

FT-IR, ¹HNMR, UV-vis studies on synthesized Co[3N2CTU2P] & Cu [3N2CTU2P] complexes

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Abstract— The biological properties of carbonyl compounds in general make them one of the prim interests of the pharmaceutical and biotechnology industries. Thiourea is an important class of carbonyl compounds which has been used extensively in medical chemistry. Starting from synthesis the study of complexes is a charming task. Besides some modern techniques viz. XRD, SEM etc. a number of other reliable tools are available for the characterization of solid complexes. Infrared studies, nuclear magnetic resonance measurements and electronic measurements are the important classical techniques. In the present work synthesis and characterization of [3-N-phenyle-thiourea-pentan-2] ligand and its copper and cobalt complexes has been carried out. Structural studies by some standard spectroscopic techniques like Fourier transforms infrared spectroscopy (FTIR), Ultra Violet visible spectroscopy (UV vis) and Nuclear Magnetic Resonance (NMR) have been done for the ligand and complexes.

IndexTerms: Synthesis of thiourea, ¹HNMR, UV-Vis, FTIR

I. INTRODUCTION

One of the most interesting aspects of organic chemistry is that dealing with the building up of complex substance from simple ones. The synthesis of organic compounds whether for scientific or industrial purpose, has been very important in the development of the science and is still of greatest importance today [1]. The biological properties of carbonyl compounds in general make them one of the prim interests of the pharmaceutical and biotechnology industries. Many modern pharmaceuticals are synthetic compounds and a large of these is phenylthiourea. In the other areas in which organic compounds are widely used, such as the paints, plastics, food, explosive, drugs, and petrochemicals and of course they form the basis of all life processes. Out of broad range of organic compounds available to date, interest in phenylthiourea-containing structures stems from their widespread occurrence in molecules that display a plethora of useful biological properties. The thiourea is an important class of carbonyl compounds, which has been used, extensively in medical chemistry. A number of techniques are available for the characterization of solid complexes. Infrared studies, nuclear magnetic resonance measurements and electronic measurements are the important characterization techniques. [2]

The present communication deals with synthesis and characterization of [3-N-phenyle-thiourea-pentan-2] ligand and its copper and cobalt complexes. Structures of the synthesized thiourea ligand and its complexes have been ascertained on the basis of FTIR, HNMR and UV-Vis spectroscopic techniques.

1.1 Fourier transforms infrared spectral studies (FTIR)

IR spectral measurements have been very helpful in deciding the actual sites of the coordination of ligand to the metal ion. The infrared spectra of the coordinated ligand differ sufficiently from that of the free ligand and it is possible to correlate changes in the spectra with the changes in the structure of the ligand. In this way, the information regarding the structure of the complex and the coordination of particular ligand may be obtained from the infrared data. Infrared spectra of organic compounds have been recognized as an important tool to provide wealth of structural information and rich array of absorption bands. The absorption of infrared radiations causes the various bonds in a molecule to stretch and bend with respect to one another. Infrared spectra are frequently used to decide the donor sites in the ligand molecule. When a ligand is coordinated to the metal ion, the metal atom is introduced in to the ligands vibrating system, and the infrared spectrum of the complex will, thus, be different from that of the free ligand. The spectra of the complex may differ from that of ligand in (i) band positions (ii) band intensity (iii) appearance of new often-weak bands and (iv) splitting of some of the bands of free ligand.

1.2 Nuclear Magnetic Resonance (¹HNMR)

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Nuclear magnetic resonance spectroscopy is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter. As a consequence, NMR spectroscopy finds applications in several areas of science. Chemists to study chemical structure using simple one-dimensional techniques routinely use NMR spectroscopy. This important and well-established application of nuclear magnetic resonance will serve to illustrate some of the novel aspects of this method. To begin with, the NMR spectrometer must be tuned to a specific nucleus, in this case the proton. The actual procedure for obtaining the spectrum varies, but the simplest is referred to as the continuous wave (CW) method.

