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Synthesis and characterization of tin(IV)/organotin(IV) complexes with 2-benzoylpyridine-N(4)cyclohexylthiosemicarbazone [HBPCT]: X-ray crystal structure of [SnCl₃(BPCT)]

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Synthesis and characterization of tin(IV)/organotin(IV) complexes with 2-benzoylpyridine-*N*(4)-cyclohexylthiosemicarbazone [HBPCT]: X-ray crystal structure of [SnCl₃(BPCT)]

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Four new tin(IV)/organotin(IV) complexes, [SnCl₃(BPCT)] (2), [MeSnCl₂(BPCT)] (3), [Me₂SnCl(BPCT)] (4), and [Ph₂SnCl(BPCT)] (5), have been synthesized by the direct reaction of 2-benzoylpyridine-N(4)-cyclohexylthiosemicarbazone [HBPCT, (1)] and stannic chloride/ organotin(IV) chloride(s) in absolute methanol under purified nitrogen. HBPCT and its tin(IV)/ organotin(IV) complexes (2–5) were characterized by CHN analyses, molar conductivity, UV-Vis, FT-IR, and ¹H NMR spectral studies. In all the complexes, tin(IV) was coordinated *via* pyridine-N, azomethine-N, and thiolato-S from 1. The molecular structure of 2 has been determined by X-ray single-crystal diffraction analysis. Complex 2 is a monomer and the central tin(IV) is six-coordinate in a distorted octahedral geometry. The crystal system of 2 is monoclinic with space group P121/n1 and the unit cell dimensions are a=8.3564(3)Å, b=23.1321(8)Å, c=11.9984(4)Å.

Keywords: Substituted thiosemicarbazone; Tin(IV)/organotin(IV) complexes; Spectral analyses; Crystal structure

1. Introduction

Thiosemicarbazones are chelating ligands, bonding through the sulfur and hydrazine nitrogen. Interest in tin(IV) thiosemicarbazones is focused on tin(IV) sulfur compounds in biological molecules, with the bonding in tin(IV) chelates derived from the skeletal $=N-NH-C(S)-NH_2$. Thiosemicarbazones and their organotin(IV) complexes are of considerable interest due to their potential biological (namely antiviral and antitumor) activities as well as their industrial and agricultural applications [1–4]. Synthesis and biological studies of substituted thiosemicarbazones have received increasing attention in recent years [5–8]. Mendes *et al.* [9] reported the synthesis of organotin(IV) complexes

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of 2-pyridineformamide-derived thiosemicarbazone, which suggested that the complexes possess an interesting pharmacological profile and are useful as cytotoxic and antibacterial agents. Suni *et al.* [10] synthesized and characterized Co(II) and Co(III) metal complexes with di-2-pyridylketone N(4)-cyclohexyl and N(4)-phenyl thiosemicarbazone ligands. However, most past works on thiosemicarbazones involved their metal complexes with transition metal ions [11–16].

Many organotin(IV) compounds are investigated for their anticancer activity [17–20]. Survey of the literature found no report on the syntheses of tin(IV)/organotin(IV) chelating 2-benzoylpyridine-N(4)-cyclohexylthiosemicarbazone or its anticancer activity and cytotoxicity. Continuing our work on organotin(IV) adducts with substituted thiosemicarbazones [21–23], we report here the synthesis and structural characterization of four new tin(IV)/organotin(IV) complexes (2–5) with 2-benzoylpyridine-N(4)-cyclohexylthiosemicarbazone [HBPCT, (1)]. Single-crystal X-ray diffraction of [SnCl₃(BPCT)] (2) is also studied.

