00	30.00	57.89	94.74	100.00	100.00	100.00	
	0.00	0.00	0.00	0.00	15.00	25.00	57.89	89.47	100.00	100.00	100.00	
(**7**)	0.00	0.00	0.00	0.00	10.00	31.58	60.00	94.74	100.00	100.00	100.00	36.03
	0.00	0.00	0.00	5.00	15.00	31.58	65.00	100.00	100.00	100.00	100.00	
	0.00	0.00	0.00	5.00	15.00	42.11	65.00	94.74	100.00	100.00	100.00	

[H_2BAS] (**1**) is less biological active compared with its organotin(IV) complexes (**2-7**) [40]. Generally, for this series, di-organotin(IV) complexes (**2-4**), which LC_{50} range from 15.49-28.84 µg/mL, are more toxic than the mono-organotin(IV) complexes (**5-7**) (36.31-44.67 µg/mL). Biological activities increase in the order CH_3<C_4H_9<C_6H_5 suggesting the more bulky/longer the R (R = CH_3, C_4H_9, C_6H_5) group, the higher the toxicity [41]. Besides the bulkness, the stucture-activity relationships for organotin(IV) derivatives and the nature of donor ligand, even the donor atoms that involved in coordination also affect biological behavior of a compound [42]. Ianelli and his co-workers [43] proposed that organotin(IV) toxicity is also influenced by their hydrophobicity.

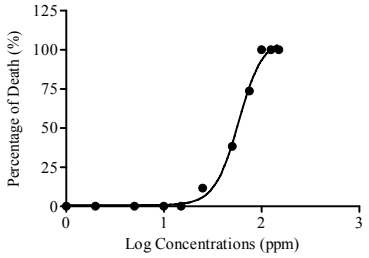


Figure 2a [H_2BAS] (**1**)

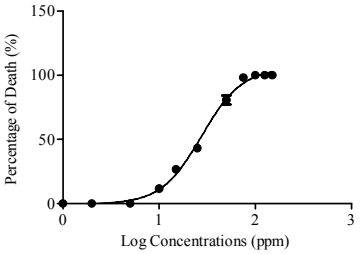


Figure 2b [Me_2Sn(BAS)] (**2**)

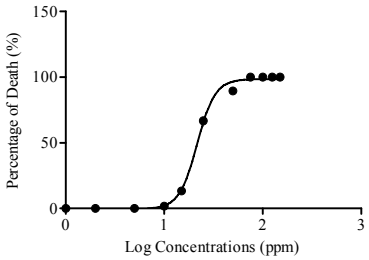


Figure 2c [nBu$_2$Sn(BAS)] (**3**)

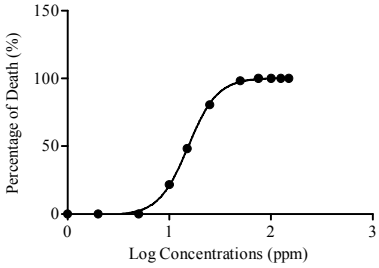


Figure 2d [Ph_2Sn(BAS)] (**4**)

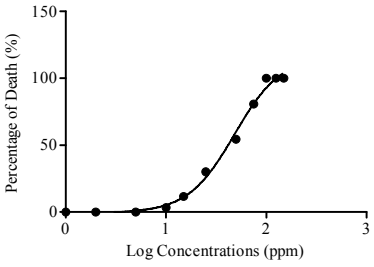


Figure 2e [MeSnCl(BAS)] (**5**)

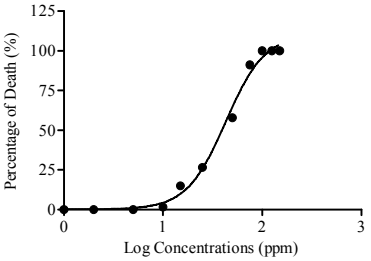


Figure 2f [nBuSnCl(BAS)] (**6**)

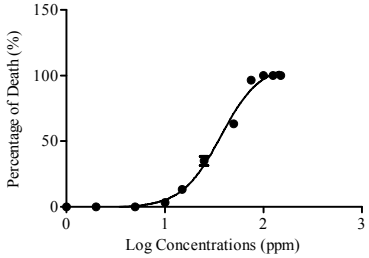


Figure 2g [PhSnCl(BAS)] (**7**)

Figure 2

Conclusion

Benzoylacetone isonicotinylhydrazone ligand [(H_2BAS), (**1**)] and its organotin(IV) complexes (**2-7**) have been synthesized and characterized. The structural characterization showed that the hydrazone ligand [H_2BAS] (**1**) acted as a dinegative tridentate nature in its organotin(IV) complexes (**2-7**) which is further confirmed by the X-ray crystal structure determination of [Me_2Sn(BAS)] (**2**) complex.

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