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Synthesis and spectroscopic characterization of organotin(IV) complexes with 2-benzoylpyridine-*N*(4)-cyclohexylthiosemicarbazone (HBPCT): X-ray crystal structure of [$PhSnCl_2$(BPCT)]

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ABSTRACT

The reaction of 2-benzoylpyridine-*N*(4)-cyclohexylthiosemicarbazone [HBPCT, (**1**)] ligand with organotin(IV) chloride(s) lead to the formation of three new organotin(IV) complexes: [$MeSnCl_2$(BPCT)] (**2**), [$PhSnCl_2$(BPCT)] (**3**) and [Ph_2SnCl(BPCT)] (**4**). The ligand (**1**) and its organotin(IV) complexes (**2–4**) have been synthesized and characterized by CHN analyses, molar conductivity, UV–Vis, FT-IR and ^{1}H NMR spectral studies. The single crystal X-ray diffraction studies indicated that [$PhSnCl_2$(BPCT)] (**3**) is six coordinated and adopts strongly a distorted octahedral configuration with the coordination through pyridine-N, azomethine-N and thiolato-S atoms of the ligand. The crystal system of [$PhSnCl_2$(BPCT)] (**3**) is orthorhombic with space group *P2ac2n* and the unit cell dimensions: $a = 28.1363(5)$ Å, $b = 9.5970(2)$ Å, $c = 9.4353(2)$ Å.

1. Introduction

A thiosemicarbazone is a chemical compound containing the thiosemicarbazide radical = N–NH–C(S)–NH_2. Thiosemicarbazones are known to have anti-viral and anti-cancer properties. For the past few years, studies of the coordination chemistry of thiosemicarbazone involved complexes with transition metal ions [1–6]. Earlier studies of the biological properties of thiosemicarbazones and their metal complexes have reported that the biological active thiosemicarbazone molecules are planar and contain a pyridine ring or derivatives giving rise to NNS-tridentate system [7]. Heterocyclic thiosemicarbazones with a group attached at 2-position have been studied and the presence of bulky group at terminal nitrogen considerably increases the biological activity. Padhye et al. (2005) have synthesized and characterized copper(II) complexes of thiosemicarbazone, derived from thiosemicarbazide and 4-alkyl/aryl-1,2-naphthoquinones. These compounds have been shown to bind DNA molecules and inhibit nuclear DNA repair enzymes. Thiosemicarbazones and their organotin(IV) complexes are of considerable interest due to their various industrial and agricultural applications as well as their antibacterial, anti-viral and antitumor activity [8–11]. Organotin(IV) salts with substituted thiosemicarbazone ligand formed important series of organotin(IV) compounds and have been increasingly reported [12–15]. Sen and Chaudhuri [6] have reported tin(IV) complexes involving ONS coordination mode of dimethyltin(IV) 4-cyclohexylthiosemicarbazone as a novel antitumor agent.

Despite this, based the literature review there is still very limited information available regarding the X-ray and biological studies of novel organotin(IV) complexes with heterocyclic *N*(4)-cyclohexylthiosemicarbazone ligands [16]. In this paper we present new organotin(IV) complexes (**2–4**) of 2-benzoylpyridine-*N*(4)-cyclohexylthiosemicarbazone [HBPCT, (**1**)]. Among them the structure of [$PhSnCl_2$(BPCT)] (**3**) was also determined by single crystal X-ray diffraction. The molecular structure of the complex (**3**) revealed that the Sn atom is six coordinated in distorted octahedral geometry.

2. Experimental

2.1. General procedure

All reagents were purchased from Fluka, Aldrich and JT Baker. All solvents were purified according to standard procedures [17]. The UV–Vis spectra were recorded with DMF solvent on a Perkin–Elmer Lambda 25 UV–Vis spectrophotometer. Infrared spectra (IR) were recorded on KBr disks using a Perkin–Elmer Spectrum GX Fourier-Transform spectrometer (4000–370 cm^{-1}). ^{1}H NMR spectra were recorded in $CDCl_3$ on a JEOL 500 MHz-NMR spectrophotometer.