2. Experimental procedure

2.1. General procedure

All reagents were purchased from Fluka, Aldrich, and JT Baker. All solvents were purified according to standard procedures [24]. UV-Vis spectra were recorded with DMF on a Perkin Elmer Lambda 25 UV-Vis spectrophotometer. Infrared (IR) spectra were recorded as KBr discs using a Perkin Elmer Spectrum GX Fourier-Transform spectrometer (4000–375 cm⁻¹). ¹H NMR spectra were recorded in CDCl₃ solution on a JEOL 500 MHz-NMR spectrophotometer. CHN analyses were recorded with a Flash EA 1112 series CHN elemental analyzer. Molar conductance values were measured in DMF using a Jenway 4510 conductivity meter. Finally, single-crystal X-ray crystallographic analyses were carried out using a CrysAlispro CCD diffractometer at Oxford Diffraction Ltd. UK.

2.2. Synthesis of N(4)-cyclohexylthiosemicarbazide

Cyclohexylisothiocyanate (1.41 g, 10 mmol) in 4 mL of ether was added dropwise 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 forming white precipitate. The white precipitate was filtered off, washed with a small amount of cold diethyl ether and dried *in vacuo* over silica gel. Yield: 2.12 g, 62%: m.p.: 146–148°C: FT-IR (KBr disc, cm⁻¹) ν_{max} : 3334 (s, NH₂), 3297 (s, NH), 2929, 2853 (s, cyclohexyl), 1349, 849 (w, C=S).

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

N(4)-cyclohexylthiosemicarbazide (0.51 g, 3 mmol) was dissolved in dry methanol (10 mL) and mixed with a dry methanolic solution of 2-benzoylpyridine (0.54 g, 3 mmol) (10 mL). 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 recrystallized from methanol and dried *in vacuo* over silica gel. Yield: 0.94 g, 89%: m.p.: 174–176°C: UV-Vis (DMF) $\lambda_{max/nm}$: 280, 300, 347: FT-IR (KBr disc, 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). ¹H NMR (CDCl₃) δ : 11.54 (*s*, 1H, N1–H), 8.81 (d, 1H, pyridine ring C19–H), 7.76 (t, 1H, pyridine ring C17–H), 7.62 (d, 2H, 1H of N2–H, 1H of CyC6–H), 7.53 (d, 1H, pyridine ring C16–H), 7.48 (t, 1H, pyridine ring C18–H), 7.29–7.25 (m, 5H, phenyl ring), 2.11–1.71 (m, Cy–H). Anal. Calcd for C₁₉H₂₂N₄S (%): C, 67.42; H, 6.55; N, 16.55. Found (%): C, 67.21; H, 6.31; N, 16.22.

2.4. Synthesis of [SnCl₃(BPCT)] (2)

HBPCT (0.34 g, 1.0 mmol) was dissolved in absolute methanol (10 mL) under a nitrogen atmosphere in a Schlenk round bottom flask. Then, a methanolic solution of stannic chloride (0.26 g, 1.0 mmol) was added dropwise, resulting in a yellow solution. The resulting reaction mixture was refluxed for 4h (scheme 2) and cooled to room temperature. Yellow microcrystals were obtained from slow evaporation of the solution at room temperature. The microcrystals were filtered off, washed with a small amount of cold methanol and dried in vacuo over silica gel. Single crystals were grown from chloroform/methanol (1:1 ratio) at room temperature. Yield: 0.48 g, 80%; m.p.: 281–283°C; molar conductance (DMF) Ω^{-1} cm² mol⁻¹: 18.10; UV-Vis (DMF) $\lambda_{max/nm}$: 298, 370, 422; FT-IR (KBr, cm⁻¹) ν_{max} : 3329 (s, NH), 2931, 2852 (s, cyclohexyl), 1596 (m, C=N-N=C), 1067 (w, N-N), 1307, 819 (m, C-S), 653 (w, pyridine in plane), 449 (w, Sn–N). ¹H NMR (CDCl₃) δ : 8.83 (d, 1H, pyridine ring C19–H), 8.15 (t, 1H, pyridine ring C17–H), 8.10 (d, 1H, pyridine ring C16–H), 7.82 (d, 2H, 1H of N2-H, 1H of CyC6-H), 7.55-7.25 (m, 6H, 1H of pyridine ring C18-H, 5H of phenyl ring), 2.20–1.72 (m, CyC–H). Anal. Calcd for $C_{19}H_{21}Cl_3N_4SSn$ (%): C, 40.57; H, 3.76; N, 10.03. Found (%): C, 40.41; H, 3.63; N, 9.92.



