



Synthesis and complexation of bis(thiourea) with Co(II) and Cu(II) ions

Abubakar Abdullahi Ahmed* Almustapha Sulaiman Chindo and Abdullahi Idi Mohammed

Department of Pure and Applied Chemistry, Faculty of Science, University of Maiduguri, P.M.B. 1069, Maiduguri, Borno State, Nigeria
abubakarabdullahiahmed28@gmail.com

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Abstract

Bis(thiourea) was synthesized from reaction of semicarbazide hydrochloride and potassium thiocyanate in 1:1 molar ratio in aqueous medium. Interaction of the bis(thiourea) with chloride salts of cobalt(II) and copper(II) yielded the respective complexes of varying colours in excellent yield of 74.52% and 64.81% respectively. The bis(thiourea) and its complexes were characterized using FT-IR spectroscopy and various physicochemical techniques. The ligand has sharp melting point of 217°C indicating its purity whereas the Co(II) and Cu(II) decomposed at 190 and 340°C respectively, suggestive of thermostability. The molar conductance measurement revealed that the Co(II) complex was electrolytic in nature while Cu(II) was non-electrolyte. The complexes were hydrated as revealed by thermal and FT-IR analysis. Moreover, the results of FT-IR affirmed the coordination of the metal(II) ions to the bis(thiourea) through the two thionic Sulphur atoms (>C=S) hence acting as a bidentate ligand. On the basis of the spectral analysis, the complexes could be formulated as $[CoL_2]Cl_2 \cdot H_2O$ and $[CuL_2(OH)_2] \cdot 3H_2O$ where L=bis(thiourea).

Keywords: Bis(thiourea), Complexation, Semicarbazide, Thermostability, Thionic.

Introduction

Bis(thiourea) are flexible ligands with capability of coordinating with array of metal centers as either neutral ligands, monoanions or dianions^{1,2}. Furthermore, multiple binding possibilities are provided by the hard nitrogen and soft sulfur donor atoms. Thiourea and its derivatives form a series of complexes of various symmetries containing different metal ions such as Ni(II), Pd(II) and Co(II). Extensive work is reported on the complexing behavior of di-substituted thiourea. In these complexes it is shown that one of the coordination sites is thiocarbonyl sulfur³. Study of the thiourea derivatives has attracted the attention of many researchers due to their selectivity for the concentration and separation of metal cations, treatment of lead and mercury poisoning in humans and as highly selective reagents for liquid-liquid extraction. Thioureas have also been shown to possess antibacterial, antifungal, antitubercular, antithyroid and insecticidal properties⁴. Most investigations showed that the complexation between transition metal ions and thiourea derivatives leads to a dramatically increase of biological activity properties⁵.

Due to their capability to act as ligands with nitrogen or oxygen/sulfur being coordinating sites; in recent time, urea, bis(thiourea) and their N-substituted derivatives have been topic of study. Infrared spectra of their metal complexes have gained much advertece in order to identify the coordinating atoms of the ligands (which is often oxygen or sulfur for majority of the first row transition elements reported). However, different structural features have also been reported. Some these are the works on Co(II) complexes with thiourea; ethylenethiourea and N,N'-diethylthiourea; N,N'-dibutylthiourea, and N,N'-

diphenylthiourea⁶; and N-methyl urea, N-ethyl urea, N,N'-dimethylurea, N,N'-diethylurea, and ethyleneurea. In general, a four-coordinate tetrahedral geometry around Co(II) has been found for thiourea and its N-substituted forms, whereas octahedral structure has been known for Co(II) complexes of urea and its substituted forms, although exceptional behaviours have been in record.

Bis(thiourea) is derived from semicarbazide hydrochloride. Semicarbazide and thiosemicarbazide have been reported to show broad biological activities. Despite their significance and that of their complexes, no much attention has been directed towards the synthesis, biological activity and complexation behaviour of bis(thiourea) with metal ions^{6,7}.

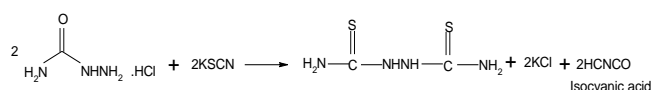
Materials and methods

All chemicals utilized in the work were of ANALAR grade and used as commercially received. This included; semicarbazide hydrochloride, potassium thiocyanate, distilled water, cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), silver nitrate, dichloromethane, acetone, tetrachloromethane, diethyl ether, ethanol and benzene.