1.3 Absorption Spectrum (UV-Vis)

UV-Vis absorption spectroscopy is a common and well-developed technique for studying electronic transition between the ground state and excited state of the atoms or molecules. A beam of light passes through a sample, and amount of light that is absorbed during the passage is measured a function of the wavelength or the frequency of light. The absorption is measured by comparing the intensity, I of the light leaving the sample with the intensity, I_0 , entering the sample. The transmittance, T , is defined as the ratio

$$T = \frac{I}{I_0} \quad (1)$$

It is often quoted as a percentage. In measuring the spectra of gases or solutions contained in cells, I_0 is usually taken to be the light intensity passing through an empty cell or a cell of pure solvent. This corrects well for reflection at the surfaces, absorption by the solvent or light scattering, which are not usually the quantities of interest. It is usually convenient to work with the decadic absorbance, A , defined by

$$A = \log\left(\frac{I_0}{I}\right) = -\log T \quad (2)$$

The modified term absorbance usually means this quantity, through some author use the Napierian absorbance $B = -\ln T$. The absorbance is so useful because it normally increases linearly with path length, l , through the sample and with the concentration, c , of the absorbing species within the sample. The relationship is usually called Beer's law:

$$A = \epsilon cl \quad (3)$$

The quantity ϵ is called the absorption coefficient, more completely the molar decadic absorption coefficient; it is characteristic of the substance and the wavelength and to a lesser extent the solvent and temperature. It is common to take path length in centimeter and concentration in moles per liter, so ϵ has units of $1 \text{ mol}^{-1} \text{cm}^{-1}$. The electronic absorption spectrum of a compound is usually shown as a plot of ϵ versus wavelength or frequency. Another useful quality related to extinction coefficient is the cross section, σ , is defined for a single atom or molecule. It may be thought of as the effective area blocking the beam at a given wavelength, and the value may be compared with the size of the molecule. The relationship is

$$\sigma = \frac{(\ln 10)\epsilon}{N_A} \quad (4)$$

where N_A is Avogadro's number. If ϵ is in $1 \text{ mol}^{-1} \text{cm}^{-1}$ and σ is desired in cm^2 the relationship may be written

$$\sigma = (3.8235 \times 10^{-21} \text{ cm}^3 \text{ mol}^{-1}) \epsilon \quad (5)$$

Electronic Spectra [3-4] of transition metal complexes plays an important role to decide their geometry. The spectral characteristics of the transition metal complexes arise from the electronic transitions that involve the various energy levels of d orbital. The movement of an electron from the ligand to the metal is known as charge transfer. Because of charge transfer transition, the complex possesses an intense colour. As the amount of conjugation increases, the ability for a charge transfer transition to occur also increases.

2. SYNTHESIS AND CHARACTERIZATION OF THIOUREA

The thiourea compounds with antimicrobial activity are of continuous interest because of the increased antimicrobial resistance developed by important pathogen. [5] Thiourea derivatives have attracted the attention of several research groups due to their potential in medicinal chemistry. [6] The broad spectra of biological activity of thiourea derivatives and their metal complexes have been investigated and diverse bioactivities, such as an antifungal and anti-malarial have been reported. [7-8] Thiourea based non-nucleoside inhibitors of HIV reverse transcriptase have also been described. Although the antimicrobial properties of thiourea have been related [7-9], they are limited in terms of both microorganism strains and structural diversity. To the best of our knowledge, no systematic screening has been reported for this class of compounds. Among the thiourea, the [3-N-(phenyl)-thiourea-pentanone-2] derivatives caught our attention because newly results concerning the low toxicity of these thiourea derivatives suggested their potential as antibiotic drugs. [9-10]

2.1 Synthesis of 3-N-(2chloro)-thiourea-pentanone-2 (3N2CTU2P) ligand

In a round-bottomed flask 6.35gm 2-Cl anilines and 3.8gm of ammonium thiocyanate were mixed in 10ml of hydrochloric acid, with constant stirring. Content were heated for 2-3 minutes and poured in to beaker. Content 50gm up to white colored precipitate of phenylthiourea with substituted anilines, was obtained in which 90% yield is formed. 1-2 pellets of NaOH were added to 2.5ml of pentone-2, 4-dione in 250ml beaker. Now 0.5mol prepared compound of phenylthiourea (with substituted anilines), added to this solution with constant stirring. After some stirring, 5ml of ethyl alcohol is added. Now the contents were transferred into porcelain dish and then heated up to 30°C with continuous stirring. After heating, now porcelain dish is kept in crushed ice with continuous stirring, after 5 minute a pale yellow precipitate of [3-N-(2chloro)-thiourea-pentanone-2], is prepared, in which 85% yield was formed.

