SYNTHESIS AND CHARACTERIZATION OF BENZIL CROWN CYCLIC SCHIFF BASE LIGAND AND ITS METAL COMPLEXES

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ABSTRACT. The reaction between benzil and hexamethylenediamine formed a new ligand [L], [(1Z,3Z)-2,3-diphenyl-5,6,7,8,9,10-hexahydro-1,4-diazecine], of the type [N_2], was synthesized by the condensation reaction through Schiff base reaction between benzil and hexamethylenediamine. The new Schiff base ligand reacts with Mn^{2+}, Ni^{2+} and Co^{2+} metal ions to give the complexes with the general formula: [M(L)Cl_2]. The elemental investigations have been used to analyze the ligand and its complexes by CHN, FT-IR, UV-Vis, TLC, mass spectrum, melting point with the study of biological activity to the formed compounds. From the data obtained, the proposed molecular structure adopts square planar structure about the metal ions. The study reveals the formation of a new ligand type [N_2] and its metal ion complexes with square planar structures metal:ligand ratio of 1:1, which can be employed in a variety of fields such as medicine and industry.

KEY WORDS: Benzil, Hexamethylenediamine, Metal complexes, Square planar structure

INTRODUCTION

Due to their many characteristics and applications, Schiff bases are an important class of chemicals. They are used as biological system models [1] and as catalysts [2] in a variety of chemical and photochemical reactions [3], these compounds have gotten a lot of attention. Antibacterial [4], antifungal [5], and anticancer [6] properties have been observed for this sort of substance. The structural elucidation of Schiff base spectra was investigated [7]. H_2N(CH_2)_3NH_2 is the formula for hexamethylenediamine, an organic molecule that made up of a hexamethylene hydrocarbon chain with amine functional groups, the amine odor is strong in the colorless solid (yellowish in certain commercial samples). Annually, over 1 billion kg are manufactured [8]. It is nearly entirely employed to make polymers, an application that takes advantage of its structure. The chemical molecule benzil also known as (1,2-diphenylethane-1,2-dione) has the formula (C_9H_7CO_2), which is commonly written as (PhCO)_2. One of the most frequent diketone is a yellow solid. Most benzil is used in the free-radical curing of polymer networks. Ultraviolet radiation decomposes benzil, generating free-radical species within the material, promoting the formation of cross-links. Benzil is a potent inhibitor of human carboxylesterases, enzymes involved in the hydrolysis of carboxylesters and many clinically used drugs [9]. The majority of benzil is primarily used in the curing of polymer networks by free radicals, It decomposes in the presence of ultraviolet radiation, generating free radical species that encourage the formation of cross-links within the material. Human carboxylesterases, which are enzymes involved in the hydrolysis of carboxyl esters, are inhibited by benzil and they are found in many therapeutically utilized medications [10]. The manuscript includes the description of the synthesis and physical characterization of [(1Z,3Z)-2,3-diphenyl-5,6,7,8,9,10-hexahydro-1,4-diazecine] ligand [N_2] type

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in the ratio of 1:1 (benzil and hexamethylenediamine), and its new square planar metal ion complexes. This proposal was supported by results obtained from analytical techniques such as FT-IR, UV-Vis, CHN elemental analysis, TLC, and mass spectrometry, with (1:1) metal:ligand ratio forming a new bands of (M-N) of a new compounds by the condensation reaction which has been characterized by FT-IR, UV-Vis, elemental analysis, thin layer chromatography (TLC), mass spectrum and study the biological activity for the ligand and its complexes.

**EXPERIMENTAL**

**Synthesis of the [N₂] Schiff base ligand**

Equimolar quantities (2.7 g, 12.84 mmol) of benzil and (1.5 g, 12.90 mmol) hexamethylenediamine with the addition of 5-6 drops of HBr, primary amine was dissolved in ethanol (40 mL). The mixture was cooked at (110 °C) in a reflux cooker for (4 h). Filtration was used to isolate the precipitate, which was recrystallized from ethanol dried under vacuum. Yield (2.2 g, 82 %), (m.p. 155 °C).

