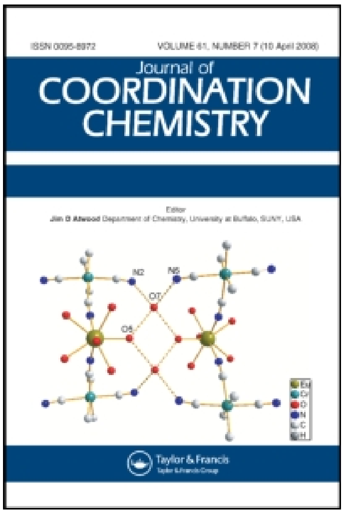

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Synthesis and characterization of metal complexes of 3-(*N*-phenyl)-thiourea-pentanone-2

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Copper and cobalt complexes derived from 3-(*N*-phenyl)-thiourea-pentanone-2 were characterized by elemental, XRD, FTIR, UV–Vis, SEM and ^{1}H NMR spectroanalytical studies. The X-ray diffraction studies indicate that 3-(*N*-phenyl)-thiourea-pentanone-2 and complexes with copper and cobalt are crystalline in nature with simple cubic lattice structure. IR spectroscopic data were used to assign characteristic vibrational frequencies of groups present in these compounds. Scanning electron micrograms were used to assign morphology and particle size.

Keywords: Thiourea; Aniline; Copper(II) complex; Cobalt(II) complex

1. Introduction

Thiourea (Tu) derivatives have a long history as ligands in coordination chemistry, coordinating via sulfur and oxygen [1, 2]. Hydrogen bonding of some thioureas have been investigated finding that intermolecular hydrogen bonds between sulphur and hydrogen on *N* is common [3, 4]. A number of thiourea derivatives have been reported to form complexes with copper and cobalt [5–7]. A number of thiourea derivatives possess antibacterial, antifungal, antitubercular, antithyroid and insecticidal properties [8, 9] and biological activities of complexes with thiourea derivatives have been screened [10–13]. 3-(*N*-phenyl)-thiourea-pentanone-2 has remarkable capacity to coordinate transition metals giving highly colored chelated structures. Hence, chelating behavior of 3-[*N*-phenyl thiourea-pentanone-2] was examined with copper and cobalt complexes followed by characterization using XRD, SEM, FTIR, ^{1}H NMR and elemental analyses. All the complexes possess simple cubic phase geometry.

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2. Experimental

2.1. *Chemicals*

All chemicals and solvents were obtained from Fluka Chemical Co., Germany, and used as received. ^{1}H NMR labeled thiourea was obtained from Isotec Co., USA, 5% ^{1}H NMR enriched Tu was made by mixing 5% labeled and 95% unlabeled Tu by weight.

2.2. *Synthesis*

2.2.1. Preparation of phenyl thiourea. In a round-bottomed flask 6.35 g aniline and 3.8 g of ammonium thiocynate were mixed in 10 mL of hydrochloric acid with constant stirring. Contents were heated for 2–3 min and poured into a beaker containing 50 g of crushed ice. Upon standing, white precipitate of phenylthiourea was obtained. The yield was 90%.

2.2.2. Preparation of 3-(*N*-phenyl)-thiourea-pent-2-one. Pellets (1–2) of NaOH were added to 2.5 mL of pentone-2,4-dione in a 250 mL beaker and 0.5 mol of phenylthiourea was added to this solution with constant stirring. After stirring, 5 mL of ethyl alcohol is added, the contents transferred to Porcelain dish and then heated to 30°C with continuous stirring. After heating, Porcelain dish is placed in crushed ice with continuous stirring; after 5 min, a pale yellow precipitate of 3-(*N*-phenyl)-thiourea-pentanone-2 in 85% yield was formed.