2.2 Synthesis of Cu (3N2CTU2P) complex

In 250ml of beaker, 1.24 mmol of 3-N-(2chloro)-thiourea-pentanone-2 is dissolved in 10ml of pure ethyl alcohol. Now, at a room temperature, solution of copper chloride was added drop wise with constant stirring in to ligand solution. A green precipitate of copper complex is formed. The precipitate was collected by filtration, washed with alcohol and dried under vacuum for overnight. With this method, copper complex of 60% yield is prepared.

2.3 Synthesis of Co (3N2CTU2P) complex

In 250ml of beaker, 1.24m mol of 3-N- (2chloro)-thiourea-pentanone-2 is dissolved in 10ml of pure ethyl alcohol. Now, at a room temperature, solution of cobalt chloride is added drop wise with constant stirring in to ligand solution. A pink precipitate of cobalt complex is formed. The precipitate was collected by filtration, washed with alcohol and dried under vacuum for overnight. With this method, cobalt complex of 70% yield is prepared.

3. RESULTS AND DISCUSSION

Structures of the synthesized thiourea ligand and its copper and cobalt complexes have been ascertained on the basis of their consistent IR, HNMR and UV-Vis assignments.

3.1 IR Spectral Studies

Infrared spectra of ligand and its complexes have been recorded in the range 4000-450 cm^{-1} in KBr pellets. Some of the important features of IR spectra of ligand and complexes, which are particularly important in assigning the position of the metal ligand bonding have been discussed. It is revealed from the IR spectra of ligand and complexes depicted in figure 1 that the high frequency N-H absorption bands in the spectrum of thiourea have not been shifted to lower frequencies on the formation of metal-thiourea complexes. This indicates that nitrogen to metal bonds is not present [11] and therefore the bonding in these complexes must be between sulfur and metal atoms. The bands observed in 3394, 3493 and 3443 cm^{-1} region are undoubtedly assigned to the N-H stretching vibrations. Which are of similar intensity in ligand and metal complexes, which suggest no involment of this moiety in complexation. The lower shift of $>\text{C}=\text{S}$ band in complex indicate involment of coordination linkage through $\text{S} \rightarrow \text{M}$. The disappearance of $-\text{OH}$ absorption band in complexes further preludes involment of this proton in complexation. This observation can be explained by considerable change in the nature of $\text{C}=\text{S}$ bond on coordination of thiourea through the sulfur atom. In general all the compounds exhibit characteristics Sp^2 , C-H stretching vibrations in between 3100-3000 cm^{-1} strong bands at 1300-1184 cm^{-1} appeared for the C-N stretching of the C-N-C=S group confirming the formation of a new C-N band.[12] Below 600 cm^{-1} modes occur due to (M-L) like 442 cm^{-1} and 446 cm^{-1} confirming the formation of copper and cobalt metal with thiourea ligand ($\text{S} \rightarrow \text{M}$). The absorption bands in the spectra of the metal-thiourea complexes, which have been assigned to the particular vibrations noted, above all indicate the presence of sulfur-to-metal bonds in these metal complexes. These specific Infrared vibrations of the complex crystal are similar with those of free phenylthiourea. [13] Infrared spectral frequencies pertaining to compounds of series are presented in Table 1.

3.2 HNMR Spectral Studies

HNMR spectra of ligand 3N2CTU2P and its copper complex Cu [3N2CTU2P] are shown in figure 2. It is revealed from the HNMR data of ligand complex that the three signals in the ranges between 1.020-3.596 ppm are for methyle-methyle protons. The characteristics singlet around $\cong 4.00$ ppm in complex and ligand can be assigned to $-\text{NH}$ proton. The presence of this $-\text{NH}$ signals in complex further confirm the non-involment of this group in metal coordination. Further specific singlet at 10.020 ppm in ligand [3N2CTU2P] due to $-\text{OH}$ proton, which is absent in the HNMR of the complex, suggest its ligation with metal. The multiplets in the region 7.00 to 8.00 ppm are due to the aromatic protons. Hence, HNMR data are also support of our structural assignments as given in Table 1.