**Synthesis Mn²⁺ complex**

Equimolar quantities (1.3 g, 4.48 mmol) of the ligand and (0.9 g, 4.55 mmol) MnCl₂.4H₂O dissolved in methanol (40 mL). The mixture was cooked with a low temperature in a reflux cooker (110 °C for 2 h). Filtration was used to isolate the precipitate that was re-crystallized from methanol and dried. Yield (0.8 g, 62%), (m.p. 190 °C) (Table 1).

| No. | Compounds       | M.wt. (g/mol) | Yield % | Colour  | m.p. °C | Found (calc. %) |
|-----|-----------------|---------------|---------|---------|---------|-----------------|
|     |                 |               |         |         |         | M   | C   | H   | N   |
| 1   | C₁₀H₁₀N₂        | 290.41        | 82      | Yellow  | 155     | -   | 80.05 | 6.61 | 9.86 |
|     |                 |               |         |         |         |     | (82.72) | (7.64) | (9.65) |
| 3   | C₁₀H₁₀Cl₂MnN₂  | 416.25        | 62      | Mustered| 190     | (13.20) | 11.22 | 55.03 | 4.44 | 6.73 |
|     |                 |               |         |         |         |     | (57.71) | (5.33) | (5.00) |
| 3   | C₁₀H₁₀Cl₂NiN₂  | 420.00        | 71      | Green   | 230     | (13.97) | 13.82 | 55.12 | 4.00 | 5.11 |
|     |                 |               |         |         |         |     | (57.19) | (5.28) | (5.67) |
| 4   | C₁₀H₁₀Cl₂CoN₂  | 420.24        | 66      | Pale Green| 177    | (14.02) | 13.01 | 53.83 | 3.81 | 5.10 |
|     |                 |               |         |         |         |     | (57.16) | (5.28) | (5.67) |

The same way has been used to prepare the Ni, Co metal ion complexes and their data shown in Table 1.

**RESULTS AND DISCUSSION**

The [N₂] type ligand was produced by reacting benzil with hexamethylenediamine in a 1:1 ratio in acidic conditions (Scheme 1).

The reaction of metal chlorides occurs according to Scheme 2 which shows the synthetic route of the ligand type [N₂]. The yield of the ligand and its complexes ranges from (62% to 71%). CHN, FT-IR, UV-Vis, melting point, mass spectrum, and thin-layer chromatography TLC were used to describe the compounds.
Synthesis and characterization of benzil crown cyclic Schiff base and its metal complexes

Scheme 1. Synthetic route for \([\text{N}_2]\) type ligand.

Scheme 2. Synthetic route for the complexes, where the \([\text{M} = \text{Mn}^\text{II}, \text{Ni}^\text{II} \text{and Co}^\text{II}]\).

Ligand\’s FT-IR spectrum

In the FT-IR spectrum of hexamethylenediamine (Figure 1A) the two bands at the range of (3400-3420 cm\(^{-1}\)) are due to the \(\nu(\text{NH}_2)\) \([11]\), while at the same time there is a strong peak at (1700 cm\(^{-1}\)) which assign to the \(\nu(\text{C}=\text{O})\) \([12]\) is belong to benzyl (Figure 1B), these peaks are vanish in the spectrum of the free ligand (Figure 1A).

As a result of the coordination between hexamethylenediamine and benzil, a new peak at (1500 cm\(^{-1}\)) that belongs to the \(\nu(\text{C}=\text{N})\) \([13]\) has appeared and replaced by a new peak at (1500 cm\(^{-1}\)) which is belongs to the \(\nu(\text{C}=\text{N})\) as a result of the coordination between hexamethylenediamine and benzil \([14]\). In contrast to the spectra of the unbound ligand, which shows Schiff base reaction, a new peak at (1500 cm\(^{-1}\)) belongs to the \(\nu(\text{C}=\text{N})\) as a result of coordination between hexamethylenediamine and benzil. As a result of the coordination action and the delocalization of electron pi density of the ring at (3077 cm\(^{-1}\)), the bands owing to the phenyl group \([15]\) of the benzil are transferred to a higher frequency as shown in Table 2.
Figure 1. (A) Hexamethylenediamine’s FT-IR spectrum and (B) FT-IR spectrum of benzil.