2.2.3. Preparation of copper and cobalt complexes with [3-(*N*-phenyl)-thiourea-pentanone-2] ligand. In a 250 mL beaker, 1.24 mol of 3-(*N*-phenyl)-thiourea-pentanone-2 was dissolved in 10 mL of pure ethyl alcohol. At room temperature, solution of copper or cobalt chloride was added dropwise with constant stirring into ligand solution. A green precipitate of copper complex and pink precipitate of cobalt complex were obtained. The precipitate was collected by filtration, washed with alcohol and dried under vacuum overnight. 60% yields were formed.

2.3. *Elemental analysis*

Elemental analyses (C, H, N, S) were performed using a Carlo Erba elemental analyzer. Melting points were determined in open capillary tubes using an electric melting point apparatus and are uncorrected. The data are reported in table 1.

2.3.1. XRD. XRD patterns were recorded by a Rigaku RINT-2000 diffractometer equipped with a rotating anode with tube voltage of 40 kV and current of 100 mA on a Philips PW3040/60 X-ray powder diffractometer. Cu target was used as the source of X-rays at $\lambda = 1.54$ Å wavelength. Results are summarized in table 2.

2.3.2. FTIR. The solid state FTIR spectrum of the ligand and their complex was recorded in the range 4000 to 400 cm^{-1} on a Perkin-Elmer 16 FPC FT-IR using KBr pellets. Results are reported in table 3.

2.3.3. NMR. ^{1}H NMR spectra (δ, ppm) were recorded on a 300 MHz Bruker spectrometer with TMS as an internal standard (see table 3).

Table 1. Physical and analytical data of the metal(II) complexes.

Complexes/Mol. Formula	M.P. (°C)	Yield (%)	Calcd (Found)% C	H	N	S
[Ligand][$C_{12}H_{14}N_3O_3S$]	250–251	65	51.4 (50.1)	5.03 (4.9)	14.9 (14.5)	11.4 (11)
[Cu(L)(Cl)$_2$][$C_{12}H_{14}N_3O_3SCuCl_2$]	230–232	58	34.7 (33.9)	3.4 (3.1)	17.1 (16.7)	7.7 (7.1)
[Co(L)(Cl)$_2$][$C_{12}H_{14}N_3O_3SCoCl_2$]	240–242	56	41.1 (40)	3.7 (3.5)	11.08 (11.04)	8.4 (8.2)

Table 2. XRD peaks and crystal thickness calculated from Scherer's formula.

Compound	2-theta maximum	hkl	Crystal size (Å)
Ligand	18.05	463	4.6
$CuLCl_2$	17.08	440	4.4
$CoLCl_2$	11.70	300	3.9

Table 3. IR, UV, and NMR spectroscopic data of the ligand and metal(II) complexes.

Ligand/complexes	IR (cm^{-1})	λ_{max} in nm (ε in $\mathrm{M}^{-1}\mathrm{cm}^{-1}$)	^{1}H-NMR (DMSO-d_6) (ppm)
Ligand	3470(NH); 3480(=C–H, Sp2); 1598(C=S); 1615(C=O); 1468(C–C, ring structure); 836,749(sub phenyl)	272(1103)	–CH_3 (2.19) –NH (6.80) Aromatic protons (7.95–8.21)
Cu complex	3330(NH); 3281(=C–H, Sp2); 1600(C=S); 1630(C=O); 1517(C=C); 1490(C–C, ring structure); 740(M → L); 921,824(sub phenyl)	241(9801), 294(9830), 364(1284)	–CH_3 (3.10) –NH (6.60) Aromatic protons (7.96–8.2)
Co complex	3500(NH); 2944(=C–H, Sp2); 1616(C=S); 1630(C=O); 1533(C=C); 1522(C–C, ring structure); 594(M → L); 927,782(sub phenyl)	(277), 382.4(227.5), –	–CH_3 (3.10) –NH (6.60) Aromatic protons (7.96–8.2)

2.3.4. Electronic spectra. Electronic spectra of 1.862×10^{-4} M solution of the ligand and complex were recorded in methanol at different time intervals in the range 500–200 nm on a UV-1700 SHIMADZU Corporation spectrophotometer with slit = 2 nm, scan speed = 60 nm min^{-1}, response = 0.2 s. The data are tabulated in table 3.