Physical Measurements: Infrared spectra were recorded on BUCK scientific model 530 infrared spectrophotometer in the 4000-600 cm^{-1} at Yobe State University, Damaturu. All measurements were carried out using Electronic balance Metre, Model XY2002C. Water of crystallization was determined using Thermostat oven: DHG-9030A, Pec medical⁸, Magnetic stirrer hot plate 85-2 Pec medical USA and Heating and refluxing were carried out on DB-1A hot plate Pec medical USA.

The conductance value of the freshly prepared 10^{-3} M solutions of the complexes in dimethylformamide (DMF) was recorded using LIDA instrument model DDS-307 conductivity meter at 32°C .

Methods: Synthesis of Bis(thiourea) ligand: Each of semicarbazide hydrochloride (12.7g, 0.11mol) and potassium thiocyanate (10.7g, 0.11mol) dissolved in 40ml distilled water were introduced into a flat bottom flask. The mixture was allowed to react under reflux for 3 hours using a refluxing set up. The mixture was allowed to stay for overnight for the formation of crystals. The crystals were filtered, washed with hot distilled water and dried in an oven for 2 hours at 100°C ⁹. The yield was recorded and the percentage yield was calculated. The route of the reaction is portrayed in Scheme-1.



Scheme-1: Preparation route for bis(thiourea).

Synthesis of Cobalt(II) and Copper(II) complexes: The complexes were prepared by adding 40ml of ethanolic solution of 0.01mol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.38g) or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.9g) to ethanolic solutions of the ligand (0.02mol, 3g). The solution was refluxed for 3 hours, resulting to change in colour with the precipitates of the complex appearing. The solution was reduced to about one third its volume by evaporation and kept overnight for the formation of crystals. The crystal formed was filtered and washed with hot ethanol and desiccated over CaCl_2 . The yield was recorded and the percentage yield was calculated⁹.

Molar Conductance Measurements: The 0.001mol of each complex was dissolved in 10ml of dimethylformamide (DMF) and the corresponding conductance values were recorded using LIDA instrument model DDS-307 conductivity meter at 32°C . From the observed conductance recorded, the specific conductance and the molar conductance of the metal complexes were calculated using equations 1 and 2 respectively¹⁰. The results obtained are shown in Table-1.

$$\text{Specific Conductance} = \frac{\text{Observed conductance}}{\text{Cell constant} \times \text{Correction factor}} \quad (1)$$

$$\text{Molar conductance} = \frac{1000 \text{ K}}{\text{Molar concentration}} \quad (2)$$

where k = specific conductance

Results and discussion

The physical characteristics of the bis(thiourea) and its metal(II) complexes are portrayed in Table-1.

The reaction between semicarbazide hydrochloride and potassium thiocyanate yielded the Bis(thiourea) Ligand with percentage yield of 31.12% and sharp melting point 217°C indicating its purity and relative thermal stability. The interaction of the ligand with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ produced ash and dark green coloured complexes with percentage yield of 74.52% and 64.81% respectively. The formation of these coloured complexes might be due to d-d transition or nature of the bis(thiourea) ligand¹¹. The decomposition temperatures of the Co(II) and Cu(II) complexes were 190°C and 340°C respectively. These temperatures are relatively high indicating good thermal stability of the complexes¹⁰.

Table-1: Physical characteristics of Bis(thiourea) and its metal(II) Chelates.

Compound	Molecular weight (g/mol)	Color	Yield (%)	Melting point / Decomposition Temperature ($^{\circ}\text{C}$)	Molar conductance Δm ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
Bis(thiourea)	300.00	White	31.12	217	-
$[\text{Co}(\text{C}_2\text{H}_6\text{N}_4\text{S}_2)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	448.38	Ash	74.52	190	109.12
$[\text{Cu}(\text{C}_2\text{H}_6\text{N}_4\text{S}_2)_2(\text{OH})_2] \cdot 3\text{H}_2\text{O}$	451.99	Dark Green	64.81	340	2.26

Table-2: Solubility profile of the synthesized bis(thiourea) its metal(II) Chelates.

