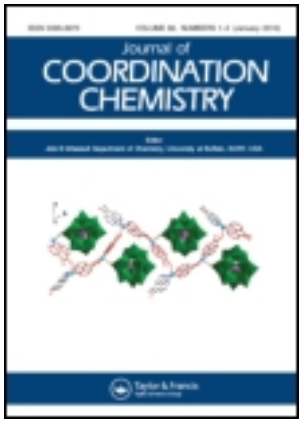

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Synthesis, characterization, and antibacterial activity of organotin(IV) complexes with 2-hydroxyacetophenone thiocarbohydrazone

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Synthesis, characterization, and antibacterial activity of organotin(IV) complexes with 2-hydroxyacetophenone thiocarbohydrazone

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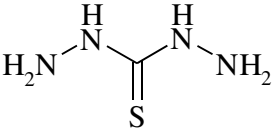
Six new organotin(IV) complexes were synthesized by direct reaction of $RSnCl_3$ (R = Me, Bu and Ph) or R_2SnCl_2 (R = Me, Bu and Ph) and 2-hydroxyacetophenone thiocarbohydrazone [H_2APTC] under purified nitrogen in the presence of base in 1 : 2 : 1 molar ratio (metal: base: ligand). Complexes **2–7** have been characterized by elemental analyses, molar conductivity, UV-Visible, IR and ^{1}H NMR spectral studies. Complexes **2–7** are non-electrolytes. The molecular structure of $[Me_2Sn(APTC)]\cdot(C_2H_5OH)$ (**5**) has been determined by X-ray diffraction analysis. The thiocarbohydrazone ligand (**1**) and **2–7** have been tested for antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Salmonella typhi* and *Enterococci aeruginosa*.

Keywords: Organotin(IV) complexes; Thiocarbohydrazone ligand; Spectral analyses; Crystal structure; Antibacterial activity

1. Introduction

Thiocarbohydrazide is a compound with hydrazine groups at both ends and a thione in the middle.



Thiocarbohydrazide is a precursor for formation of macrocyclic ligands, where wide varieties of metals can attach to the thiocarbohydrazide donor [1]. Both hydrazines of thiocarbohydrazide are reactive and can form *bis*-derivatives with an aldehyde and a

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ketone to form thiocarbohydrazone. Recently, thiocarbohydrazone has received much attention due to promising chemical and biological applications [2]. The chelating ability of thiocarbohydrazones plays an important role for compounds to serve as analytical reagents for extraction, photometric and flourimetric determination of many transition metals [3]. Chelating behavior of thiocarbohydrazones with iron(II), cobalt(II), nickel(II) [2], copper(II), zinc(II), cerium(III), vanadyl(IV), uranyl(IV), and thorium(IV) ions have been studied [4, 5]. Thiocarbohydrazone also shows antimicrobial, antiproliferative, and anti-carcinogenic activity [4, 5]. From literature review, very little work has been reported on organotin(IV) complexes with thiocarbohydrazone [6]. Therefore, we report the synthesis, spectroscopic characterization, and biological activities of the 2-hydroxyacetophenone thiocarbohydrazone (H_2APTC) and its organotin(IV) complexes. The crystal structure of **5** has been determined by X-ray crystallography.

2. Experimental

2.1. *General and instrumental*

Chemicals were purchased from Aldrich, Fluka, Acros, and J.T Baker. All solvents were distilled and purified by standard methods [7]. The reactions were carried out in Schlenk apparatus under nitrogen. The elemental analyses were performed using a FlashEA® 1112. Molecular weight determinations were carried out by the Rast camphor method. Melting points of the compounds were determined with a Stuart SMP3 melting point apparatus in open capillaries. FT-IR spectra were obtained on a Perkin Elmer Spectrum GX Fourier Transform spectrophotometer using KBr discs from 4000–375 cm^{-1}. Electronic spectra were recorded on a Perkin Elmer Lambda 25 from 260–550 nm in DMF. Molar conductivities of the organotin(IV) compounds were measured using a Jenway 4510 conductivity meter at room temperature. ^{1}H NMR spectra were recorded on a Jeol 500 MHz in DMSO-d_6. Single X-ray analyses were carried out using a CrysAlisPro diffractometer at Oxford Diffraction, UK.

