



Synthesis and infrared spectroscopic study of N, N'-bis(4-methoxybenzylidene)thiourea with its Co(II) and Ni(II) homobinuclear complexes

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ABSTRACT

New homobinuclear complexes of Co(II) and Ni(II) with a Schiff base, N,N'-bis(4-methoxybenzylidene)thiourea derived from [2+1] condensation reaction of 4-methoxybenzaldehyde and thiourea have been synthesized by conventional method. The Schiff base ligand and the complexes were characterized as appropriate by gravimetric determination of chloride content, thermogravimetric estimation of uncoordinated water, melting point, molar conductance measurement and infrared spectroscopy. The ligand was white crystalline solid of sharp melting point (150 °C) whereas the Co(II) and Ni(II) complexes were blue and golden colour with decomposition temperature of 190 °C and 198 °C, allusive of thermostability. Both complexes were hydrated and non-electrolytic in nature with four chloride ions coordinated to the bimetallic ions. The infrared spectroscopic study revealed that the ligand is a neutral tridentate diazamonothio moiety coordinated to the Co(II) and Ni(II) ions through its two azomethine nitrogen atoms (C=N) and thione sulphur (>C=S). The resultant data suggested formation of the homobinuclear complexes as $[M_2LCl_4] \cdot nH_2O$, (where $M^{2+} = Co$ or Ni , $L =$ Schiff base ligand and $n = 4$ for Co and 6 for Ni complex), possessing square planar structure.

1. Introduction

Thiourea which is also known as thiocarbamide is a white crystalline solid compound that consist of sulphur and nitrogen atoms [1]. The chemical attention of thiourea derivatives lies in the fact that they are ambidentate ligands with nitrogen and sulphur atoms susceptible for coordination and they have binding sites relevant to those in living organisms [2]. They possess two potential donor atoms (N and S), showing amazingly rich coordination chemistry. This remarkable tendency as hosts has facilitated the use of thiourea derivatives in ramifying new applications in the field of binding chemistry [3].

Plenty of research work have been done on ordinary complexes, chelates and mixed ligand complexes [4-6]. In order to fiddle with the properties of the complexes originating due to metal ions, polynuclear complexes with inclusion of more than one homo or hetero metals is imperative [7].

In a study, Kafi-Ahmadi *et al.* [8] synthesized a new Schiff base ligand by condensation reaction of 4-dimethylaminobenzaldehyde and 1,3-phenylenediamine. Treatment of this Schiff base ligand with Zinc(II) nitrate and Cadmium(II) nitrate in ethanol medium afforded the corresponding metal complexes. The synthesized ligand and complexes were characterized by their UV-Vis, FT-IR and ¹H-NMR, ¹³C-NMR spectral data and elemental analysis. The spectral data suggest an octahedral geometry for these complexes. Antibacterial activities of both synthesized free ligand and complexes were investigated against *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis* bacteria. The complexes showed better antibacterial activity in comparison with that of the free ligand against selective bacteria.

In this paper, we reported the synthesis of homobinuclear transition metal complexes with Schiff base containing thiourea in order to investigate its coordination behaviour.

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2. Results and Discussion

The physicochemical characteristics of the Schiff base and its homobinuclear complexes are shown in Table 1. Condensation reaction of 4-methoxybenzaldehyde and thiourea in 2:1 molar ratio in an ethanolic medium produced white crystalline Schiff base, N, N'-bis(4-methoxybenzylidene)thiourea with 19.13 % yield. Upon interaction of the Schiff base with the corresponding metal salts in 2:1 metal-ligand ratio led to the obtainment of the homobinuclear complexes, $[\text{Co}_2\text{LCl}_4]\cdot 4\text{H}_2\text{O}$ and $[\text{Ni}_2\text{LCl}_4]\cdot 6\text{H}_2\text{O}$ in low yield of 40.66 % and 23.47 % respectively. The percentage yields of the complexes usually vary due to different factors such as the variation in electronic configuration of the metal ion in d-orbital, size of ion, nature of the electron donating atoms on the ligand and reaction conditions [9]. The quite low percentage yield recorded for the complexes under investigation could be due to difficulties in optimizing all the reaction conditions such as temperature and solution concentration. Instead of that, some of the products were

inevitably lost during physical manipulation involved in isolating the product from reaction mixture [10]. Besides, the difference in metal ion size might have also contributed.