Mn complex’s FT-IR

There is a significant band at (1500 cm\(^{-1}\)) assigned to \(\nu(C=N)\) of the (ligand-metal) ion interface as a result of the coordination between both of them as shown in Figure 2A. This band has been pushed to a higher frequency in comparison to the spectrum of the Mn complex (Figure 2B). The characteristic new created band at (500 cm\(^{-1}\)) was ascribed to the \(\nu(Mn-N)\) \[^{[1]}\] for the produced complexes in Table 2.

Table 2. FT-IR spectral data for the ligand and its complexes.

| No. | Compounds       | \(\nu(NH_2)\) cm\(^{-1}\) | \(\nu(C_6H_5)\) ring cm\(^{-1}\) | \(\nu(C=O)\) cm\(^{-1}\) | \(\nu(C=N)\) cm\(^{-1}\) | \(\nu(M-N)\) cm\(^{-1}\) |
|-----|-----------------|---------------------------|-----------------------------|-------------------------|-----------------------|-------------------------|
| A   | Hexamethylenediamine | 3400-3420                | -                          | -                       | -                     | -                       |
| B   | Benzil          | -                         | 3077                       | 1700                    | -                     | -                       |
| 1   | C\(_6\)H\(_5\)N\(_2\) | -                         | 3100                       | -                       | 1500                  | -                       |
| 2   | C\(_6\)H\(_5\)Cl\(_2\)MnN\(_2\) | -                         | 3095                       | -                       | 1540                  | 500                     |
| 3   | C\(_6\)H\(_5\)Cl\(_2\)NiN\(_2\) | -                         | 3087                       | -                       | 1570                  | 490                     |
| 4   | C\(_6\)H\(_5\)Cl\(_2\)CoN\(_2\) | -                         | 3070                       | -                       | 1520                  | 480                     |
Synthesis and characterization of benzil crown cyclic Schiff base and its metal complexes

Figure 2. (A) FT-IR spectrum of the free ligand. (B) Mn$^n$ complex's FT-IR spectrum.

Figure 3. The starting materials’s (benzil and hexamethylenediamine) UV-Vis spectrum.
The UV-Vis spectrum for the ligand

The electronic spectra of the complexes were obtained using (UV-Visible) spectrophotometer type Shimadzu in the range (900-200 nm) by using quartz cells of (1.0 cm) length and concentration of (10⁻³ M) in DMSO solvent. The UV-Vis spectrum for the ligand (Figure 3A) shows two peaks at the ligand field which are due to the (π → π*) and (n → π*) transitions, these two peaks are differ from the ligand field transitions of the starting materials (benzyl and hexamethylenediamine) as shown in Figure 3. all the data are in Table 1.

In the UV-Vis spectrum (Figure 3A) two significant absorption peaks may be seen at (225 nm), (4444 cm⁻¹), ( εmax = 1640 molar⁻¹. cm⁻¹) and (265 nm), (37735 cm⁻¹), (εmax= 1100 molar⁻¹. cm⁻¹) which are due to the (π → π*) and (n → π*) transitions respectively [17] (Table 3).

Table 3. The ligand and its complexes’ electronic spectrum data are listed in.

| No. | Compounds               | Band Position | Electronic transition(cm⁻¹) | εmax (dm³ mol⁻¹ cm⁻¹) | Assignme nt | Suggested configuration |
|-----|-------------------------|---------------|-----------------------------|------------------------|-------------|-------------------------|
| A   | hexamethylene diamine)  | 290           | 34482                       | 900                    | π→π*        |                         |
|     |                         | 350           | 28571                       | 700                    | n→π*        |                         |
| B   | Benzil                  | 215           | 46511                       | 780                    | π→π*        |                         |
|     |                         | 260           | 38461                       | 8100                   | n→π*        |                         |
| 1   | C₁₉H₂₀N₂                 | 225           | 44444                       | 1640                   | π→π*        |                         |
|     |                         | 265           | 37735                       | 1100                   | n→π*        |                         |
| 2   | C₁₉H₂₀Cl₂MnN₂            | 235           | 42553                       | 1590                   | π→π*        |                         |
|     |                         | 270           | 37037                       | 900                    | n→π*        |                         |
|     |                         | 565           | 17699                       | 100                    | d-d         | S.P                     |
| 3   | C₁₉H₂₀Cl₂NiN₂            | 240           | 41666                       | 1400                   | π→π*        |                         |
|     |                         | 290           | 34482                       | 720                    | n→π*        |                         |
|     |                         | 510           | 19607                       | 110                    | d-d         | S.P                     |
| 4   | C₁₉H₂₀Cl₂CoN₂            | 260           | 38461                       | 1450                   | π→π*        |                         |
|     |                         | 295           | 3898                        | 820                    | n→π*        |                         |
|     |                         | 620           | 16129                       | 100                    | d-d         | S.P                     |