Compound	Solvents													
	Distilled water		Acetone		Benzene		Ethanol		Diethyl ether		Chloroform		DMF	
	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
Bis(thiourea)	IS	S	IS	IS	IS	IS	IS	S	IS	IS	IS	IS	S	S
$[\text{Co}(\text{C}_2\text{H}_6\text{N}_4\text{S}_2)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	IS	S	IS	IS	IS	IS	IS	S	IS	IS	IS	IS	IS	S
$[\text{Cu}(\text{C}_2\text{H}_6\text{N}_4\text{S}_2)_2(\text{OH})_2] \cdot 3\text{H}_2\text{O}$	IS	IS	IS	IS	IS	IS	IS	S	IS	IS	IS	IS	IS	S

Where: S=Soluble, SS= Slightly soluble, IS=Insoluble, DMF= Dimethylformamide.

Table-3: Significant IR Frequencies (cm^{-1}) of the synthesized compounds.

Compound	Spectral Bands (cm^{-1})					
	$\nu(\text{N-H})$	$\nu(\text{OH})/\text{H}_2\text{O}$	$\nu(\text{N-N})$	$\nu(\text{C-N})$	$\nu(\text{C=S})$	$\nu(\text{M-S})$
Bis(thiourea)	3214, 3308 w, sh	-	1084 m, sh	1323 w	862 w	-
$[\text{Co}(\text{C}_2\text{H}_6\text{N}_4\text{S}_2)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	3216 b, sh	3352 b, sh	1082 m, sh	1326 m	760 w	2376w, sh
$[\text{Cu}(\text{C}_2\text{H}_6\text{N}_4\text{S}_2)_2(\text{OH})_2] \cdot 3\text{H}_2\text{O}$	3213 w	3346 b, sh	1084 m, sh	1387 w	842 w	2394w, sh

W=weak,b=broad, sh=sharp.