The Schiff base ligand has sharp melting point (150 °C) portraying purity [11]. Furthermore, the high decomposition temperature could be due to the higher melting point of the metals as a result of their closed packed structure which in turn results in strong metallic bond and small atomic radii, thus more energy would be required to break the metal ions [11,12]. Moreover, the change in colour from white (Schiff base ligand) to blue and golden for Co(II) and Ni(II) homobinuclear complexes respectively is another allusion that complex formation has taken place [12]. The colour of the complexes is ascribed to d-d transition of electrons from one energy level to another, by their magnitude of splitting, which in turn depends on the geometry of the complex, nature of the ligand and charge transfer [13].

Table 1. Physical and analytical data of N, N'-bis(4-methoxybenzylidene)thiourea (ATU) and its metal(II) complexes

Compounds	Molecular Weight (g/mol)	Colour	%Yield	M.P/D.T (°C)	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
ATU	312.42	White	19.13	150	-
$[\text{Co}_2\text{LCl}_4]\cdot 4\text{H}_2\text{O}$	644.28	Blue	40.66	190	2.59
$[\text{Ni}_2\text{LCl}_4]\cdot 6\text{H}_2\text{O}$	679.78	Golden	23.47	198	2.44

L = ATU = $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$, M.P = melting point, D.T = decomposition temperature

The solubility of the Schiff base and its homobinuclear complexes were analyzed in various solvents. Both the Schiff base and complexes showed solubility in water and DMF. The Schiff base ligand was found soluble in water, methanol, acetone, tetrachloromethane and diethyl ether whereas the Co(II) complex dissolve in CCl_4 and diethyl ether as Ni(II) complex dissolves in ethanol and methanol in addition to the CCl_4 . This signifies that there is an interaction between the binuclear complexes and these solvents. Therefore, the structure of the compounds is assumed to partly constitute hydrophobic and hydrophilic portions [14].

4.2.2 Elemental Gravimetric Analysis

The percentage composition of the metal, chloride and water of crystallization in the metal(II) homobinuclear complexes as obtained from gravimetric analysis are summarized in Table 2. The qualitative determination of chloride indicated no chloride ions were present as counter ions as no precipitate was formed on addition of AgNO_3 to the solution of the complexes. However, precipitates were only formed when nitric acid-digested complexes were used. Quantitative gravimetric analysis

revealed the presence of four chloride ions inside the coordination sphere as four moles of AgCl were precipitated when AgNO_3 solution was added to the acid-digested solution of the complexes [15]. Within the limit of experimental error, the values obtained are in concordance with the theoretical values and suggest 2:1:4 M:L:Cl ratio.

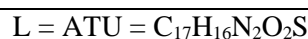
The presence of uncoordinated water molecules was detected by the use of cobalt(II) chloride paper and the percentage of water of crystallization was calculated from the weight loss resulting from heating the complexes to constant weight. It was found that the observed and calculated percentages are in good agreement. These were analyzed to be equivalent to 4 and 6 molecules of water of crystallization. Therefore, the Co(II) complex was inferred to be tetrahydrate while Ni(II) complex as hexahydrate.

4.2.3 Molar Conductivity Measurement

The molar conductivity of the homobinuclear complexes have been determined in DMF. The result shows low value of 2.59 and 2.44 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for the Co(II) and Ni(II) complexes respectively.