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CHN analyses were recorded with a Flash EA 1112 series CHN elemental analyzer. Molar conductance values were measured with DMF solvent using a Jenway 4510 conductivity meter. Single crystal X-ray analyses were carried out using a Bruker 300 MHz CCD diffractometer.

2.2. Synthesis of N(4)-cyclohexylthiosemicarbazide

Cyclohexylisothiocyanate (1.41 g, 10 mmol) in 4 mL of ether was added drop-wise into 4 mL of ether solution of hydrazine hydrate (2 g, 40 mmol). The mixture was stirred vigorously for 5 h. Then, 5 mL petroleum ether was added into the resulting solution and stirred for another 1 h and white precipitate was formed. The white precipitate was filtered, washed with a small amount of cool diethyl ether and dried in vacuo over silica gel. Yield: 2.12 g, 62%: Mp.: 146–148 °C: FT-IR (KBr disk, cm^{-1}) ν_{max}: 3334 (s, NH_2), 3297 (s, NH), 2929, 2853 (s, cyclohexyl), 1349, 849 (w, C=S).

2.3. Synthesis of 2-benzoylpyridine-N(4)-cyclohexylthiosemicarbazone [HBPCT (**1**)]

The *N*(4)-cyclohexylthiosemicarbazide (0.51 g, 3 mmol) was dissolved in 10 mL of dry methanol before mixing it with 10 mL of dry methanolic solution of 2-benzoylpyridine (0.54 g, 3 mmol). The resulting mixture was refluxed for 4 h (Scheme 1) and cooled to room temperature. White microcrystals were formed and filtered off. The microcrystals were washed several times with small amounts of cold methanol and subsequently with cold hexane. The microcrystals were recrystallised from methanol and dried in vacuo over silica gel. Yield: 0.94 g, 89%: Mp.: 174–176 °C: UV–Vis (DMF) $\lambda_{max/nm}$: 280, 300, 347: FT-IR (KBr, cm^{-1}) ν_{max}: 3335 (s, NH), 2938, 2845 (s, cyclohexyl), 1583 (w, C=N), 984 (m, N–N), 1345, 863 (w, C=S), 608 (m, pyridine in plane). ^{1}H NMR ($CDCl_3$) δ: 10.80 (*s*, 1H, N4–H), 8.81 (d, 1H, pyridine ring C31–H), 7.76 (t, 1H, pyridine ring C33–H), 7.62 (d, 2H, 1H of N1–H, 1H of CyC1–H), 7.53 (d, 1H, , pyridine ring C34–H), 7.48 (t, 1H, pyridine ring C32–H), 7.29–7.25 (m, 5H, phenyl ring), 2.11–1.71 (m, Cy-H). *Anal.* Calc. for $C_{19}H_{22}N_4S$: C, 67.42; H, 6.55; N, 16.55. Found: C, 67.11; H, 5.61; N, 16.07%.

2.4. Synthesis of [$MeSnCl_2$(BPCT)] (**2**)

The [HBPCT, (**1**)] ligand (0.34 g, 1.0 mmol) was dissolved in 10 mL of absolute methanol under a nitrogen atmosphere in a Schlenk round bottom flask. Then, 10 mL methanolic solution of methyltin(IV) trichloride (0.24 g 1.0 mmol) was added drop-wise, and resulted in a yellow solution. The yellow solution was refluxed for 4 h (Scheme 2) and cooled to room temperature. The yellow microcrystals were obtained from slow evaporation of the solution at room temperature. The microcrystals were filtered, washed with a small amount of cold methanol and dried in vacuo over silica gel. Yield: 0.48 g, 84%: Mp.: 202–204 °C: Molar conductance (DMF) Ω^{-1} cm^2 mol^{-1}: 11.3.