2.2. *Preparation of 2-hydroxyacetophenone thiocarbohydrazone (H_2APTC) (1)*

To a solution containing 2-hydroxyacetophenone (1.36 g, 0.010 mol) in 10 mL of ethanol was added thiocarbohydrazide (0.53 g, 0.005 mol) dissolved in minimum ethanol : water mixture (10/5 v/v). The reaction mixture was heated under reflux for 4–6 h in the presence of 2–3 drops of glacial acetic acid and constantly stirred. The reaction mixture was allowed to cool to room temperature for an hour. Pale yellow microcrystals were filtered off and washed several times with absolute ethanol. Then microcrystals were purified by recrystallization from hot absolute ethanol and dried *in vacuo* over anhydrous silica gel. Colorless crystals were obtained by slow evaporation of acetone solution at room temperature. Yield: 1.66 g, 88%, m.p: 221–223°C. UV-Visible (DMF) λ_{max}(nm): 303, 355. IR (ν_{max} cm^{-1}) (KBr): 3561 (lattice OH_2), 3391 (phenolic OH), 3230 (NH), 1619 (C=N), 1300 (C–O phenolic), 1232 (C=S), 963 (N–N). ^{1}H NMR δ ppm: 12.71 (s, 2H, OH), 10.74 (s, 2H, NH), 6.89–7.61 (m, 8H, aromatic protons), 2.02 (s, 6H, CH_3). Anal. Calcd for $C_{17}H_{18}N_4O_2S$ (%): C, 59.65; H, 5.30;

N, 16.36. Found: C, 59.60; H, 5.26; N, 16.33. Molecular weight Calcd for $C_{17}H_{18}N_4O_2S$ ($g\,mol^{-1}$): 342. Found: 341.

2.3. *Synthesis of [MeSnCl(APTC)] (2)*

H_2APTC (0.66 g, 0.002 mol) was dissolved in hot absolute methanol (10 mL) in a Schlenk round bottom flask under nitrogen. Potassium hydroxide (KOH) (0.23 g, 0.004 mol) dissolved in methanol was added dropwise to the ligand solution and the color changed from yellow to orange. The resulting mixture was refluxed under nitrogen for one hour. A methanolic solution of methyltin(IV) trichloride (0.438 g, 0.002 mol) was added dropwise into the resulting mixture causing the solution to change from orange to yellow. The solution was further refluxed for 3–5 h and allowed to cool to room temperature. Potassium chloride (KCl) was filtered off and the solution dried *in vacuo* over anhydrous silica gel. The methyltin(IV) complex was obtained as an intense yellow compound by recrystallization from methanol. Yield: 0.94 g, 72%, m.p: 290°C [dec]. Molar conductivity (DMF) $\Omega^{-1}\,cm^2\,mol^{-1}$: 8.12. UV-Visible (DMF) λ_{max}(nm): 348, 375, 421. IR (ν_{max} cm^{-1}) (KBr) : 3350 (phenolic OH), 3232 (NH), 1599 (C=N–N=C), 1062 (C–O phenolic), 1037 (N–N), 745 (C–S), 518 (Sn–O), 436 (Sn–N). ^{1}H NMR δ ppm: 13.17 (s, 1H, OH), 10.57 (s, 1H, NH), 6.77–7.60 (m, 8H, aromatic ring protons), 2.70 (s, 3H, N=C–CH_3), 2.08 (s, 3H, N=C–CH_3), 1.03 (s, 3H, Sn–CH_3). Anal. Calcd for $C_{18}H_{19}N_4O_2SSnCl$ (%): C, 42.42; H, 3.76; N, 10.99. Found: C, 42.38; H, 3.73; N, 10.97. Molecular weight Calcd for $C_{18}H_{19}N_4O_2SSnCl$ ($g\,mol^{-1}$): 509. Found: 508.

Complexes **3**–**7** were synthesized using the same procedure as for **2** with appropriate organotin(IV) chloride(s).