Table 2. Percentage elemental and water contents in the homobinuclear metal(II) complexes

Compounds	% Found (Calculated)			Equivalent number		
	M	Cl	H ₂ O	M	Cl	H ₂ O
[Co ₂ LCl ₄].4H ₂ O	17.99(18.29)	21.46(22.00)	12.00(11.18)	2	4	4
[Ni ₂ LCl ₄].6H ₂ O	17.03(17.27)	21.37(20.89)	15.20(15.89)	2	4	6



These values are too low to account for any dissociation hence non-electrolytic nature of the complexes [16].

4.2.4 Infrared Spectral Analysis

In the absence of sophisticated techniques such as x-ray crystallography, IR spectroscopy provides valuable information on the bonding mode of the ligand to the metal ions. Thus, in order to elucidate the structures of the binuclear complexes, IR spectra of the starting materials, Schiff base ligand and metal complexes are studied as per similarities and differences. The significant IR bands are shown in Table 3 and spectra of the Schiff and complexes are shown in Fig. 1-3.

The FT-IR spectrum of the Schiff base ligand displayed distinct strong band at 1622.66 cm⁻¹ attributable to $\nu(\text{C}=\text{N})$ group [17,18]. The band due to $\nu(\text{C}=\text{S})$ group was observed at 1036.71 cm⁻¹ [3]. In the spectra of the binuclear complexes, the peak due to $\nu(\text{C}=\text{N})$ exhibits hypsochromic shift to 1638.55 and 1626.55 cm⁻¹ for Ni(II) and Co(II) binuclear complexes

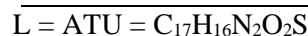
respectively, suggesting coordination through the azomethine nitrogen atom. Similarly, the band due to $\nu(\text{C}=\text{S})$ shifted to lower (1102.42 cm⁻¹) and higher (1111.97 cm⁻¹) frequencies indicating complexation *via* the sulphur atom of the thiourea moiety [19].

The emergence of new weak peaks in the binuclear complexes at 748.30 and 682.43 cm⁻¹ in Ni(II) complex and 730.45; and 648.10 cm⁻¹ in Co(II) complex may respectively be ascribed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$. These new bands inferred the formation of the complexes through azomethine nitrogen and thiocarbonyl sulphur groups [7,19]. The broad and strong peaks exhibited in the spectra of the binuclear complexes at 3210.4 and 3300.04 cm⁻¹ for Ni(II) and Co(II) complexes respectively are characteristics of water of crystallization [20,21].

The coordinated chloride ions could not be detected due to limitation of instrument. However, white precipitate of AgCl is only observed when AgNO₃ is added to nitric acid-digested binuclear complex solution indicating that the chloride ions are inside the coordination sphere as supported by conductivity measurement [17].

Table 3. Significant Infrared Bands (cm⁻¹) of the Schiff base and its Binuclear Complexes

Compounds	$\nu(\text{H}_2\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
ATU	-	1622.66	1036.71	-	-
[Co ₂ LCl ₄].4H ₂ O	3300.04	1626.55	1111.97	730.45	648.10
[Ni ₂ LCl ₄].6H ₂ O	3210.40	1638.55	1102.42	748.30	682.43