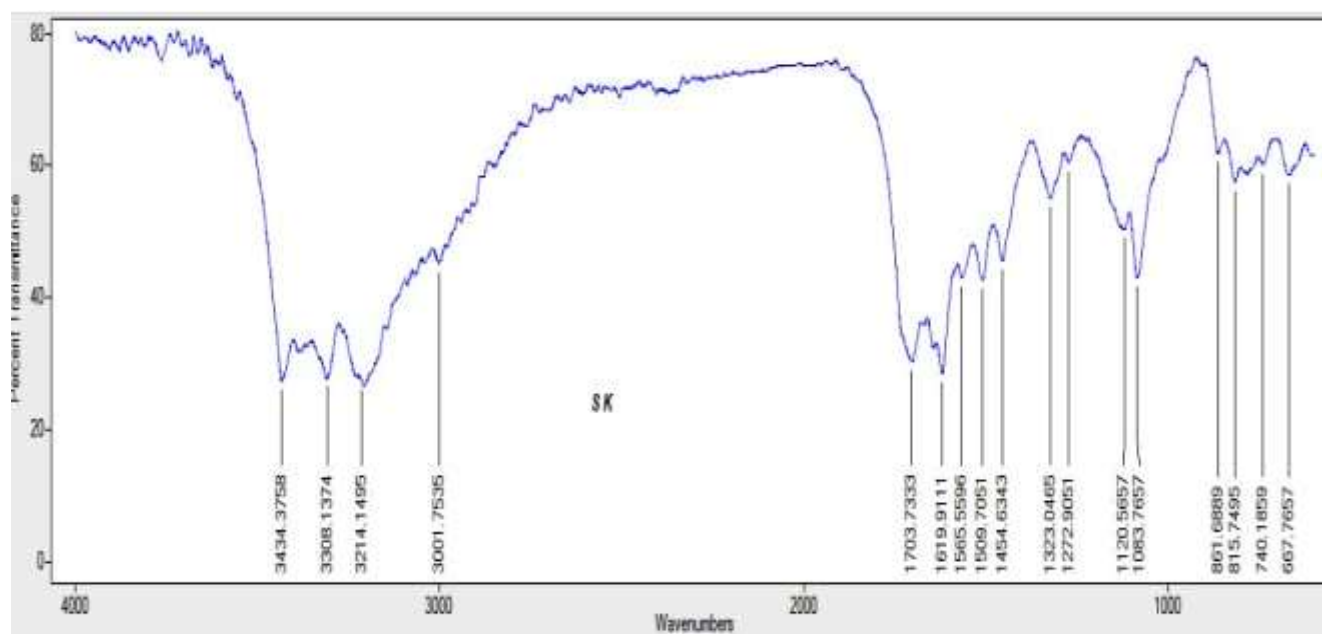


Figure-1: FT-IR- Spectrum of Bis(thiourea).

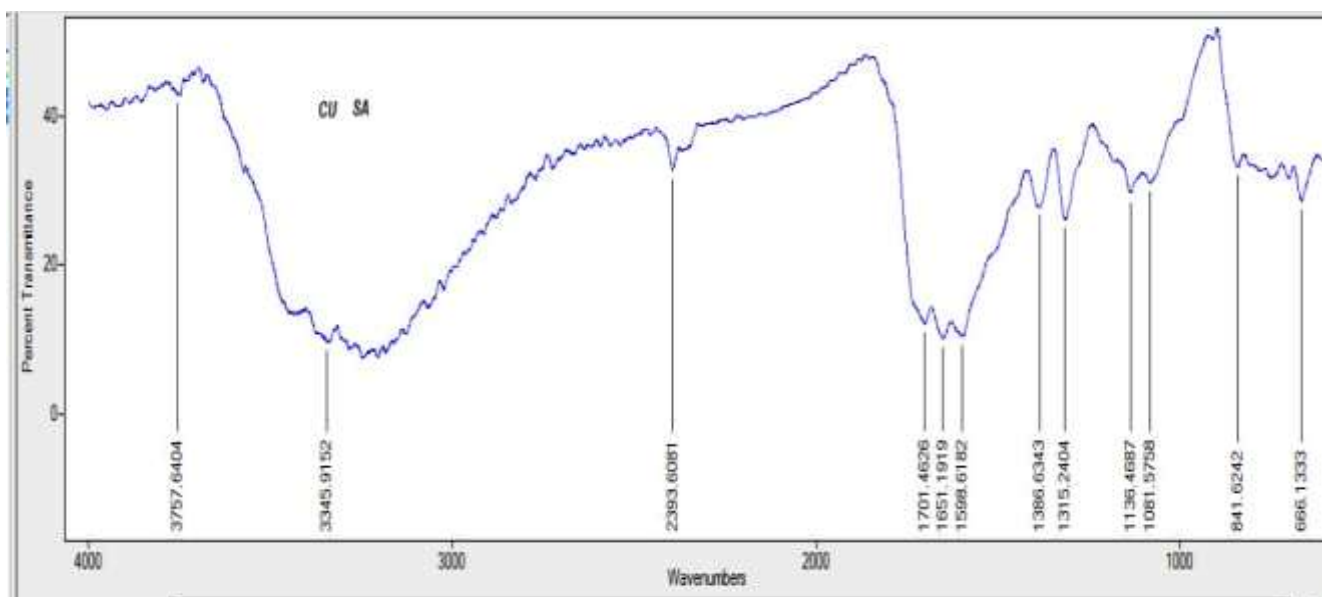


Figure-2: FT-IR-Spectrum of Cu(II) complex.