2.4. *[BuSnCl(APTC)] (3)*

Yield: 1.01 g, 70%, m.p: decomposed >327°C. Molar conductivity (DMF) $\Omega^{-1}\,cm^2\,mol^{-1}$: 15.92. UV-Visible (DMF) λ_{max}(nm): 338, 384, 397. IR (ν_{max} cm^{-1}) (KBr): 3494 (phenolic OH), 3278 (NH), 1597 (C=N–N=C), 1108 (C–O phenolic), 1034 (N–N), 746 (C–S), 564 (Sn–O), 487 (Sn–N). ^{1}H NMR δ ppm: 13.12 (s, 1H, OH), 10.69 (s, 1H, NH), 6.77–7.60 (m, 8H, aromatic ring protons), 2.69 (s, 3H, N=C–CH_3), 2.08 (s, 3H, N=C–CH_3), 0.90–1.68 (m, 9H, Sn–$CH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{21}H_{25}N_4O_2SSnCl$ (%): C, 45.72; H, 4.57; N, 10.16. Found: C, 45.69; H, 4.52; N, 10.14. Molecular weight Calcd for $C_{21}H_{25}N_4O_2SSnCl$ ($g\,mol^{-1}$): 552. Found: 551.

2.5. *[PhSnCl(APTC)] (4)*

Yield: 0.900 g, 60%, m.p: decomposed >330°C. Molar conductivity (DMF) $\Omega^{-1}\,cm^2\,mol^{-1}$: 24.4. UV-Visible (DMF) λ_{max}(nm): 304, 390, 403. IR (ν_{max} cm^{-1}) (KBr): 3443 (phenolic OH), 3256 (NH), 1599 (C=N–N=C), 1061 (C–O phenolic), 1033 (N–N), 747 (C–S), 525 (Sn–O), 428 (Sn–N). ^{1}H NMR δ ppm: 13.10 (s, 1H, OH), 10.96 (s, 1H, NH), 6.42–7.70 (m, overlapping of aromatic ring protons and phenyl ring protons attached to the tin(IV) atom), 2.76 (s, 3H, N=C–CH_3), 2.08 (s, 3H, N=C–CH_3). Anal. Calcd for $C_{23}H_{21}N_4O_2SSnCl$ (%): C, 48.32; H, 3.70; N, 9.80. Found: C, 48.28; H, 3.68; N, 9.78. Molecular weight Calcd for $C_{23}H_{21}N_4O_2SSnCl$ ($g\,mol^{-1}$): 571. Found: 571.

2.6. *[Me$_2$Sn(APTC)]·(C$_2$H$_5$OH) (5)*

Yield: 0.83 g, 63%, m.p: 120–122°C. Molar conductivity (DMF) $\Omega^{-1}\,cm^2\,mol^{-1}$: 1.71. UV-Visible (DMF) λ_{max}(nm): 337, 387, 410. IR (ν_{max} cm^{-1}) (KBr): 3440 (phenolic OH), 3191 (NH), 1596 (C=N–N=C), 1083 (C–O phenolic), 1034 (N–N), 750 (C–S), 515 (Sn–O), 419 (Sn–N). ^{1}H NMR δ ppm: 13.17 (s, 1H, OH), 10.56 (s, 1H, NH), 6.73–7.56 (m, 8H, aromatic ring protons), 2.74 (s, 3H, N=C–CH$_3$), 2.08 (s, 3H, N=C–CH$_3$), 0.68 (s, 6H, Sn–(CH$_3$)$_2$). Anal. Calcd for $C_{19}H_{22}N_4O_2SSn$ (%): C, 46.65; H, 4.53; N, 11.45. Found: C, 46.50; H, 4.43; N, 11.30. Molecular weight Calcd for $C_{19}H_{22}N_4O_2SSn$ (g/mol): 535. Found: 534.