UV–Vis (DMF) $\lambda_{max/nm}$: 295, 334, 385, 417: FT-IR (KBr, cm^{-1}) ν_{max}: 3360 (s, NH), 2933, 2852 (s, cyclohexyl), 1596 (m, C=N–N=C), 1028 (w, N–N), 1308, 816 (m, C–S), 649 (w, pyridine in plane), 578 (w,Sn–C), 484 (w, Sn–N). ^{1}H NMR ($CDCl_3$) δ: 8.83 (d, 1H, pyridine ring C31–H), 8.01 (t, 1H, pyridine ring C33–H), 7.96 (d, 1H, , pyridine ring C34–H), 7.66 (d, 2H, 1H of N1–H, 1H of CyC1–H), 7.51–7.25 (m, 6H, 1H of pyridine ring C32–H, 5H of phenyl ring), 2.15–1.73 (m, Cy-H), 1.08 (s, 3H, Sn–CH_3). *Anal.* Calc. for $C_{20}H_{23}N_4SSnCl_2$: C, 47.19; H, 4.55; N, 11. Found: C, 46.92; H, 4.37; N, 10.74%.

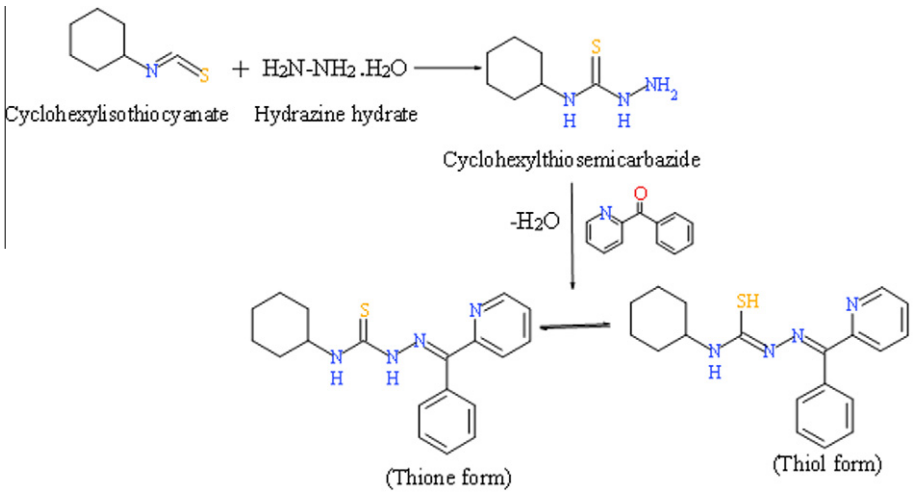
The other complexes (**3**–**4**) were synthesized using a similar procedure to organotin(IV) complex (2) using appropriate organotin(IV) chloride(s).