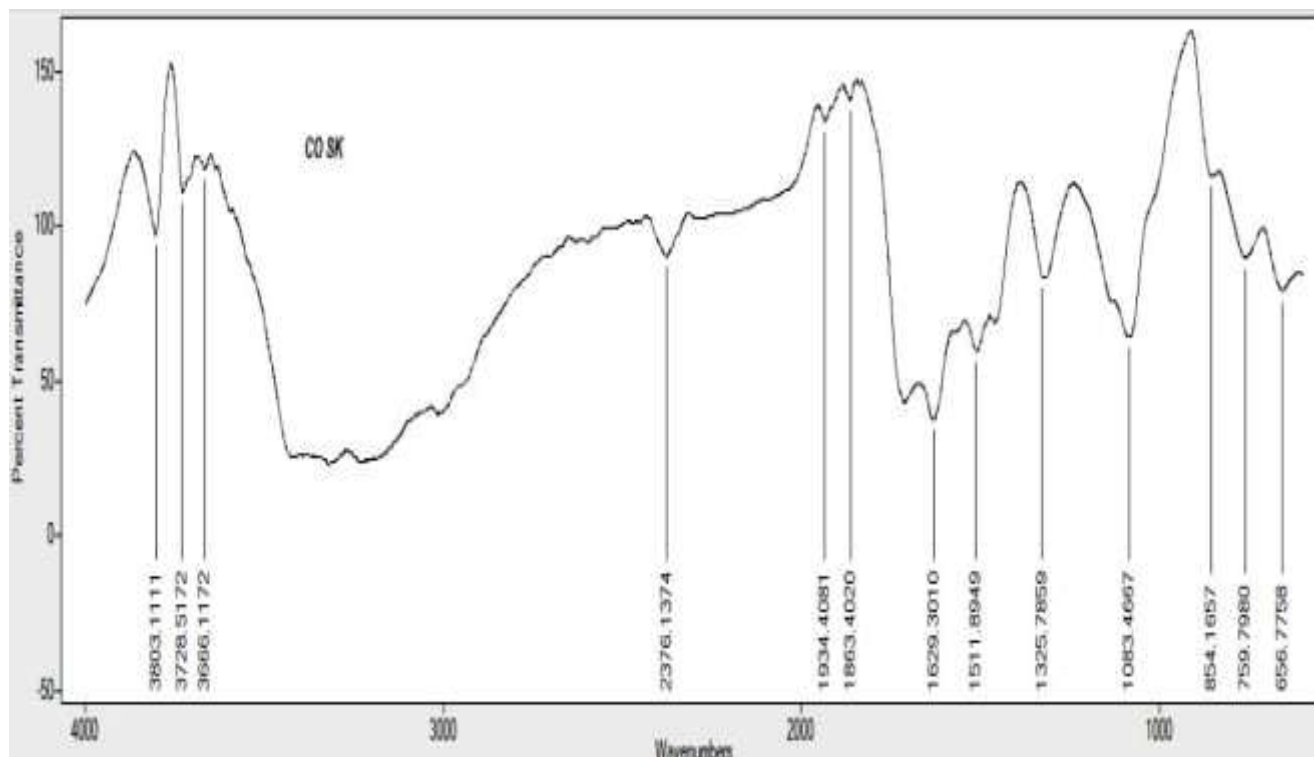


Figure-3: FT-IR Spectrum of Co(II) Complex.

Solubility studies of the synthesized compounds: The solubility of the bis(thiourea) and its metal(II) complexes was studied in different polar and non-polar solvents. The results are shown in Table-2. The result shows that the bis(thiourea) ligand and complexes were not soluble in hot and cold acetone, benzene and diethyl ether but soluble in hot distilled water, ethanol and dimethylformamide. This could be attributed to the interaction between the hydrogen ion in these compounds under investigation and the oxygen atom in the solvents which results in the formation of hydrogen bond¹².

Chloride content and conductivity measurement: White precipitate of AgCl was observed when AgNO₃ solution was dropped to the solution of the Co(II) complex. This revealed that the chloride ions are found in the outer ionization sphere. This is further affirmed by the molar conductance value 109.12 Ω⁻¹cm²mol⁻¹ consistent with 1:2 electrolyte¹³. In contrast, the copper(II) complex showed molar conductance of 2.26Ω⁻¹cm²mol⁻¹ indicative of non-electrolytic nature. The result is shown in Table-1.