Scheme 1. Synthesis of 2-benzoylpyridine-N(4)-cyclohexylthiosemicarbazone [HBPCT, (1)].



Scheme 2. The reaction scheme for the synthesis of 2-5.

The other complexes (3-5) were synthesized using a similar procedure to 2 using appropriate organotin(IV) chloride(s).

2.5. Synthesis of [MeSnCl₂(BPCT)] (3)

Yield: 0.48 g, 84%: m.p.: 202–204°C: Molar conductance (DMF) Ω^{-1} cm² mol⁻¹: 11.3: UV-Vis (DMF) $\lambda_{\text{max/nm}}$: 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). ¹H NMR (CDCl₃, ²*J*[¹¹⁹Sn, ¹H]) δ : 8.83 (d, 1H, pyridine ring C19–H), 8.01 (t, 1H, pyridine ring C17–H), 7.96 (d, 1H, pyridine ring C16–H), 7.66 (d, 2H, 1H of N2–H, 1H of CyC6–H), 7.51–7.25

(m, 6H, 1H of pyridine ring C18–H, 5H of phenyl ring), 2.15–1.73 (m, CyC–H), 1.08 (s, 3H, Sn–CH₃), [92.5 Hz]. Anal. Calcd for $C_{20}H_{24}N_4SSnCl_2$ (%): C, 44.31; H, 4.46; N, 10.33. Found (%): C, 44.31; H, 4.38; N, 10.27.

2.6. Synthesis of [Me₂SnCl(BPCT)] (4)

Yield: 0.45 g, 81%: m.p.: 180–182°C: Molar conductance (DMF) Ω^{-1} cm² mol⁻¹: 12.84: UV-Vis (DMF) $\lambda_{\text{max/nm}}$: 298, 339, 386, 412: FT-IR (KBr, cm⁻¹) ν_{max} : 3335 (s, NH), 2939, 2852 (s, cyclohexyl), 1583 (m, C=N–N=C), 1074 (w, N–N), 1320, 833 (m, C–S), 652 (w, pyridine in plane), 531 (w, Sn–C), 479 (w, Sn–N). ¹H NMR (CDCl₃, ²*J*]¹¹⁹Sn, ¹H]) δ : 8.82 (d, 1H, pyridine ring C19–H), 8.55 (t, 1H, pyridine ring C17–H), 7.76 (d, 1H, pyridine ring C16–H), 7.63 (d, 2H, 1H of N2–H, 1H of CyC6–H), 7.47–7.25 (m, 6H, 1H of pyridine ring C18–H, 5H of phenyl ring), 2.15–1.63 (m, CyC–H), 1.17 (s, 6H, Sn–CH₃), [110 Hz]. Anal. Calcd for C₂₁H₂₇N₄SSnCl (%): C, 48.34; H, 5.21; N, 10.73. Found (%): C, 48.28; H, 5.14; N, 10.62.

2.7. Synthesis of $[Ph_2SnCl(BPCT)]$ (5)

Yield: 0.52 g, 76%: m.p.: 192–195°C: Molar conductance (DMF) Ω^{-1} cm² 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). ¹H NMR (CDCl₃) δ : 8.82 (d, 1H, pyridine ring C19–H), 8.60 (t, 1H, pyridine ring C17–H), 8.55 (d, 1H, pyridine ring C16–H), 7.70 (d, 2H, 1H of N2–H, 1H of CyC6–H), 7.27–7.25 (m, 16H, 1H of pyridine ring C18–H, 15H of phenyl ring), 2.15–1.74 (m, Cy–H). Anal. Calcd for C₃₁H₃₁N₄SSnCl (%): C, 57.65; H, 4.83; N, 8.67. Found (%): C, 57.34; H, 4.62; N, 8.48.