2.7. *[Bu$_2$Sn(APTC)] (6)*

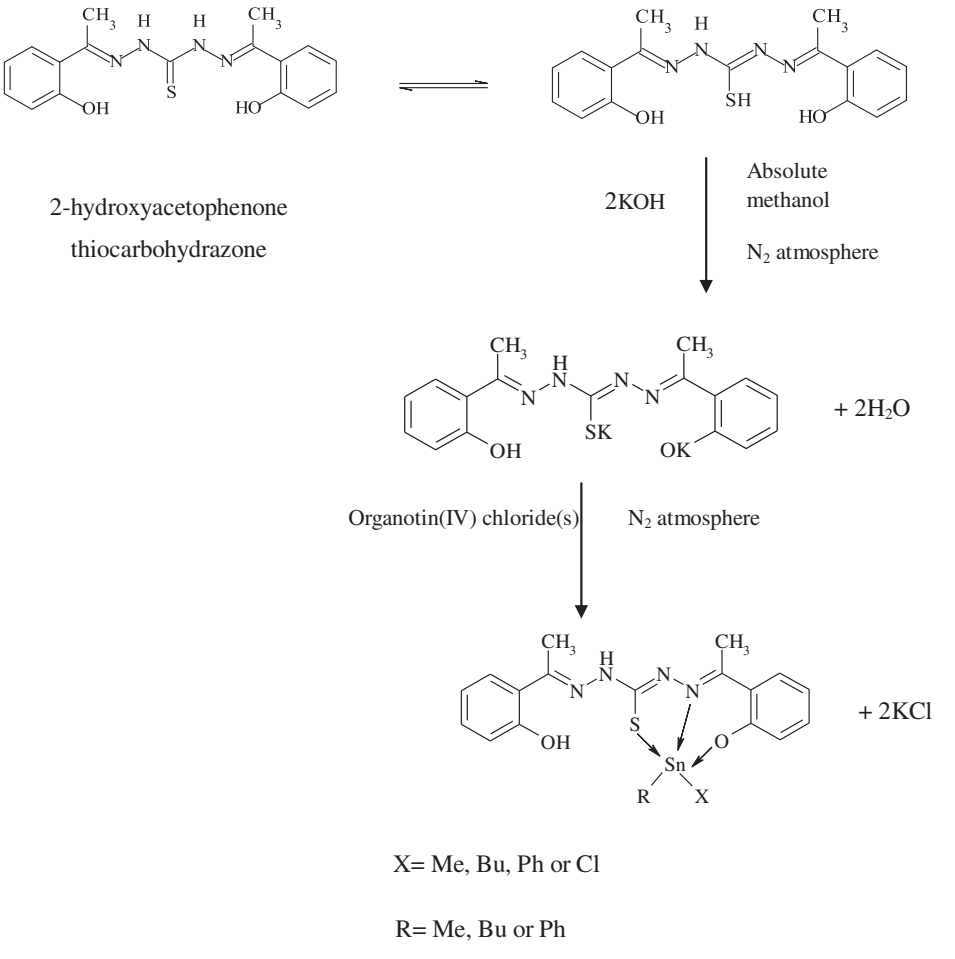
Yield: 0.94 g, 63%, m.p: 132–135°C. Molar conductivity (DMF) $\Omega^{-1}\,cm^2\,mol^{-1}$: 1.72. UV-Visible (DMF) λ_{max}(nm): 338, 389,410. IR (ν_{max} cm^{-1}) (KBr): 3448 (phenolic OH), 3209 (NH), 1596 (C=N–N=C), 1108 (C–O phenolic), 1035 (N–N), 747 (C–S), 515 (Sn–O), 419 (Sn–N). ^{1}H NMR δ ppm: 13.13 (s, 1H, OH), 10.62 (s, 1H, NH), 6.74–7.56 (m, 8H, aromatic ring protons), 2.75 (s, 3H, N=C–CH$_3$), 2.08 (s, 3H, N=C–CH$_3$), 0.63–1.56 (m, 18H, Sn-(CH$_2$CH$_2$CH$_2$CH$_3$)$_2$). Anal. Calcd for $C_{25}H_{34}N_4O_2SSn$ (%): C, 52.37; H, 5.98; N, 9.77. Found: C, 52.35; H, 5.92; N, 9.70. Molecular weight Calcd for $C_{25}H_{34}N_4O_2SSn$ ($g\,mol^{-1}$): 573. Found: 572.