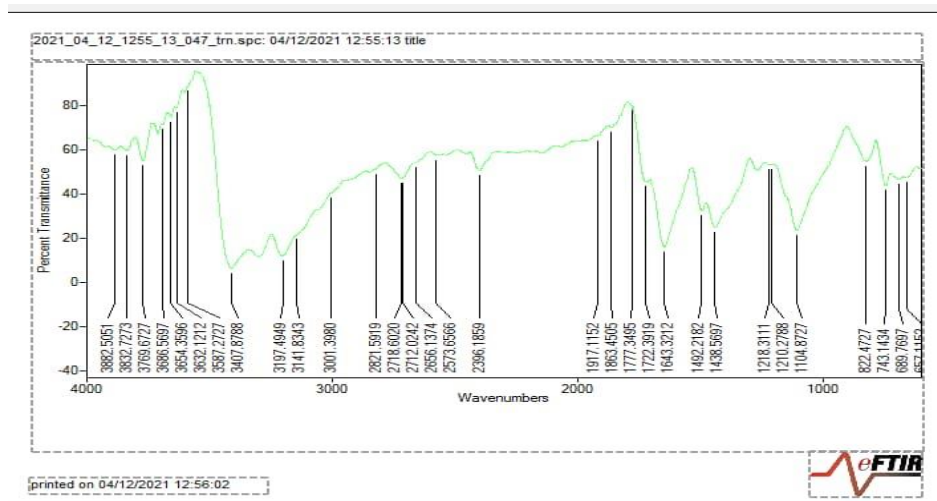


Fig. 1: FTIR Spectrum of Schiff base ligand

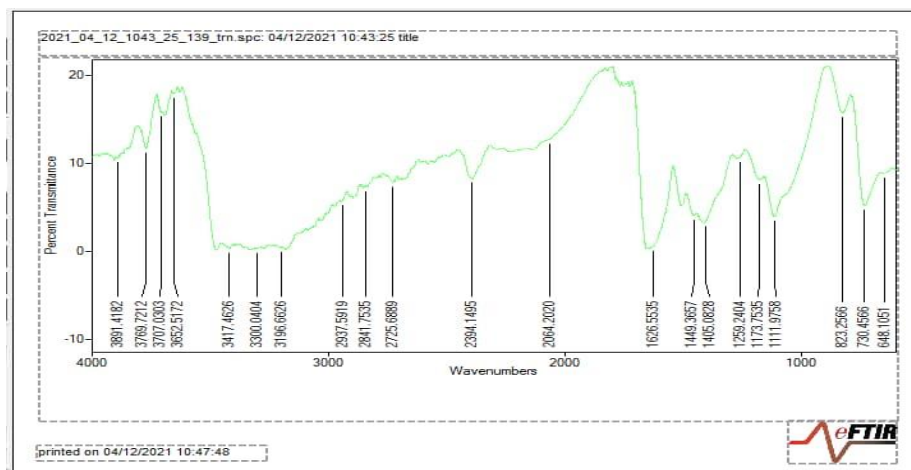


Fig. 2: FTIR Spectrum of Co(II) Complex

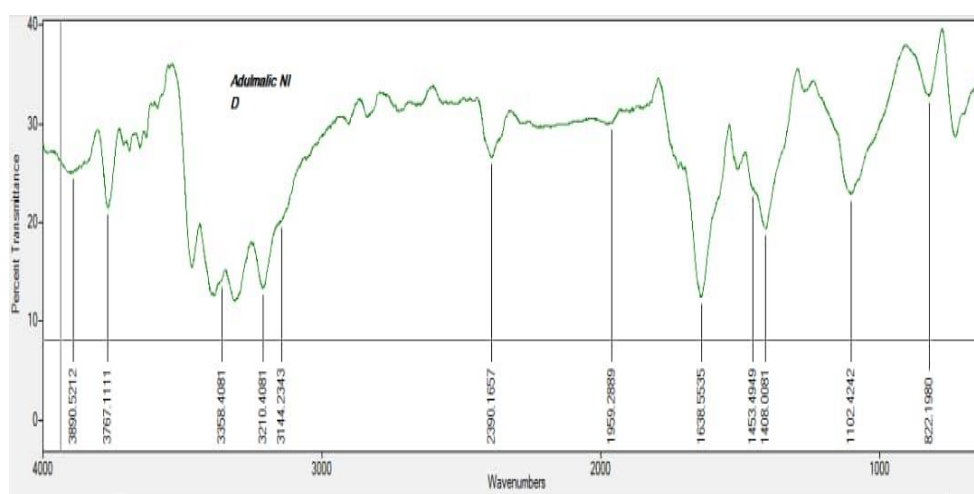
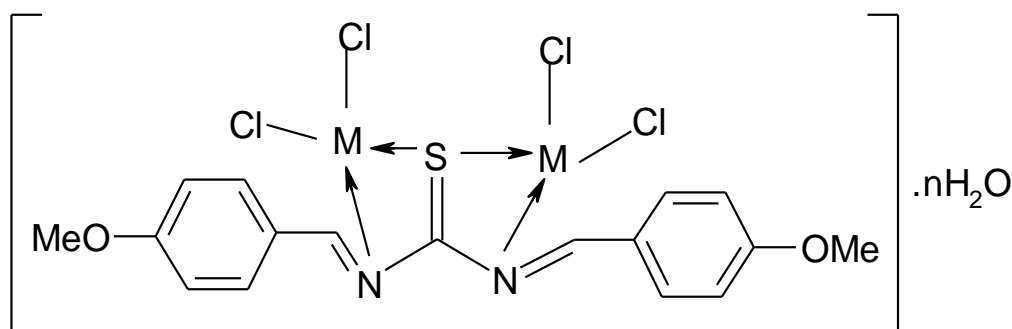