3. Results and discussion

HBPCT was prepared by the condensation of cyclohexylthiosemicarbazide and 2-benzoylpyridine in absolute methanol in 1:1 mole ratio. It has two tautomers within the structure, existing as either thione or thiol tautomer (scheme 1). Four new tin(IV)/organotin(IV) complexes (2–5) with 1 were synthesized in acceptable yields (scheme 2). The physical properties and analytical data of 1–5 are given in section 2. Complexes 2–5 are solids and are stable under N₂. They are more soluble in polar than in nonpolar solvents. Complexes 2–5 are proposed to have octahedral configuration; all are neutral and nonelectrolytes [25].

3.1. UV-Vis spectroscopy

The UV-Vis spectra of 1–5 were carried out in DMF $(10^{-4} \text{mol L}^{-1})$ at room temperature. 1 exhibited three bands at 280, 300, and 347 nm assigned to the HOMO/LUMO transition of pyridine, azomethine, thiolate functions and benzene ring system, respectively [26]. On complexation, the UV-Vis spectra of 2–5 exhibit one new

absorption at 412–422 nm, assigned to the HOMO/LUMO transition of the ligandmetal charge transfer [27]. The shift of the HOMO/LUMO band from the ligand to the complexes was a clear indication that coordination occurred between tin(IV) and 1.

3.2. IR spectroscopy

The IR spectrum of **1** displayed absorptions at 3335, 2938, 2845, 1583, 984, 1345, 863, and 608 cm^{-1} attributable to $\nu(\text{NH})$, $\nu(\text{cyclohexyl})$, $\nu(\text{C=N})$, $\nu(\text{N-N})$, $\nu(\text{C=S})$, and pyridine in plane, respectively. Upon complexation, several significant changes occurred. The spectrum of the free ligand exhibits a strong band at 1583 cm⁻¹ due to ν (C=N). The newly formed C=N-N=C bond showed medium to strong absorptions at $1583-1596 \text{ cm}^{-1}$ in spectra of 2–5, indicating coordination of azomethine nitrogen (N3) to tin(IV) [28]. The ν (N–N) at 984 cm⁻¹ in 1 is shifted to higher frequencies, $1020-1074 \text{ cm}^{-1}$, in 2–5, supporting the coordination of azomethine nitrogen to Sn(IV). This is further supported by the formation of a new v(Sn-N) at 449–484 cm⁻¹ in 2–5 [29]. The ν (C=S) and bending vibrations observed at 1345 and 863 cm⁻¹ in the spectrum of 1 shift to lower frequencies, 1302-1320 and 811-833 cm⁻¹, in spectra of 2-5, suggesting coordination of tin(IV) through sulfur after deprotonation and formation of thiolate sulfur [30, 31]. The pyridine in-plane sharp band at 608 cm^{-1} in free 1 shifts to $648-699 \text{ cm}^{-1}$ in 2-5, suggesting coordination of the pyridine nitrogen to tin(IV) [32]. Based on the IR spectra of 2-5, substituted thiosemicarbazone coordinates through azomethine-N, pyridine-N, and thiolato-S.