2.8. *[Ph$_2$Sn(APTC)] (7)*

Yield: 1.02 g, 65%, m.p: decomposed >333°C. Molar conductivity (DMF) $\Omega^{-1}\,cm^2\,mol^{-1}$: 9.37. UV-Visible (DMF) λ_{max}(nm): 303, 363, 415. IR (ν_{max} cm^{-1}) (KBr): 3314 (phenolic OH), 3042 (NH), 1600 (C=N–N=C), 1083 (C–O phenolic), 1033 (N–N), 748 (C–S), 525 (Sn–O), 430 (Sn–N). ^{1}H NMR δ ppm: 13.12 (s, 1H, OH), 10.89 (s, 1H, NH), 6.42–7.71 (m, overlapping of aromatic ring protons and phenyl ring protons attached to tin(IV) atom), 2.75 (s, 3H, N=C–CH$_3$), 2.08 (s, 3H, N=C–CH$_3$). Anal. Calcd for $C_{29}H_{26}N_4O_2SSn$ (%): C, 56.79; H, 4.27; N, 9.14. Found: C, 56.68; H, 4.23; N, 9.12. Molecular weight Calcd $C_{29}H_{26}N_4O_2SSn$ ($g\,mol^{-1}$): 613. Found: 612.

2.9. *Antibacterial test*

Antibacterial test of pathogens was carried out by using the disc diffusion method [8]. The bacteria from stock culture were lightly inoculated into the Mueller Hinton Broth (MHB) and let grow overnight at 37°C in an ambient air incubator. The culture was diluted with new MHB in order to achieve optical density of 2.0×10^6 colony forming units ($CFU\,mL^{-1}$) or 0.168 at wavelength of 550 nm in the spectrophotometer. Later, a sterile cotton swab was dipped into the broth culture and inoculated on the Mueller Hinton Agar (MHA). Sterile paper discs with 6 mm diameter were placed on the agar at equal distance. Subsequently, 10 µL aliquot of organotin(IV) compounds at concentration of $200\,mg\,mL^{-1}$ in 0.5% DMSO and 95% MHB were dispensed individually to each of the discs. The agar plate was incubated at 37°C overnight. For each plate, doxycycline dissolved in 5% DMSO and 95% MHB acted as positive control, while DMSO was used as negative control. The inhibition zone on the plate was recorded and measured in diameter, mm.



Scheme 1. The general synthesis of organotin(IV) complexes **2–7**.

3. Results and discussion

3.1. *Synthesis*

2-Hydroxyacetophenone thiocarbohydrazone [H_2APTC (**1**)] was synthesized by condensation of thiocarbohydrazide and 2-hydroxyacetophenone in 1 : 2 mol ratio in ethanol:water (10/5 w/v). H_2APTC exists as the thione form in the solid state and in the thiol form in solution. Six new organotin(IV) complexes (**2–7**) were synthesized by direct reaction of organotin(IV) chlorides with **1** under nitrogen in the presence of KOH as shown in scheme 1. The resulting complexes were obtained in good yield (60–71%). All the complexes are solids and soluble in DMSO, DMF and THF at room temperature. The molar conductivity of **2–7** in DMF are 1.71–24.4 $\Omega^{-1}\,cm^2\,mol^{-1}$ showing that the complexes are non-electrolytes [9]. UV-Visible, IR and ^{1}H NMR spectral data are given in the experimental section. Analytical data are in good agreement with the proposed molecular geometry of **2–7**.

3.2. *UV-Vis spectra*

Electronic spectra of H_2APTC and **2**–**7** were recorded in DMF (10^{-4} M) at room temperature from 260–550 nm, respectively. Compound **1** exhibited two intense peaks at 303 and 355 nm, corresponding to the π–π^* (benzene) and π–π^* (C=N) transitions, respectively. After complexation, the complexes showed three absorptions at 304–338, 363–390 and 397–403 nm, respectively [10]. The new absorption at 397–403 nm, observed in the spectra of the complexes, is assigned to ligand-metal charge transfer transition (LMCT) [11]. The shift of λ_{max} from the ligand to the complexes is a clear indication of coordination between tin(IV) and ligand.