3.3 UV/Vis Spectral Studies

The electronic spectral data of the ligand [3N2CTU2P] and copper [3N2CTU2P] and cobalt [3N2CTU2P] complexes is given in Table 1. UV-Vis absorption spectra of ligand [3N2CTU2P] and copper [3N2CTU2P] and cobalt [3N2CTU2P] complexes are shown in figure 3. UV-Vis absorption spectrum of ligand show characteristics peaks in the region 327nm. Spectrum of copper complex shows additional peaks in left hand side in the region 295nm, and for cobalt complex additional peaks in right hand side of the spectra in the region 281nm respectively. It was tentatively, contributed to a charge transfer (CT) transition. The CT transition has been universally observed in thiourea compounds and metal-ligand coordination compounds. [14] In complexes, d-d transitions observed which suggests octahedral geometry for each complex. [15] This absorption and strength of UV spectra in the spectrum of ligand and metal complexes are different indicating the ligand coordination to metal ion. These results are in accordance with the results of IR spectra. A comparison of the electronic spectra of the ligand with those of the corresponding metal complexes showing a shift in the position of peak, and this can be considered as evidence for the complex formation.

Based on the reported results and discussion, the suggested general structure for ligand [3N2CTU2P] is as shown in figure 4.

TABLE 1
IR, HNMR AND UV-VIS SPECTRAL DATA FOR
LIGAND [3N2CTU2P] AND ITS COPPER AND COBALT COMPLEXES

ELEMENT	IR (N _{KBR} , CM ⁻¹)	HNMR (Δ PPM)	UV-VIS
Ligand [3N2CTU2P]	3394(N-H), 2604 (sp ² -C-H), 1094(C=S), 672(Sub. Phenyl), 495 (C-Cl)	(1.02-3.5, s), (4.0 N-H), (10.02,O-H), (7.0-8.0, Ar- proton)	λ _{max} = 327 (nm)
Complex Cu [3N2CTU2P]	3493(N-H), 1094(C=S), 609 (Sub. Phenyl), 442 (Cu-S)	(1.02-3.5, s), (4.0 N-H), (7.0-8.0, Ar- proton)	λ _{max} = 295 (nm)
Complex Co [3N2CTU2P]	3443(N-H), 2928(sp ² -C-H), 1094(C=S), 672(Sub. Phenyl), 446 (Co-S)	(1.05-3.8, s), (4.3 N-H), (7.0-8.0, Ar- proton)	λ _{max} = 281 (nm)