2.5. Synthesis of [$PhSnCl_2$(BPCT)] (**3**)

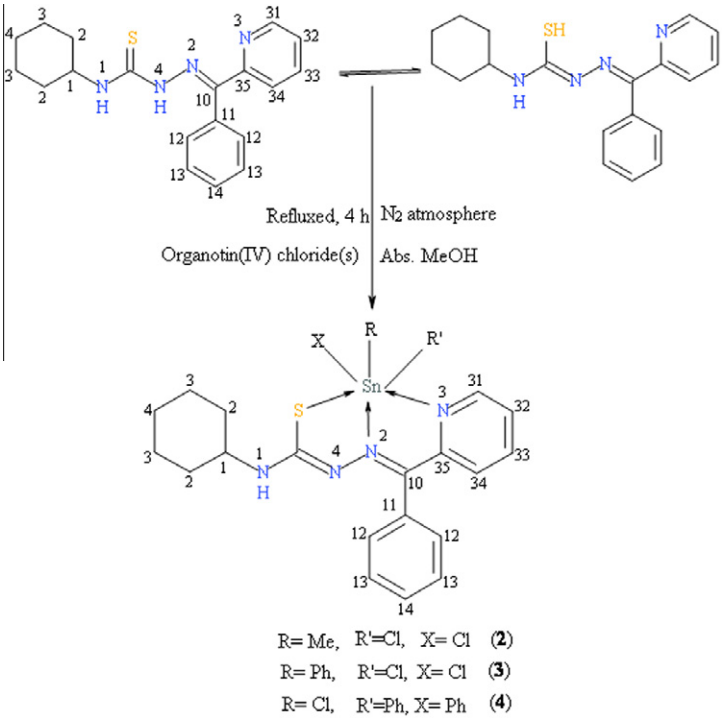
Yield: 0.473 g, 81.27%: Mp.: 297–299 °C: Molar conductance (DMF) Ω^{-1} cm^2 mol^{-1}: 15.18: UV–Vis (DMF) $\lambda_{max/nm}$: 289, 312, 367, 422; FT-IR (KBr, cm^{-1}) ν_{max}: 3378 (s, NH), 2924, 2846 (s, cyclohexyl), 1595 (m, C=N–N=C), 1063 (w, N–N), 1305, 817 (m, C–S), 653 (w, pyridine in plane), 579 (w, Sn–C), 484 (w, Sn–N). ^{1}H NMR ($CDCl_3$) δ: 8.82 (d, 1H, pyridine ring C31–H), 8.41 (t, 1H, pyridine ring C33–H), 8.28 (d, 1H pyridine ring C34–H), 7.95 (d, 2H, 1H of N1–H, 1H of CyC1–H), 7.58–7.25 (m, 11H, 1H of pyridine ring C32-H, 10H of phenyl ring), 2.20–1.70 (m, Cy-H). *Anal.* Calc. for $C_{25}H_{26}N_4SSnCl_2$: C, 49.70; H, 4.33; N, 9.27. Found: C, 49.23; H, 4.12; N, 9.08%.

2.6. Synthesis of [Ph_2SnCl(BPCT)] (**4**)

Yield: 0.52.g, 76%: Mp.: 192–195 °C: Molar conductance (DMF) Ω^{-1} cm^2 mol^{-1}: 8.15: UV–Vis (DMF) $\lambda_{max/nm}$: 295, 306, 368, 417: FT-IR (KBr, cm^{-1}) ν_{max}: 3379 (s, NH), 2929, 2851 (s, cyclohexyl), 1592 (m, C=N–N=C), 1020 (w, N–N), 1302, 811 (m, C–S), 636 (w, pyridine in plane), 588 (w, Sn–C), 457 (w, Sn–N). ^{1}H NMR ($CDCl_3$) δ: 8.82 (d, 1H, pyridine ring C31–H), 8.60 (t, 1H, pyridine ring C33–H), 8.55 (d, 1H, pyridine ring C34–H), 7.70 (d, 2H, 1H of



Scheme 1. Synthesis of 2-benzoylpyridine-*N*(4)-cyclohexyl thiosemicarbazone [HBPCT, (**1**)] ligand.



Scheme 2. The reaction scheme for the synthesis of organotin(IV) complexes (**2–4**).

N1–H, 1H of CyC1–H), 7.27–7.25 (m, 16H, 1H of pyridine ring C32–H, 15H of phenyl ring), 2.15–1.74 (m, Cy-H). *Anal.* Calc. for $C_{31}H_{31}N_4SSnCl$: C, 57.65; H, 4.83; N, 8.67. Found: C, 57.14; H, 4.62; N, 8.41%.

