



# Synthesis, structure and spectroscopic properties of cobalt(III) complexes with 1-benzoyl-(3,3-disubstituted)thiourea



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## ABSTRACT

Reactions of Co(II) acetate with 1-benzoyl-(3-methyl-3-R)thiourea (R = ethyl, propyl, cyclohexyl and phenyl) and 1-benzoyl-(3-ethyl-3-benzyl)thiourea ligands, herein refer to as 1-benzoyl-(3,3-disubstituted)thiourea, derived from secondary alkyl- and arylamines gave [tris(1-benzoyl-(3,3-disubstituted)thiourea)cobalt(III)] complexes. The neutral cobalt(III) complexes were afforded through a one-pot reaction between a deprotonated 1-benzoyl-(3,3-disubstituted)thiourea ligands with cobalt(II) acetate with a 1:3 ratio in methanol. These complexes were characterized on the basis of elemental analysis, mass spectrometry, magnetic susceptibility measurement, X-ray crystallography and spectroscopic techniques namely infrared, UV–Vis and nuclear magnetic resonance. Based on the magnetic susceptibility and spectroscopic data as well as X-ray crystallographic structure of the octahedron [tris(1-benzoyl-(3-methyl-3-phenyl)thiourea)cobalt(III)] complex, it can be concluded that the ligands behave as bidentate O,S chelate.

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## 1. Introduction

Transition metal complexes containing ligand, i.e. thiourea with N-, S- and O-donor atoms play an important role in biological activities [1–6]. Thioureas are versatile bidentate donor ligands for transition metal ions [7]. Since the days of Werner and Jørgensen, cobalt complexes have interesting structural features for the development of coordination chemistry. The most common oxidation states for cobalt are +2 and +3, where the +2 and +3 ions resulted in the formation of paramagnetic and diamagnetic complexes. In the 3+ oxidation state, cobalt complexes are kinetically non-labile, which make them ideal for spectroscopic study [8]. In the case of cobalt benzoylthiourea, the Co(III) centre is coordinated to the S and O atoms of three acylthiourea ligands in a slightly distorted octahedral geometry. The three O atoms are arranged *fac*, as are the three S atoms [9–11].

The presence of hard O and N, and soft S-donor atoms in the backbones of benzoylthiourea ligands assist them to react readily with transition metal ions, yielding stable metal complexes [12]. Most of benzoylthiourea derivatives derived from a primary amine tend to be a monodentate ligand and prefers to coordinate with

metal centre through the S-donor atom [13–20]. However, benzoylthiourea derivatives derived from secondary amine behave differently and are more likely to act as *cis*-bidentate chelate via S- and O-donor atoms [21–33]. For example, 1-benzoyl-(3,3-disubstituted)thiourea ligands adopts a *cis-trans* configuration with respect to the thiono C=S group across the thiourea C–N bond. However, the coordination of this class of ligands have almost exclusively behaved as a bidentate chelate via the O,S donors [34–39].

In the present work, cobalt(II) acetate was used to react with benzoylthiourea ligands with a 1:3 ratio in methanol to give neutral Co(III) complexes with benzoylthiourea ligands. The oxidative reaction of Co(II) ions was reported earlier under similar reaction conditions [18]. The benzoylthiourea ligands namely 1-benzoyl-(3-ethyl-3-methyl)thiourea (HL<sup>1</sup>), 1-benzoyl-(3-propyl-3-methyl)thiourea (HL<sup>2</sup>), 1-benzoyl-(3-cyclohexyl-3-methyl)thiourea (HL<sup>3</sup>), 1-benzoyl-(3-methyl-3-phenyl)thiourea (HL<sup>4</sup>), and 1-benzoyl-(3-benzyl-3-ethyl)thiourea (HL<sup>5</sup>) were derived from their respective secondary amines. The effect of different alkyl and aryl groups attached to the N-atom of the tertiary amine on the chemistry and structural properties of the complexes were investigated by spectroscopy techniques (IR, UV–Vis, NMR), mass spectrometry, magnetic susceptibility measurement and X-ray crystallography studies. The results are presented and discussed in this communication.

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## 2. Experimental

### 2.1. Chemicals and Instrumentation

Cobalt(II) acetate,  $\text{Co}(\text{OO-CCH}_3)_2 \cdot 4\text{H}_2\text{O}$  and *N*-methylcyclohexylamine were purchased from Fluka (Malaysia), *N*-ethylmethylamine, *N*-ethylbenzylamine and *N*-methylphenylamine were obtained from Aldrich (Malaysia) and *N*-methylpropylamine was purchased from Merck (Malaysia). All solvents were of reagent grade quality, obtained from commercial suppliers, and used without further purification.