2.3.5. SEM. The surface morphologies of samples were examined using scanning electron microscopy on a JEOL JSM 5600 SEM.

3. Results and discussion

The XRD pattern of 3-(*N*-phenyl)-thiourea pentanone-2] and its complexes show sharp intense peaks throughout the spectrum indicating crystalline sample. Some sharp peaks disappear when the ligand is attached to copper and additional sharp peaks are observed when the ligand is attached to cobalt. X-ray diffraction main peaks have been indexed by trial and error method [14]. The crystal size, hkl and 2-theta maximum are reported in table 2.

IR spectra of complexes in comparison to 3-(*N*-phenyl)-thiourea-pentenone-2 are listed in table 3. Medium peaks at 3470, 3330 and 3500 cm^{-1} for ligand and their complexes are attributed to stretching of the N–H group adjacent to the carbonyl [15]. A strong absorption (1615 cm^{-1} for ligand) ascribed to the carbonyl group shifts upon complexation [15]. Deprotonation induces delocalization of C=O stretching vibration ($\sim$180 cm^{-1} decrease) in agreement with the literature [16, 17] confirming coordination through oxygen. The C=S modes of thiourea were observed at a lower frequency (1598 cm^{-1}) compared to that of their complex with copper and cobalt (1616, 1600 cm^{-1}). The characteristic absorption peaks in the IR spectra of all the complexes are similar and in agreement with those reported for other thiourea complexes [18, 19].

For free Tu the *n*–π^* transition occurs at 272 nm [20] (λ) with molar extinction coefficient (ε) of 1103 cm^{-1}M^{-1}. For the copper complex (figure 1), three prominent

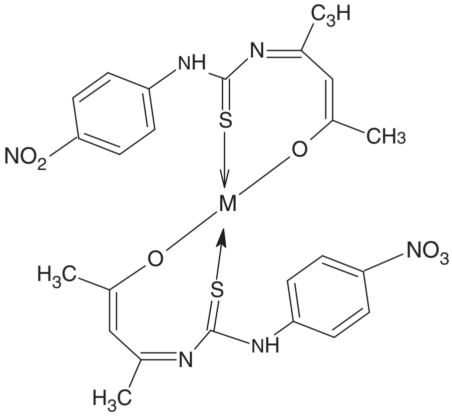

Figure 1. The structure of 3-(*N*-phenyl)-thiourea pentanone-2 M-(Cu and Co).

absorptions at 241, 294 and 364 nm with molar extinction coefficients of 9801, 9830 and 1284 $cm^{-1}M^{-1}$, respectively, are observed and for cobalt, two at 277 and 371.5 nm with molar extinction coefficient of 9826 and 12900 $cm^{-1}M^{-1}$, respectively. The absorptions at 364 and 371 nm indicate ligand to metal charge transfer (LMTC). In ^1H NMR spectra broad signals between 7.9 and 8.2 ppm indicate thiourea. El-Etri and coworkers [21] reported the H signals of $-NH_2$ in free Tu. In the present study this was observed at 7.34 and 7.40 ppm, as reported earlier [22]. Resonances for Cu and Co bonded with thiourea at 7.66 and 7.96 ppm indicate Cu–S and Co–S bond formation.

Scanning electron microscopy is a convenient technique to study the microstructure of powdered samples [23]. The surface morphology of 3-(*N*-phenyl)-thiourea-pentanone-2 and their complexes with copper and cobalt are shown in Supplementary Material. Small fibers structure for 3-(*N*-phenyl)-thiourea pentanone-2, the pyramidal structure for copper complex, and needle structure is observed for Co complex. From the figures, we estimated that the grain size of the ligand is 4 µm and the complexes are 5 µm and 3 µm.

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