3. Results and discussion

The ligand 2-benzoylpyridine-*N*(4)-cyclohexylthiosemicarbazone [HBPCT, (**1**)] was synthesized by the condensation reaction of *N*(4)-cyclohexylthiosemicarbazide and 2-benzoylpyridine in dry methanol. It has two tautomerization features within the structure, thus in the solid state, it exist as thione form but it converted a thiol form when it is in solution (Scheme 1). Three new organotin (IV) complexes (**2–4**) with [HBPCT, (**1**)] ligand have been synthesized with high purities (Scheme 2). The physical properties and elemental analysis of ligand (**1**) and its organotin(IV) complexes (**2–4**) are given in the experimental section. All organotin(IV) complexes (**2–4**) are stable under N_2 atmosphere and soluble in CH_2Cl_2, $CHCl_3$, DMF, DMSO and MeCN solvents. The molar conductivity of the complexes (**2–4**) in DMF was measured at room temperature. All organotin(IV) complexes (**2–4**) were found to be non electrolytic in nature [18]. The ligand (**1**) acted as mononegative tridentate in all the organotin(IV) complexes (**2–4**).

3.1. UV–Vis spectroscopy

The UV–Vis spectra analyses of ligand (**1**) and its organotin(IV) complexes (**2–4**) were carried out in DMF (10^{-4} M) at room temperature. The bands at 280, 300 and 347 nm correspond to the n–π^* transition of pyridine ring, azomethine, thiolate functions and benzene group, respectively [19]. After complexation, the UV–Vis spectra of the complexes (**2–4**) showed absorption bands in the region at 289–295, 306–334, 368–385 and 417–422 nm, respectively. In the spectra of organotin(IV) complexes (**2–4**), the new absorption band which appeared at 417–422 nm were due to the n–π^* transition band of the ligand–metal charge transfer (LMCT) [20]. The shift of the λ_{max} band from the ligand to the complexes is a clear indication that coordination occurred between tin(IV) and ligand (**1**).

3.2. Infrared spectroscopy

The IR spectrum of the free ligand (**1**) showed absorption bands at 3335, 2938, 2845, 1583, 984, 1345, 863, and 608 cm^{-1} due to ν(NH), ν(cyclohexyl), ν(C=N), ν(N–N), ν(C=S) and pyridine ring in plane, respectively. Upon, complexation, there are significant changes with respect to the free ligand (**1**) and its organotin complexes (**2–4**). The newly formed C=N–N=C bond showed medium to strong absorption peaks within the range of 1592–1595 cm^{-1} in the spectra of the complexes (**2–4**), indicating the coordination of the azomethine nitrogen (N2) to tin(IV) atom [21–22]. The ν(N–N) stretching vibration band at 984 cm^{-1} in the free ligand (**1**) is shifted to higher frequencies at 1020–1073 cm^{-1} in the organotin(IV) complexes (**2–4**). This observation also supported the coordination of azomethine nitrogen to Sn(IV) ion. This is further supported by the formation of new ν(Sn–N) band at 484–485 cm^{-1} in the spectra of the complexes (**2–4**) [23]. The ν(C=S) stretching and bending vibration bands at 1345 and 863 cm^{-1} in [HBPCT, (**1**)] ligand is shifted to lower frequencies in the range of 1302–1308 cm^{-1} and 833–811 cm^{-1} in the spectra of the complexes (**2–4**), indicating the coordination of sulfur in the thiolate form rather than thiol form to the tin(IV) atom. The lowering in values is assumed to be resulted of the deprotonation and formation of a new C–S single bond [24]. A sharp band at 608 cm^{-1} of the pyridine ring in plane in the spectrum of the free ligand [HBPCT, (**1**)] is shifted to higher frequencies in the range of 648–699 cm^{-1} in the complexes (**2–4**), suggesting the coordination of the pyridine ring nitrogen to tin(IV) ion [25]. The IR bands observed at the 579–580 cm^{-1} range were tentatively assigned to ν(Sn–C) mode of the complexes (**2–4**). The IR observation indicated the coordination of ligand (**1**) to the tin(IV) core of the complexes (**2–4**) via pyridine-N, azomethine-N and thiolato-S atoms.

