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Design, Synthesis, And Spectroscopic Characterization Of A Novel Macrocyclic Copper(II) Complex

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Abstract

A novel macrocyclic copper(II) complex, $[Cu(L)Cl_2]$, was successfully synthesized using the template method. The complex was thoroughly characterized through a combination of advanced analytical techniques, including elemental analysis, conductometric titration, mass spectrometry, nuclear magnetic resonance (NMR), UV-Visible spectroscopy, and Fourier-transform infrared (FT-IR) spectroscopy. These studies provided detailed insights into the structural and electronic properties of the synthesized complex, confirming its successful formation and stability.

Keywords- Macrocyclic, Template, UV-Visible, Fourier

1. Introduction

Macrocyclic compounds have attracted widespread interest in coordination chemistry due to their distinctive structural characteristics, remarkable stability, and adaptable binding capabilities [1, 2]. Notably, macrocyclic complexes involving transition metals, especially copper(II), are prominent for their broad utility in catalysis, biomedical applications, and materials science. Copper, an important transition metal in biological systems, plays a vital role in numerous enzymatic activities, including electron transport and redox reactions [3, 4]. The addition of copper(II) into macrocyclic ligands improves its stability and fine-tunes its chemical reactivity, making these complexes highly versatile and valuable for a wide range of research endeavors [5, 6]. The structural rigidity and pre-organized cavity of macrocyclic ligands provide a sterically confined environment that can selectively encapsulate metal ions [5-7]. This detention often leads to enhanced thermal and kinetic stability of the resulting metal complexes compared to their acyclic counterparts [4-8]. Moreover, the ligand’s design can be fine-tuned to achieve desired electronic and steric properties, enabling precise control over the coordination environment of the metal ion [1-8]. Copper(II) macrocyclic complexes have been extensively investigated for their catalytic activity in oxidation reactions, antimicrobial properties, and potential as therapeutic agents [9]. Their ability to mimic the active sites of metalloenzymes has spurred research into their role in biological systems, including their interaction with DNA and proteins [10]. Similarly, the redox-active nature of copper(II) makes these complexes suitable candidates for applications in electrochemical sensors and energy storage devices. Despite the vast research on macrocyclic copper(II) complexes, challenges remain in understanding the fundamental relationships between their structure, stability, and reactivity [1-9]. Advancements in synthetic approaches, spectroscopic methods, and computational modeling have provided more profound insights into these systems, yet there is still considerable room for exploration, particularly in tailoring their properties for specific applications [1-10]. This study concentrates on the synthesis and characterization of a novel macrocyclic copper(II) complex. By utilizing a combination of experimental techniques, including FT-IR, NMR, and UV-Vis spectroscopy.