Fig. 3: FTIR Spectrum of Ni(II) Complex

On the basis of the results of FT-IR spectroscopy, molar conductance, chloride and water content as well as report from similar studies, square planar structure has been

proposed for the homobinuclear complexes. The structure is shown in Fig. 4.



Where M = Co or Ni and n = 4 Co-complex and 6 for Ni-complex.

Fig. 4. Proposed structure of homobinuclear metal(II) complexes

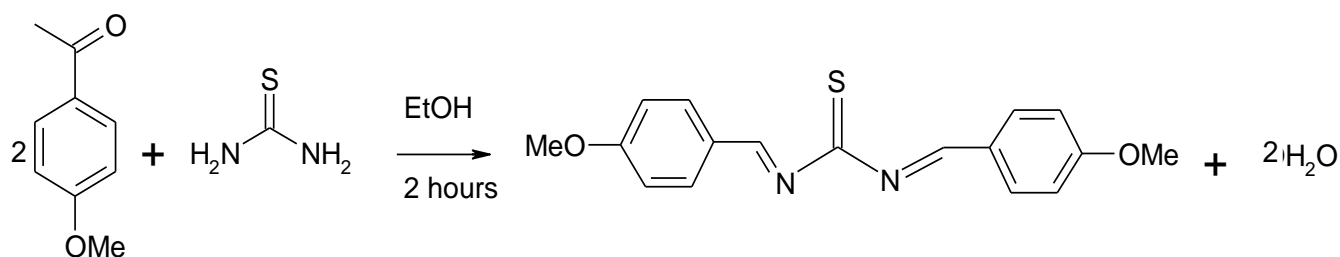
3. Experimental

3.1. Physical measurements

Chemicals utilized in the study were of analar grade. 4-methoxybenzaldehyde and thiourea were obtained from BDH. All metal salts used as chlorides ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were obtained from JHD. Melting points were measured on an Electrothermal 9100 apparatus. Electrical conductivity was recorded using LIDA instrument model DDS-307 conductivity meter. The IR spectra were determined on BUCK Scientific Fourier transform IR model M 530 spectrophotometer. Water of crystallization was determined using Thermostat oven: DHG-9030A, Pec medical. All solvents used were of high percentage purity. Distilled water was utilized for all preparations according to standard procedures.