4. ^{1}H NMR spectra

The ^{1}H NMR spectra of ligand [HBPCT, (**1**)] and the complexes (**2–4**) were carried out and interpreted based on the atom leveling in Scheme 2. In the ^{1}H NMR, the spectrum of [HBPCT, (**1**)] revealed a singlet at 10.80 ppm, corresponding to the resonance signal of N4–H. In pyridine ring, the electronic effect of the adjacent pyridyl nitrogen shifts the signals to a lower field and more downfield. The pyridine protons gave four resonance signals at 8.81, 7.76, 7.53 and 7.48 ppm corresponded to the C31–H, C33–H, C34–H and C32–H, respectively. A doublet at 7.62 ppm corresponded to N1–H which is probably overlapping with CyC1–H. The multiplet signals of aromatic-H in the ligand (**1**) were observed at 7.29–7.25 ppm. The cyclohexyl moiety exists in chair conformation and the equatorial protons are observed at more down field compared to their axial counterparts. The resonance signals of the cyclohexyl protons were observed at 2.11–1.71 ppm. Upon complexation, the N4–H signal is absent in the spectra of the complexes (**2–4**), indicating converted to thiol from thione and suggesting coordinated to tin(IV) core after deprotonation. The signals of pyridine ring hydrogen undergo significant shifts. The resonance signals of the C31–H in the complexes (**2–4**) were observed at 8.82–8.83 ppm shifted downfield compared to the free ligand (**1**). The resonance signal of the C33-H and C34–H were observed at a range of between 8.60–8.01 and 8.55–7.96 ppm which are shifted downfield compared to the free ligand (**1**), respectively. This downfield shift also supported the observation that pyridine ring nitrogen (N3) is coordinated with the Sn atom, which is also supported by the IR spectrum of the complexes (**2–4**). The proton resonance signal for N1–H which is overlapping with CyC1–H atoms appeared in the 7.95–7.70 ppm range in the complexes (**2–4**). The C32–H of pyridine ring which is probably overlapping with proton signal of aromatic-H in the complexes (**2–4**) was observed at 7.58–7.25 ppm and found to be downfield as compared to the free ligand (**1**). This downfield may be due to the depletion of electron density from the ring to the Sn atom. This downfield shift also supports the coordination of $C_6H_5C{=}N$ nitrogen to the Sn(IV) atom. In cyclohexyl, the resonance signals of the protons in the complexes (**2–4**) were observed at 2.20–1.73 ppm compared to the free ligand**.** The sharp signal attributed to the methyl group attached to the tin(IV) atom appeared as a singlet at 1.08 ppm in complex (**2**). However, the resonance signal of the methyl group, aromatic ring and cyclohexyl ring protons do not take part in the coordination but after complexation there are slight chemical shifts due to the delocalization of electron density in the system.

4.1. X-ray crystallography diffraction analyses

Suitable single crystals of phenyltin(IV) complex (**3**) were grown from methanol at room temperature. A summary of crystal data, experimental details and refinement results of the complex (**3**) are listed in Table 1. Selected bond length (Å) and bond angle (°) of the complex **(3)** are summarized in Table 2. The molecular structure of the complex (**3**) with appropriate numbering is shown in Fig. 1. In the molecular structure of (**3**), the tin(IV) atom adopts a distorted octahedral geometry with the *N*(4)-cyclohexylthiosemicarbazone ligand (**1**) coordinated to it as a mononegative tridentate chelating agent via pyridine-N, azomethine-N and thiolato-S atoms (Fig. 1). The equatorial position is occupied by S, N(2) and N(3) and remaining sites are occupied by the two chlorine atoms and one carbon atom of the phenyl group. The two chlorines do not occupy the exact axial positions as a result the (Cl1–Sn–Cl1) angle is 165.34°, which showed the significant distortion from linear angle 180°. The deviation of the axial plane from linearity might be due to the steric hindrance by the bulky phenyl groups. The angle C20–Sn–Cl1 (96.191(14)°) is larger than S–Sn–Cl1 (91.623(12)°).

Table 1
Crystal data, structure solution method and refinement for complex (**3**).