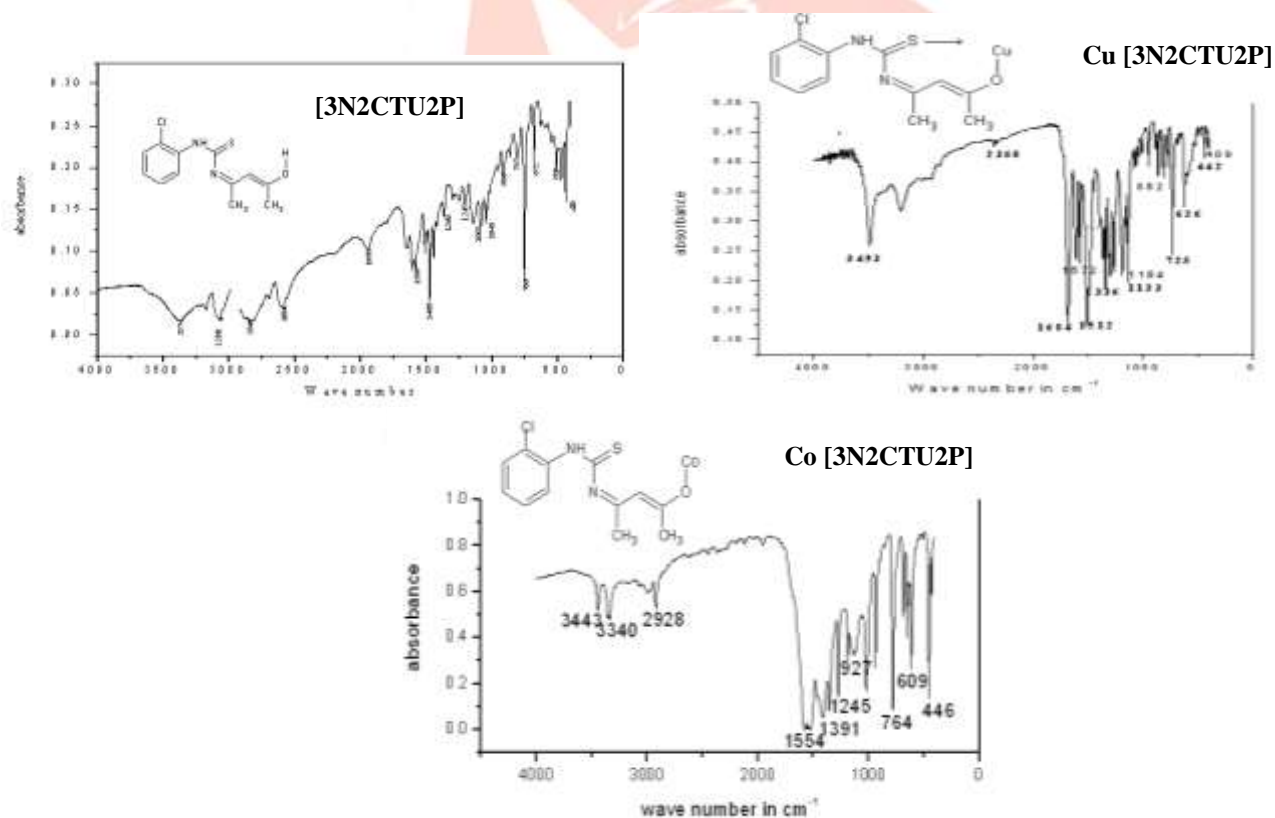
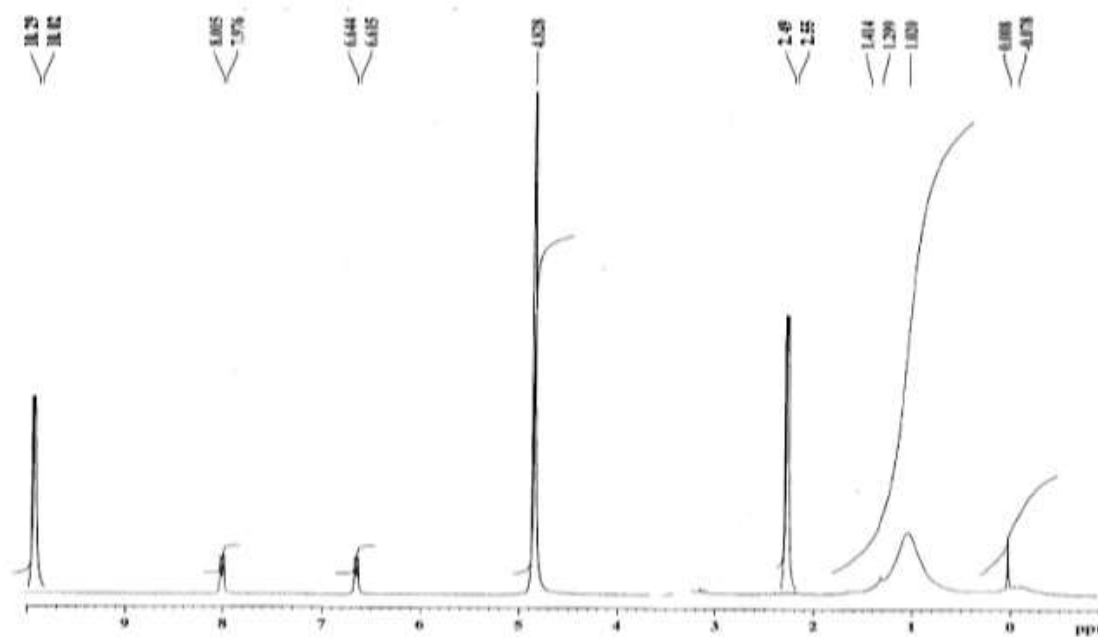