Analysis of infrared spectral data: The most important IR bands, their relative intensities and possible assignments are summarized in Table-3. The somewhat dual spiky broad band's positioned at 3214 and 3308cm⁻¹ in the spectrum of the bis(thiourea) is a characteristic of ν(N-H) stretching vibration. The negligible shift in the positions of these peaks after complexation precludes the involvement of the group in coordination¹⁴. The spectrum of the ligand also shows a peak at

862cm⁻¹ ascribable to ν(C=S) stretching vibration. However, in the spectra of the complexes, this peak shifted to lower wave number by 20-98cm⁻¹^{14,15}. This was due to the reduction in the repulsion between the lone pairs of electrons on the sulphur atoms as a result of the coordination via the thionic Sulphur atom¹⁶. As a consequence, the ν(C-N) observed at 1323cm⁻¹ should increase. This was obvious from the bathochromic shift by 13-54cm⁻¹ observed in the spectra of the complexes^{14,17}. The band due to ν(N-N) was observed at 1084cm⁻¹ in the ligand¹⁸. This band virtually remain unchanged in the spectra of the complexes, hence do not involve in coordination^{19,20}. A conclusive support of the coordination of the metal ions via the sulphur atom is observed from the appearance of distinct new peaks in the spectra of the complexes at 2376 and 2394cm⁻¹ ascribed to ν(M-S) bond²¹. The broad bands found at 3352 and 3346cm⁻¹ are due to the existence of the water molecules in the complexes. The band due to the hydroxyl group in the Cu(II) complex overlapped with the position of water molecules²².

From the IR data, it could be concluded that the bis(thiourea) ligand acted as neutral symmetrical bidentate ligand with the thionic sulphur atoms acting as the coordination sites. The FT-IR spectra of the bis(thiourea) and its metal(II) complexes are shown in Figure-1,3.

According to the results obtained from IR, chloride content estimation, alongside conductivity and melting point measurements for the prepared complexes, a square planar geometry was proposed for Co(II) complex (Figure-4)⁹ and an octahedral structure for the Cu(II) complex (Figure-5).

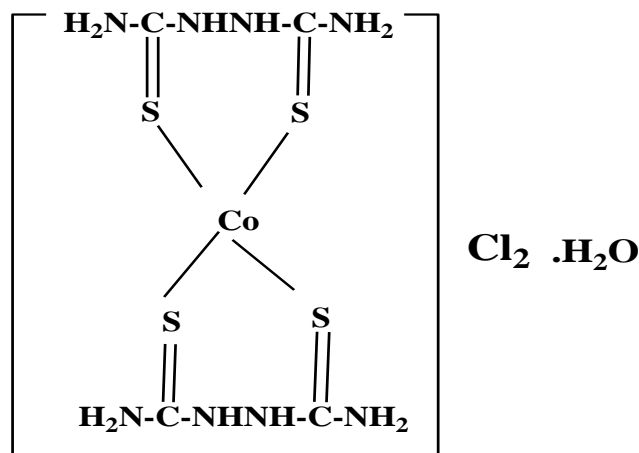


Figure-4: Probable structure of the Co(II) Complex.

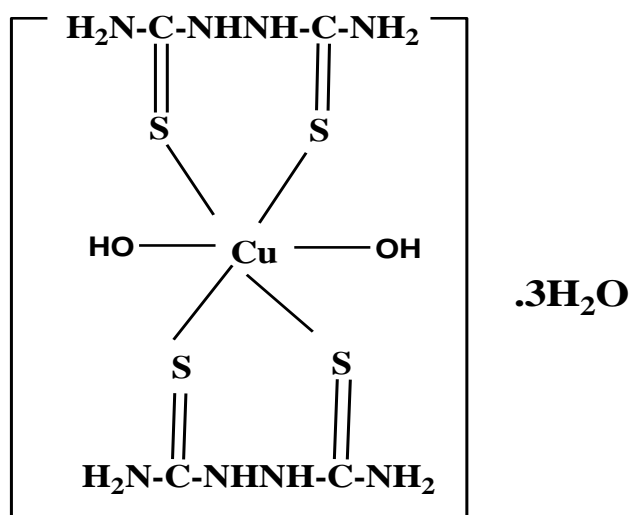


Figure-5: Probable structure of the Cu(II) Complex.

Conclusion

Bis(thiourea), derived from semicarbazide hydrochloride and potassium thiocyanate and its corresponding cobalt(II) and copper(II) coordination compounds have been successfully prepared and characterized. The bis(thiourea) and its metal chelates were soluble in some organic solvents. It was established from results of the physicochemical and spectroscopic analysis that the bis(thiourea) coordinated with Co(II) and Cu(II) ions as bidentate ligand with the two sulphur atoms being the donor atoms.

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