3.3. *Infrared spectra*

Several characteristic bands were observed in **1** at 3391, 3230, 1619, 1300, and 963 cm^{-1}, attributed to ν(OH), ν(NH), ν(C=N), ν(C–O), and ν(N–N), respectively. In spectra of the organotin(IV) complexes, a broad medium to weak band at 3494–3314 cm^{-1} indicates the presence of intramolecular H-bonded-OH. IR spectra of the complexes also show ν(NH) at 3278–3042 cm^{-1}, showing that one NH does not participate in complexation. A medium to strong band at 1600–1596 cm^{-1} is associated with the conjugated >C=N–N=C< fragment of the complexes which is lower compared to free ligand, supporting coordination of nitrogen of azomethine to tin(IV). The ligand hydrazinic ν(N–N) at 963 cm^{-1} shifts to 1037–1033 cm^{-1} in spectra of **2**–**7**, further supporting coordination of azomethine nitrogen to tin(IV) [10]. This increase in frequency is due to repulsion between lone pairs of adjacent nitrogens being reduced after complexation. The absence of ν(C=S) in **2**–**7** supports coordination of the thiolato-S with tin(IV). A new band at 750–745 cm^{-1} is attributed to ν(C–S), supporting the occurrence of thiol tautomer and bonding to tin(IV) in its deprotonated form [12]. There are two new bands at 564–515 cm^{-1} and 489–419 cm^{-1}, respectively, tentatively assigned to ν(Sn–O) and ν(Sn–N) [13].

3.4. *^{1}H NMR spectra*

The ligand showed resonances at 12.71, 10.74, 6.89–7.61, and 2.02 ppm, attributed to OH, NH, aromatic ring protons and CH_3–C=N, respectively. In ^{1}H NMR spectra of the complexes, there was still OH resonance at 13.10–13.17 ppm, indicating that one phenolic OH was not involved in coordination. A new NH signal at 10.56–10.96 ppm is from free NH of **1** which is not involved in coordination to tin(IV) in **2**–**7**. Two resonances appeared for the azomethine (CH_3C=N) group at 2.08 and 2.69–2.76 ppm; the 2.08 ppm is from azomethine not coordinated to tin, while the resonance at 2.69–2.76 ppm is from azomethine involved in coordination. The downfield chemical shift compared to the free ligand supported coordination of azomethine nitrogen to tin(IV) (Sn $\leftarrow$ N) [13]. For **2**, the methyl is at 1.03 ppm whereas in **5**, the two methyls attached to tin(IV) are at 0.68 ppm with ^{2}J(^{119}Sn^{-1}H) of 82 Hz. The coupling constant value is similar to those previously reported for five-coordinate tin(IV) [14]. In **3**, multiplet resonances for *n*-butyl appeared at 0.90–1.68 ppm while in **6**, the multiplets for *n*-butyl groups are at 0.68–1.07 ppm. Complexes **4** and **7** showed multiplets at

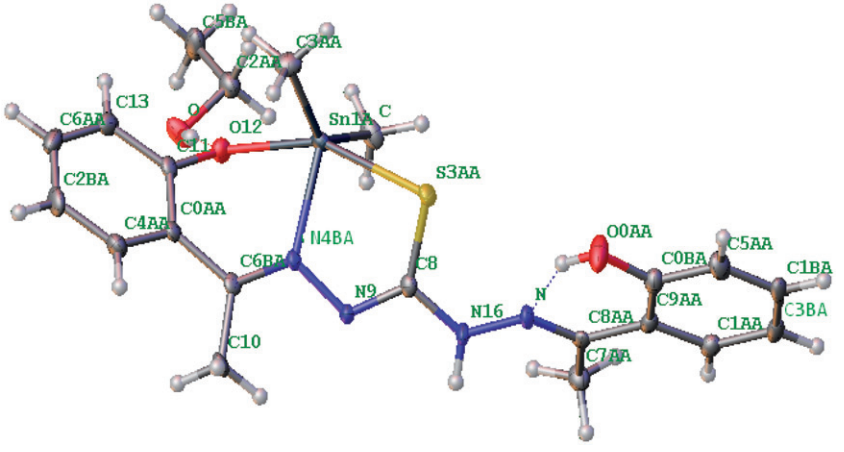


Figure 1. Molecular structure of $[Me_2Sn(APTC)\cdot(C_2H_5OH)]$.