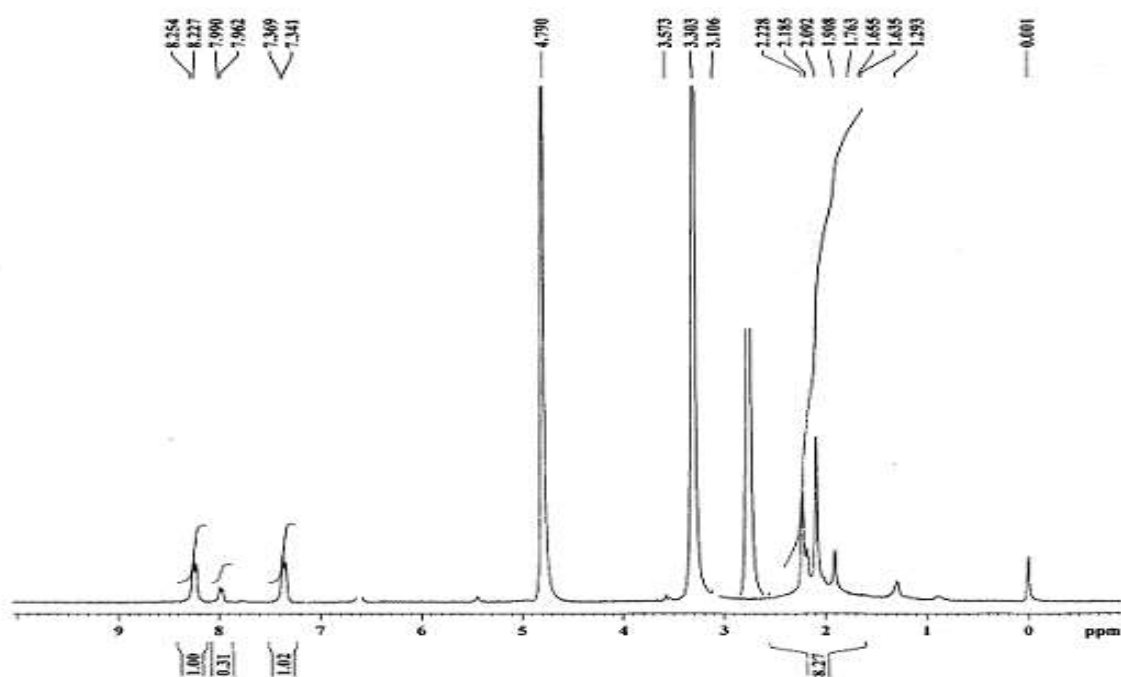


