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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%.

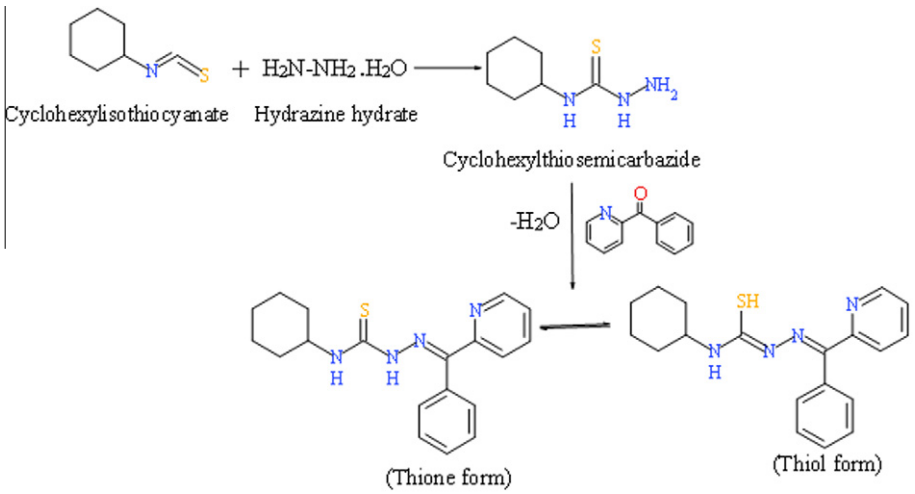
The other complexes (**3**–**4**) were synthesized using a similar procedure to organotin(IV) complex (2) using appropriate organotin(IV) chloride(s).

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.