Table 1. Crystal and refinement data of **5**.

Compound	$[Me_2Sn(APTC)]\cdot(C_2H_5OH)$ (**5**)
Empirical formula	$C_{21}H_{28}N_4O_3SnS$
Formula weight	535.22
Temperature (K)	150(1)K
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	7.7842(3)
b	15.2213(4)
c	19.4731(6)
α	90
β	101.436(3)
γ	90.0
Volume (Å^3)	2261.48
Calculated density (Mg m^{-3})	1.572
Crystal size (mm^3)	$0.061 \times 0.069 \times 0.191$
Goodness-of-fit on F^2	1.020
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0322$, $wR_2 = 0.0669$
R indices (all data)	$R_1 = 0.0406$, $wR_2 = 0.0713$

6.42–7.70 ppm and 6.42–7.71 ppm which also overlapped with the aromatic ring protons and could not be properly assigned.

3.5. *X-ray crystallography diffraction analyses*

The X-ray crystal structure of $[Me_2Sn(APTC)]\cdot(C_2H_5OH)$ revealed tridentate dibasic thiocarbohydrazone *bis*-(2-hydroxyacetophenone). The molecular structure of **5** is shown in figure 1 and crystal parameters are tabulated in table 1. Selected bond lengths (Å) and angles (°) are shown in table 2. The crystal structure confirmed that tin(IV) has

Table 2. Selected bond lengths (Å) and angles (°) for **5**.

Sn1A–C2	2.110(4)	N4BA–N9	1.397(4)
Sn1A–C3AA	2.115(4)	N9–C8	1.307(4)
Sn1A–O12	2.121(2)	C11–O12	1.332(4)
Sn1A–C3BA	2.200(3)	C11–O13	1.403(5)
Sn1A–S3AA	2.5867(9)	C11–C0AA	1.429(5)
S3AA–C8	1.734(3)	C0AA–C4AA	1.384(5)
N4BA–C6BA	1.291(4)	C8–N16	1.366(4)
C–Sn1A–C3AA	136.48(15)	N(9) –N4BA–Sn1A	117.0(2)
C–Sn1A–O12	92.92(12)	C3AA–Sn1A–S3AA	96.73(10)
C3AA–Sn1A–O12	94.56(12)	O12–Sn1A–S3AA	153.59(7)
C–Sn1A–N4BA	111.61(13)	N4BA–Sn1A–S3AA	74.53(7)
C3AA–Sn1A–N4BA	111.91(13)	C8–S3AA–Sn1A	90.21(11)
O12–Sn1A–N4BA	79.11(9)	C6BA–N4BA–N9	117.6(3)
C–Sn1A–S3AA	95.16(10)	C6BA–N4BA–Sn1A	125.3(2)