3.3. ¹H NMR spectra

The ¹H NMR spectra of 1–5 were interpreted based on the atom labeling in scheme 2. In HBPCT a singlet at 11.54 ppm indicates a proton at N1–H. The pyridyl protons have four resonances; two doublets at 8.81 and 7.53 ppm correspond to C19-H and C16-H, while two triplets at 7.76 and 7.48 ppm belong to C17–H and C18–H, respectively. The proton resonance on N2 and CyC6-H appear as a doublet at 7.76 ppm which is overlapping. The aromatic resonances of the ligand were observed as multiplets at 7.29-7.25 ppm. In the cyclohexyl, the equatorial protons were observed at 2.11 ppm compared to their axial protons at 1.71 ppm. Upon complexation, the ¹H NMR spectra of 2–5 undergo some changes in chemical shifts as a result of coordination. The N1–H signal was absent in spectra of 2-5, indicating deprotonation and coordination of thiolate sulfur to tin(IV). The C19–H resonance was observed at 8.83–8.82 ppm in 2–5, shifted downfield compared to 1, supporting coordination through pyridyl nitrogen (N4). The C18–H resonance of the pyridine ring probably overlaps with aromatic ring protons at 7.55–7.25 ppm in 2–5, downfield compared to the free ligand. C17–H and C16-H of pyridine were downfield compared to 1. Some aromatic resonances are multiplets, making it difficult to distinguish the individual signals. A doublet at 7.82-7.63 ppm in 2-5 corresponds to N2-H and CyC6-H overlapping. The methyl groups attached to tin(IV) in 3 and 4 give a singlet at 1.08 and 1.17 ppm, respectively. The ${}^{2}J$ [¹¹⁹Sn, ¹H] values, 92.5 Hz for 3 and 110 Hz for 4, support the six-coordinate environments around tin(IV) [33].



Figure 1. Molecular structure of 2.

3.4. X-ray crystallography diffraction analyses

The molecular structure of **2** is shown in figure 1 together with the atomic numbering. Crystal data and structural refinement parameters are given in table 1. Selected bond lengths (Å) and angles (°) are given in table 2. In the molecular structure of 2, Sn adopts a distorted octahedral geometry with 1 coordinated as a mononegative tridentate chelating agent via pyridine-N, azomethine-N, and thiolato-S. The distorted octahedral tin(IV) has meridional chlorides. Cl2 and Cl1 are *trans* to each other, while Cl3 is *trans* to N14. The two *trans* chlorides show slightly longer bond lengths [d(Sn-Cl1) = 2.433(1) Å and $d(Sn-Cl_2) = 2.415(1)$ Å] in [SnCl₃(FPT)] to 2.4289(5) and 2.4306(4) Å to tin(IV), whereas the *trans* chloride and nitrogen [d(Sn-Cl3) = 2.360(1) Å and d(Sn-N2) = 2.194(2) Å] in [SnCl₃(FPT)] to 2.3610(5) and 2.1906(16)Å were observed [34]. The Sn1–S17 bond distance is 2.4474(5) Å, close to the sum of the covalent radii of tin and sulfur 2.42 Å [35], but much smaller than the van der Waals radii 4.0 A [36], confirming sulfur is coordinated in the thiolate form. The Sn1-N14 and Sn1-N1 bond lengths are 2.1907(16) and 2.2047(15) Å, respectively, close to the sum of the covalent radii of Sn-N (2.15Å), indicating strong bond interaction of Sn1 with N14 and N1 [37]. The N14-C7 and N15–C16 bond distances are 1.307(2) and 1.333(2) Å, respectively, in conformity with a

$[SnCl_3(BPCT)]$ (2)
C ₁₉ H ₂₁ Cl ₃ N ₄ SSn
562.50
150(2)
0.71073
Monoclinic
P121/n1
8.3564(3)
23.1321(8)
11.9984(4)
90.0
106.139(4)
90.0
2227.93(13), 4
1.677
Mo-Ka
1120
$0.599 \times 0.248 \times 0.17$
Yellow
3.1723-26.3154
1.613
Multi-scan
1.0 and 0.83781
1.023
3910/0/253
$R_1 = 0.0206,$
$wR_2 = 0.0447$
$R_1 = 0.0276,$
$wR_2 = 0.0462$

Table 1. Crystal data, structure solution, and refinement for 2.