3.2. Synthesis of N, N'-bis(4-methoxybenzylidene)thiourea (ATU)

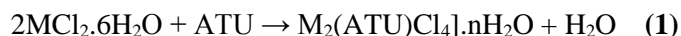
The Schiff base, N, N'-bis(4-methoxybenzylidene)thiourea (ATU) was synthesized by adopting the method described by Abdseed and El-ajaily [4] and adopted by Siraj and Sambo [22]. This was done as follows. To 70 ml ethanolic solution of 4-methoxybenzaldehyde (0.24 mol, 29.2 ml) was added isovolumic amount of ethanolic solution of thiourea (0.12 mol, 9.1344 g), then few drops of 10 % NaOH were added to adjust pH. The obtained reaction mixture was magnetically stirred under reflux at 70 °C for two hours. A pale-yellow solution formed was allowed to stand to precipitate the product, which was filtrated, washed severally with ethanol and stored in a vacuum over calcium chloride. The depiction of the reaction is shown in scheme 1.



Scheme 1: Preparation route for N, N'-bis(4-methoxybenzylidene)thiourea (ATU)

3.3. General procedure for the synthesis of Homobinuclear Cobalt(II) and Nickel(II) Complexes

To 20 ml ethanolic solution of the synthesized Schiff base ligand (4.2 mmol, 1.3122 g), 15 ml ethanolic solution of 8.4 mmol of metal chlorides ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1.9966 g; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 1.9986 g) were added accordingly, refluxed at 70 °C with constant stirring for 2 hours [19]. The reaction is represented in equation 1.



3.4 Characterization

3.4.1 Estimation of Water of Crystallization in the Complexes

Water of crystallization in the complexes was estimated by heating the samples to a constant weight, testing the gas evolved with cobalt (II) chloride paper. The loss in weight is considered the net water of crystallization [15]. This was calculated as reported in the literature [23].

3.4.2 Gravimetric Estimation of Metal Content in the Complexes

The metal content of the complexes was determined by precipitation method subsequent to the digestion of the metal complexes with HNO₃. The Co(II) and Ni(II) were precipitated as dimethylglyoxime and dipyridine thiocyanate complexes respectively [7,24].

3.4.3 Gravimetric Estimation of Cl⁻ in the complexes

To the solutions of each of the complexes, aqueous silver nitrate was added in drops, then in excess. The amount of AgCl precipitated was dried and measured [25]. The composition by mass of the chloride ion and its percentage were calculated as presented in equation (2) and (3) respectively.

$$\text{Chloride (wt)} = \frac{\text{RAM}}{\text{Molecular mass of AgCl} \left(\frac{\text{g}}{\text{mol}}\right)} \times W \quad (2)$$

Where, RAM = Relative atomic mass of Chlorine (g/mol),

W = weight of precipitate from complex sample (g)

$$\% \text{ Chloride} = \frac{\text{weight of chloride obtained (g)}}{\text{weight of complex sample used (g)}} \times 100 \% \quad (3)$$

3.4.4 Molar Conductance Measurements

The 0.001 mol of the complex was dissolved in 10 ml of dimethylformamide (DMF) and the corresponding conductance value was recorded using LIDA instrument model DDS-307 conductivity meter at 33 °C. From the observed conductance recorded, the specific conductance and the molar conductance of the metal complex were calculated using equations (4) and (5) respectively [26]. The results obtained are shown in Table 1.

$$\text{Specific Conductance} = \frac{\text{Observed conductance}}{\text{Cell constant} \times \text{Correction factor}} \quad (4)$$

$$\text{Molar conductance} = \frac{1000 \text{ K}}{\text{Molar concentration}} \quad (5)$$

where k = specific conductance

4. Conclusion

The tridentate diazathio Schiff base ligand derived from the condensation reaction between 4-methoxybenzaldehyde and thiourea have been synthesized and subjected to complexation to yield homobinuclear complexes of the formula [M₂LCl₄].nH₂O (where M= Co(II) or Ni(II), L= Schiff base ligand and n=4 for Co(II) and 6 for Ni(II). The complexes were thermally stable and non-electrolytic in nature. The Schiff base coordinated to the metal(II) ions as tridentate through the two imine nitrogen and thione sulphur,

thereby forming a square planar geometry with two chloride ions.

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