Fig. 1-IR spectra of [3N2CTU2P] ligand, Cu [3N2CTU2P] and Co [3N2CTU2P] complexes



Cu [3N2CTU2P]



Co [3N2CTU2P]

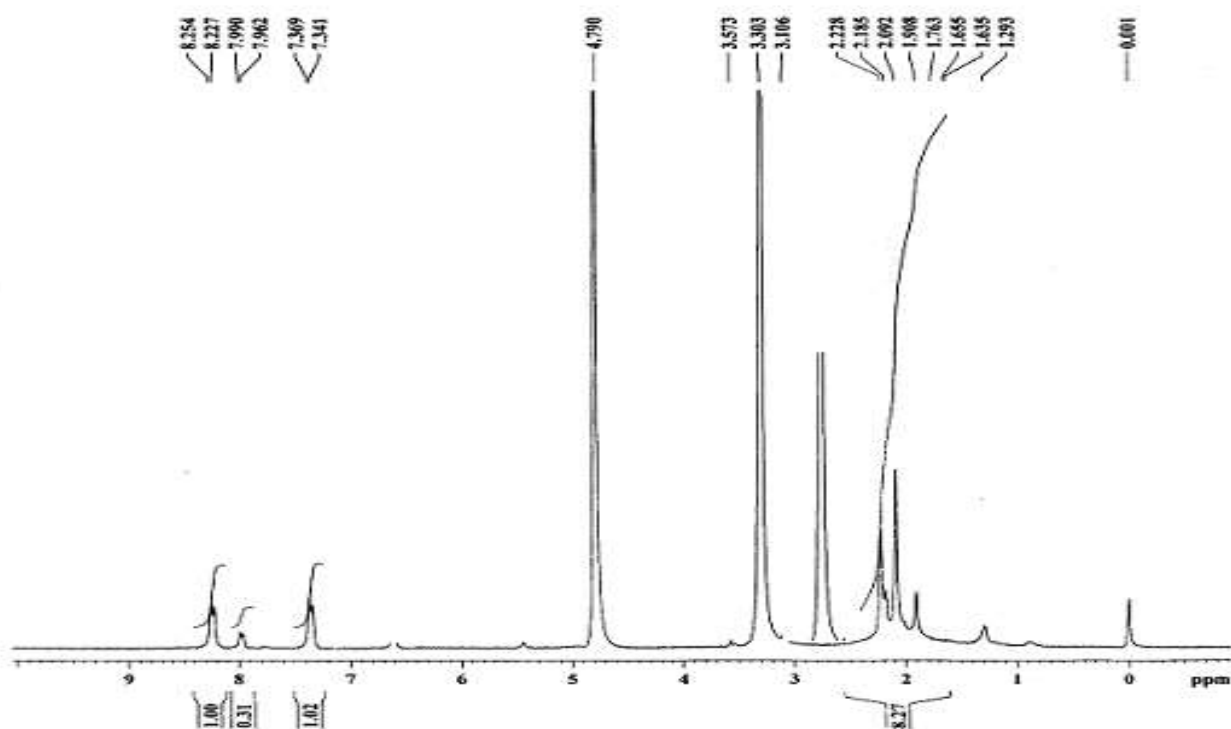


Fig. 2- ^1H NMR spectra of [3N2CTU2P] ligand, Cu [3N2CTU2P] and Co [3N2CTU2P] complexes

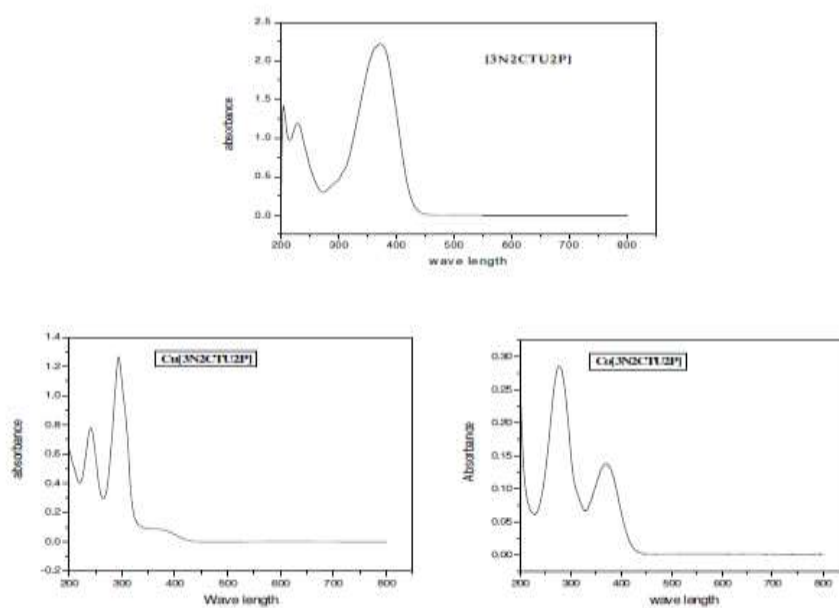


Fig. 3- UV-Vis absorption spectra of [3N2CTU2P] ligand, Cu [3N2CTU2P] and Co [3N2CTU2P] complexes

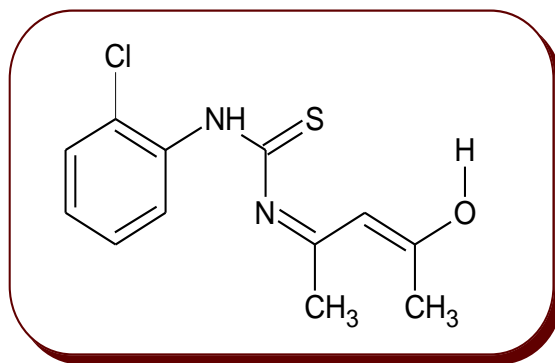


Fig. 4- Structure of 3-N-(2-chloro)-thiourea-pentan-2-one (3N2CTU2P) ligand

4. CONCLUSIONS

Synthesis and characterization of [3-N-phenyle-thiourea-pentan-2-one] ligand and its copper and cobalt complexes have been carried out. Structures of the synthesized thiourea ligand and its complexes have been ascertained on the basis of FTIR, ^1H NMR and UV-Vis spectroscopic techniques. On the basis of spectroscopic studies a general structure of the studied ligand and its metal complexes has been proposed.

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