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

Sn1-Cl1	2.4289(5)	Cl1-Sn1-Cl2	171.129(17)
Sn1-Cl2	2.4306(5)	Cl1-Sn1-S17	93.509(19)
Sn1-S14	2.4474(5)	Cl2-Sn1-S17	94.334(19)
Sn1-Cl3	2.3610(5)	Cl3-Sn1-Cl1	90.479(19)
Sn1-N14	2.1907(16)	Cl3-Sn1-Cl2	90.941(19)
Sn1-N1	2.2047(15)	Cl3-Sn1-S17	108.609(18)
S17-C16	1.760(2)	N14-Sn1-Cl1	87.29(4)
C6-N1	1.349(2)	N14-Sn1-Cl2	89.89(4)
C6-C5	1.390(3)	N14-Sn1-S17	80.69(4)
C6-C7	1.478(3)	N14-Sn1-Cl3	170.57(4)
N14-N15	1.346(2)	N14-Sn1-N1	73.92(6)
N14-C7	1.307(2)	N18-C19-C24	110.11(15)
N18-C19	1.474(3)	N15-N14-Sn1	121.01(11)
N18-C16	1.325(3)	N1-Sn1-Cl1	86.41(4)
N15C16	1.333(2)	N1-Sn1-Cl2	84.73(4)
N1-C2	1.333(2)	N1-Sn1-S17	154.58(4)
C5-C4	1.383(3)	N1-Sn1-C13	96.81 (4)
C19-C24	1.521(3)	N1-C2-C3	121.89(19)
C3–C2	1.378(3)	C5-C6-N1	119.95(18)
C3–C4	1.374(3)	C3-C4-C5	120.10(18)
C7–C8	1.477(3)	C2-N1-C6	120.63(16)
C8-C13	1.389(3)	C4-C5-C6	119.07(18)
C8–C9	1.395(3)	C4–C3–C2	118.35(19)

formal C=N double bond (1.28 Å). The values are similar, indicating the consistency of the thiol tautomeric form. Although the latter are a little longer than the former, these differences in bond distance are due to delocalization along N15-C16-S17. It is clear from the structural study that the complex is by elimination of HCl from the interaction of the SH group of the thiol form of 1 and SnCl₄. Therefore, the C16–S17 bond changes from a double bond to a predominately single bond, whereas C16–N15 acquires some double bond characteristics. Two *trans* chlorides have Cl2–Sn1–Cl1 angle of 171.129(17)°, showing significant distortion from linear. The S17–Sn1–N1 bond angle $(154.58(4)^{\circ})$ is much less than expected. The sum of the angles S17–Sn1–N14 (80.69(4)°). N14-Sn1-N1 (73.92(6)°), and S17-Sn1-N1 (154.58(4)°) is 309.19°, showing distortion. The sum of the angles S17-Sn1-C13 (108.609(18)°), S17-Sn1-N14 (80.69(4)°), N14-Sn1-N1 (73.92(6)°), and Cl3–Sn1–N1 (96.81(4)°) is 360°, thus Cl3, Sn1, S17, N1, and N14 are coplanar. In the pyridine ring, the angles are C2-N-C6 (120.63(16)°), N1-C2-C3 (121.89(19)°), C2–C3–C4 (118.35(19)°), C3–C4–C5 (120.11(18)°), C4–C5–C6 $(119.07(18)^\circ)$, and C5–C6–N1 $(119.95(15)^\circ)$; thus all the atoms in the pyridine ring are not the same, perhaps due to the electronic effect of the adjacent electronegative pyridyl nitrogen.

4. Conclusion

HBPCT and its tin(IV)/organotin(IV) complexes (2–5) were synthesized and characterized. 2–5 are proposed to be six-coordinate, where 1 is coordinated to tin(IV) through thiolato-S, azomethine-N, and pyridine ring-N. X-ray diffraction has revealed that 2 is a distorted octahedron.

Supplementary material

CCDC reference number 782929 contains the supplementary crystallographic data for [SnCl₃(BPCT)] (2). This data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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