Compound	[$PhSnCl_2$(BPCT)] (**3**)
Empirical formula	$C_{25}H_{26}Cl_2N_4SSn$
Formula weight	604.15
Temperature (K)	103(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	*P*2*ac*2*n*
Unit cell dimensions	
a (Å)	28.1363(5)
b (Å)	9.5970(2)
c (Å)	9.4353(2)
β (°)	90.0
Volume (Å3)	2547.76(9)
Z	2
Calculated density (mg m^3)	1.575
F(0 0 0)	1216
Crystal size (mm)	0.5 × 0.5 × 0.44
Crystal color	yellow
Scan range *θ* (°)	2.28–30.59
Absorption coefficient (*μ*) (mm^{-1})	1.316
Absorption correction	SADABS
Maximum and minimum transmission	0.5952 and 0.5591
Goodness-of-fit (GOF) on F^2	1.318
Data/restrains/parameters	3915/0/178
R_{obs}, wR_{obs}	0.0301, 0.0737
R_{all}, wR_{all}	0.0312, 0.0741

Table 2
Selected bond lengths (Å) and angles (°) of [$PhSnCl_2$(BPCT)] (**3**).

Bond lengths (Å)		Bond angles (°)	
Sn–C20	2.137(3)	C20–Sn–N2	171.59(10)
Sn–N2	2.222(2)	C20–Sn–N3	98.77(10)
Sn–N3	2.255(3)	N2–Sn–N3	72.82(8)
Sn–C11	2.4740(5)	C20–Sn–Cl1	96.191(14)
Sn–S	2.4746(7)	N2–Sn–Cl1	83.302(13)
C7–S	1.752(3)	N3–Sn–Cl1	85.196(14)
N1-–C7	1.335(4)	Cl1–Sn–Cl1	165.34(3)
N2–C10	1.307(4)	C20–Sn–S	109.45(8)
N2–N4	1.348(3)	N2–Sn–S	78.96(7)
N3–C31	1.343(3)	N3–Sn–S	151.79
N3–C35	1.350(4)	Cl1–Sn–S	91.623(13)
C7–N4	1.334(4)	C7–Sn–S	95.46(10)
C1–C2	1.522(3)	C10–N2–N4	119.4(3)
C10–C35	1.460(4)	C10–N2–Sn	118.26(19)
C10–C11	1.486)4)	N4–N2–Sn	122.31(19)
C11–C12	1.390(3)	C31–N3–C35	120.6(3)
C20–C21	1.392(3)	C31–N3–Sn	124.1(2)
C31–C32	1.388(2)	C7–N4–N2	114.7(2)
C32–C33	1.386(5)	N3–C31–C32	121.6 (3)
C34–C35	1.389(4)	C31–C32–C33	118.7(3)
C21–C22	1.394(3)	C32–C33–C34	119.3(3)
C22–C23	1.397(3)	C33–C34–C34	119.6(3)
C1–N1	1.467(4)	C34–C35–N3	120.2(3)

The sum of the equatorial angles S–Sn–N2 (78.96(7)°), N2–Sn–N3 (72.82(8)°) and S–Sn–N3 (151.79°) is 303.57° showing more distortion from ideal bond angle 360°. The sum of the angle S–Sn–C20 (109.45(8)°), S–Sn–N2 (78.96(7)°), N2–Sn–N3 (72.82(8)°) and C20–Sn–N3 (98.77(10)°) is 360°. Thus the atoms Sn, S, C20, N3 and N2 are coplanar. The angle C31–N3–C35 (120.6(3)°), N3–C31–C32 (121.6(3)°), C31–C32–C33 (118.7(3)°), C32–C33–C34 (119.3(3)°), C33–C34–C35 (119.6(3)°) and C34–C35–N3 (120.2(3)°) are not 120°; thus all the atoms in the pyridine ring are not in the same. The Sn–S bond distance is 2.4746(6) Å, which is close to the sum of the covalent radii of tin and sulfur 2.42 Å [26], but much smaller than the Van der Waals radii 4.0 Å [27], indicating the S atom is coordinated in the thiolate form. The Sn–N2 and