Thin layer chromatography (TLC) (Merck, Malaysia) was performed on silica gel plates with DCM/*n*-hexane as eluent. The IR spectra were recorded on Perkin-Elmer Paragon 500 spectrophotometer in the range of  $4000\text{--}250\text{ cm}^{-1}$ . Electronic spectra were obtained as dichloromethane solution on a UV-1650 PC Shimadzu Fision. Elemental microanalyses for carbon, hydrogen and nitrogen were performed using a Carlo Erba EA1108 elemental analyzer. Magnetic susceptibility measurements were determined on a Sherwood Scientific MSB-AUTO, at room temperature ( $20\text{ }^\circ\text{C}$ ) using  $\text{HgCo}(\text{SCN})_4$  as calibrant and the diamagnetic susceptibility corrections were calculated from Pascal's constants. Melting points were determined on an Electrothermal 9100. The mass spectra were

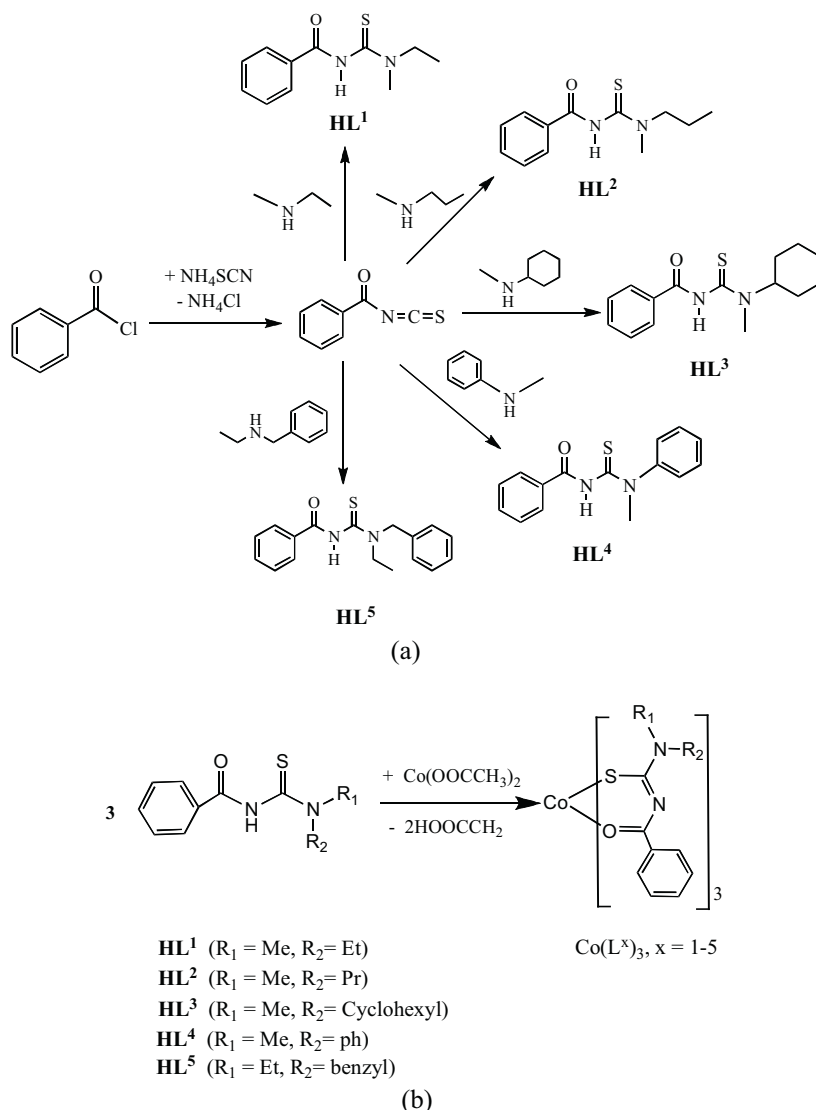
recorded on a Shimadzu QP5050A DI50 spectrometer and were determined by electron impact (EI) technique with the source maintained at  $200\text{ }^\circ\text{C}$ , the pressure in the source was approximately  $2 \times 10^{-7}$  Torr. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained from a Cryo-Probe FT-NMR 600 with  $\text{CDCl}_3$  solution.

### 2.2. Synthesis of the benzoylthiourea ligands

The benzoylthiourea ligands were prepared according to the published literature methods [38,40,41]. Firstly, benzoyl chloride was converted to benzoyl isothiocyanate and followed by condensation process with the appropriate secondary amine derivatives namely, *N*-ethylmethylamine, *N*-methylpropylamine, *N*-cyclohexylmethylamine, *N*-benzylethylamine and *N*-methylphenylamine, in acetone (Scheme 1a). The resulting mixture was stirred for 4 h. The solid product was washed with cold water to give white precipitate, which was further purified by re-crystallization from an acetone solution. The structures of the HL<sup>1</sup>–HL<sup>5</sup> ligands are shown in Fig. 1.

#### 2.2.1. 1-Benzoyl-(3-ethyl-3-methyl)thiourea HL<sup>1</sup>

Yield: 55.75%. Elemental Anal. Calc. for C, 59.43; H, 6.35; N, 12.60. Found: C, 59.29; H, 6.00; N, 13.12%. FTIR ( $\text{cm}^{-1}$ ):  $\nu(\text{NH})$



**Scheme 1.** Schematic reactions for (a) the synthesis of benzoylthiourea ligands, and (b) the corresponding cobalt(III) complexes.

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