Figure 4. The ligand’s UV-Vis spectrum (A) and the Mn ion complex’s UV-Vis spectrum (B).
Synthesis and characterization of benzil crown cyclic Schiff base and its metal complexes

*UV-Vis of the Mn complex*

The Manganese complex spectrum (Figure 4B) discovered two notable peaks in the ranges of (235 nm), (42553 cm⁻¹), (εmax = 1590 molar⁻¹ cm⁻¹) and (270 nm), (37037 cm⁻¹), (εmax = 900 molar⁻¹ cm⁻¹), respectively [18]. The d-d electronic transition ("d→d" transition) is credited to the visible area's third peak, which was discovered at (565 nm), (17699 cm⁻¹) (εmax = 100 molar⁻¹ cm⁻¹). The electronic spectral data are listed in Table 3.

*Thin layer chromatography (TLC) of the ligand and its complexes*

After the sample has been applied on the plate, a solvent or solvent mixture (known as the mobile phase) is drawn up the plate via capillary action. Because different analytes ascend the TLC plate at different rates, separation is achieved. The TLC for the complexes revealed the appearance of new spots with varied characteristics of Rf than the Rf of the ligand. Metal ion complexes of Mn, Ni, and Co revealed the development of the complexes. Because the positions of the spots in metal ion complexes varies from the position of the ligand's spot (Table 4).

**Table 4. The [N2] ligand T.L.C. complexes.**

| No. | Structural formula | Range of Rf (mm) |
|-----|-------------------|-----------------|
| 1   | C19H20N2          | 1.8             |
| 2   | C19H20ClMnN2      | 3.5             |
| 3   | C19H20ClNiN2      | 2.9             |
| 4   | C19H20ClCoN2      | 4.9             |

**Mass spectrum**

The spectrum of the ligand has a peak that corresponds to the molecular ion (m/z 289), showing that the base peak represents relative abundance. The other peaks indicate pieces of ions. The molecular structure of the ligand is frequently revealed by the type of the fragments (Figure 5).

**Figure 5. Mass spectrum of the ligand.**

**Biological processes**

The antibacterial activity of substances was assessed in vitro using the agar ditch method against *S. aureus*, *S. facials*, and *E. coli* [19]. The stock solution was made by dissolving (40 mg) of each component in 1 mL of N,N-dimethylformamide (DMF), from which two-fold serial dilutions were obtained. The inhibition diameter of the ligand and its complexes with three different concentrations (25%, 50%, and 100%) for (24 h) has been shown in (25%, 50 h) has been shown in Table 5 [20].
CONCLUSION

The ligand $[N_2]$ type was made by generating a novel complex with Mn, Ni, and Co metal ions through a Schiff base reaction between benzil and hexamethylenediamine, and it has a square planar structure around the metal ions. Spectroscopic tests have confirmed this. The type of the fragments in the mass spectrum can often reveal the ligand's molecular structure. In compared to the free ligand's spot, the TLC for the complexes displays different spots. The visible area's third peak for complexes in the UV-Vis reveals ligand-metal coordination, and the primary transitions assign to the square planar structure around the metal ions. While the FT-IR spectra the $\nu(C=\text{N})$ and $\nu(\text{NH}_2)$ of benzyl and hexamethylenediamine respectively has been diapered and replaced by a new band $\nu(C=\text{N})$ in the range of (1500-1520) for the complexes. The antibacterial activity of the produced compounds [ligands and complexes] examined in DMF was shown to be reliant on both the Schiff base substituent and the solvent medium. Because it demonstrated more inhibitory effect at lower concentrations examined. Gram-positive bacteria were inhibited by all of the produced chemicals. As a result, these compounds can be utilized to make narrow-spectrum antibiotics for the treatment of gram-positive and gram-negative bacterial infections, particularly *S. aureus*, *S. facials*, and *E. coli*.

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