five-coordinate distorted trigonal bipyramidal geometry. The meridional plane of $[Me_2Sn(APTC)]\cdot(C_2H_5OH)$ is taken up by the hydrazinic nitrogen (N4BA) and two methyls. The sum of the bond angles [(C3–Sn1A–C) + (C3–Sn1A–N4BA) + (N4BA–Sn1A–C)] is 360° showing that they are in the same plane. The axial plane of the complex is comprised by the enolic oxygen, O12 and S3 of the thiocarbohydrazone. The O12-Sn–N4BA bond angle is 79.11° whereas the N4BA–Sn1A–S3 bond angle is 74.53° showing that $[Me_2Sn(APTC)]\cdot(C_2H_5OH)$ has a distorted trigonal bipyramidal configuration as the sum of (O12–Sn–S3) angle is 153.64°, significantly deviated from 180°. The distortion is due to the rigidity of the chelate rings, together with the large covalent radius of tin(IV). Five and six-membered rings formed upon chelation of the tin to the ligand. The distorted trigonal bipyramidal geometry results from strain imposed by the non-planar five and six-membered chelate rings, Sn1A–S3AA–C8–N9–N4BA and Sn1A–O12–C11–C0AA–C6BA–N4BA. $[Me_2Sn(APTC)]\cdot(C_2H_5OH)$ has 136.48° (C–SN1A–C3AA), 111.61° (C–Sn1A–N4BA) and 111.91 (C3AA–Sn1A–N4BA) for C, C3AA and N4BA located at the three edges of the trigonal plane. Angles C–Sn1A–N4BA and C3AA–Sn1A–N4BA are slightly smaller than 120°, whereas C–SN1A–C3AA is slightly bigger. This might be due to the repulsion induced by the two methyls at tin(IV). The Sn1A–N4BA bond length is 2.20 Å, longer than the sum of the covalent radii of Sn–N (2.15 Å) [15], indicating significant bonding of tin(IV) with N4BA. The Sn1A-O12 (2.12 Å) of the crystal structure is similar with the covalent radii of Sn–O (2.10 Å) and comparable with the Sn–O (2.14 Å) of a published report [16]. The bond length of Sn1A–C2 (2.11 Å) and Sn1A–C3AA (2.11 Å) are comparable with another reported dimethyltin(IV) complex $[SnMe_2(C_{15}H_{10}N_3S)_2]$ [17]. The Sn1A-S3 of the $[Me_2Sn(APTC)]\cdot(C_2H_5OH)$ is 2.59 Å, comparable with the reported values for Sn–S in $[Sn(CH_3)_2(aptsc)Cl)$ [18], but much smaller than the van der Waals radii 4.0 Å [19]. In $[Me_2Sn(APTC)]\cdot(C_2H_5OH)$, the C_2H_5OH is located in holes within the network with no noteworthy intermolecular hydrogen bonding.

3.6. *Antibacterial activity*

1 and **2**–**7** were screened for antibacterial activity by the paper disc diffusion method and the zone of inhibition is measured in millimeters (table 3). Generally, **1** and its

Table 3. Relative diameter of inhibition zone of *Staphylococcus aureus*, *Escherichia coli*, *Enterococci aeruginosa* and *Salmonella typhi* exhibited by **1** and **2–7**.

	Diameter of inhibition (mm)			
Sample	*St. aureus*	*E. coli*	*E. aeruginosa*	*Sa. typhi*
H_2APTC (**1**)	9.0	–	–	–
[$MeSnCl_2$(APTC)] (**2**)	–	–	–	–
[$BuSnCl_2$(APTC)] (**3**)	8.0	–	–	–
[$PhSnCl_2$(APTC)] (**4**)	–	–	–	–
[Me_2Sn(APTC)] (**5**)	–	–	–	–
[Bu_2Sn(APTC)] (**6**)	12.0	–	–	–
[Ph_2Sn(APTC)] (**7**)	12.0	–	12.0	–
Doxycycline (positive control)	26.0	15.0	15.0	15.0

organotin(IV) complexes show weak to moderate activity against tested bacteria. The diphenyltin(IV) complex (**7**) gives the largest inhibition area against *St. aureus* and *E. aeruginosa* while the dibutyltin(IV) complex (**6**) gives moderate activity against *St. aureus*. **1** also gives weak inhibition towards *St. aureus* growth. The organotin(IV) complexes significantly inhibit gram positive bacteria growth [20, 21]. In general tin(IV) chelated complexes deactivate various cellular enzymes which play important roles in different metabolic pathways for the microorganisms. However, the antibacterial activity of **1** and **2–7** are lower than reported mono-/di-organotin(IV) complexes [21, 22].

4. Conclusions

2-Hydroxyacetophenone thiocarbohydrazone [(H_2APTC) (**1**)] and its organotin(IV) complexes (**2–7**) were synthesized and characterized. The ligand coordinates to the organotin(IV) dinegative tridentate *via* its thiolato-S, azomethine-N and phenolic-O. The characterizations are uniform, so it can be concluded that **2–7** have similar trigonal bipyramidal geometry. **5** was also characterized by X-ray crystal structure analysis. The diphenyltin(IV) and dibutyltin(IV) complexes showed good antibacterial activity against *S. aureus*, while **1** and its organotin(IV) complexes **2–7** are lower than other reported mono-/di-organotin(IV) complexes.

Supplementary material

CCDC783099 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK via http://ccdc.cam.ac.uk/data_request/cif.

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