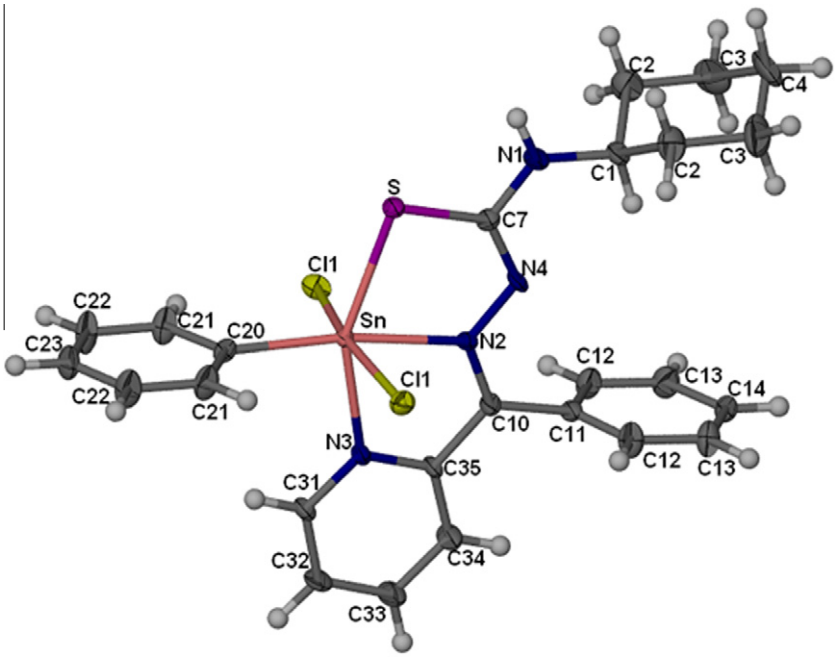


Fig. 1. Molecular structure of [$PhSnCl_2$(BPCT)] (**3**).

Sn–N3 bond lengths are 2.222(2) Å and 2.255(3) Å, respectively, which is close to the sum of the covalent radii of Sn–N (2.15 Å), indicating significant bonding of the Sn atom with N2 and N3, respectively [28]. In general, the Sn–N bond distances reported here can be considered within the usual range reported for other related tin(IV)–thiosemicarbazone complexes [29]. The expected lengthening of the C–S bond from 1.69 Å in H2Am4DH to 1.75 Å in [(*n*-Bu)–Sn(2Am4DH)Cl_2] together with shortening of the C7–N4 bond length from 1.358 Å in [(*n*-Bu)–Sn(2Am4DH)Cl_2] to 1.33 Å were observed. Therefore, the C–S bond changes from a double bond to a predominantly single bond whereas C7–N4 acquires some double bond character. The remaining sites are occupied by the negative charged phenyl group [d(Sn–C20) = 2.137(3) Å] and by two chlorine atoms [d(Sn–Cl1) = 2.4740(5) Å]. The bond length Sn–C20 (2.137(3) Å is very much longer than C20–C21 (1.392(3) Å, C21–C22 (1.394(3) Å and C22–C23 (1.397(3) Å in a phenyl ring, it may due to steric hindrance of the central Sn atom.

5. Conclusion

The ligand [HBPCT, (**1**)] and its organotin(IV) complexes (**2–4**) were synthesized and characterized successfully. The ligand (**1**) exists in thione form in a solid state but it takes on a thiol form when it is in solution. The results obtained from the spectroscopic characterization support the proposed six coordinated structures of the complexes (**2–4**). The ligand (**1**) is coordinated to the tin(IV) atom through thiolato-S, azomethine-N and pyridine ring-N atoms. The X-ray crystallography diffraction has also revealed that the phenyltin (IV) complex (**3**) is rendered a distorted octahedral geometry.

Acknowledgments

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Appendix A. Supplementary material

CCDC 7385951 contains the supplementary crystallographic data for [PhSnCl2(BPCT)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.11.002.

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