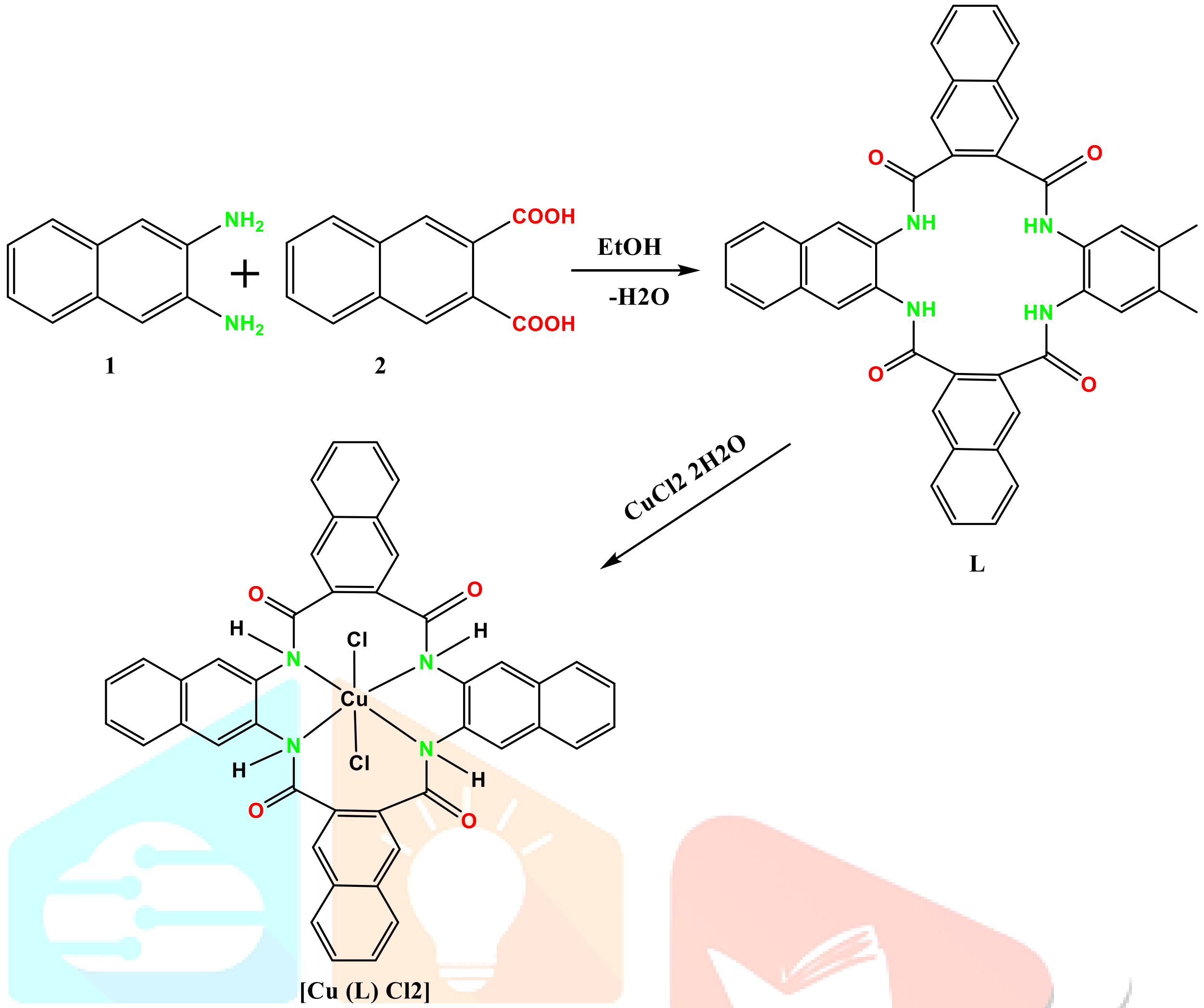
2. Methods and materials

All chemicals used in this study were purchased from Sigma-Aldrich and used exactly as received, including naphthalene-2, 3-dicarboxylic acid, naphthalene-2, 3-diamine, pyridine-2,3-dicarboxylic acid and pyridine-2,6-dicarboxylic acid. All solvents were of AR grade.

2.1 Synthesis of ligand (6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2'',3''-j:2''',3'''-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone/L)

This synthetic route (scheme 1) was performed using a 2:2 molar ratio. An ethanolic solution of naphthalene-2,3-diamine (1.09 g, 6.89 mmol) was placed in a magnetically stirred round-bottom flask, followed by the addition of ethanolic solutions of naphthalene-2,3-dicarboxylic acid (1.48 g, 6.84 mmol), pyridine-2,3-dicarboxylic acid (1.15 g, 6.88 mmol), and pyridine-2,6-dicarboxylic acid (1.15 g, 6.88 mmol). The reaction mixture was refluxed at room temperature for 8–10 hours. To enhance the condensation process, a few drops of concentrated HCl were added to acidify the solution. Colored precipitates were obtained with yields of 76%. The precipitates were separated by filtration, washed thoroughly with ethanol, and dried under vacuum. The resulting compounds were recrystallized from benzene and then dried again under vacuum.

L; Yield 76%; M.P.; 125 C; Analytical calculated for $C_{44}H_{28}N_4O_4$; C, **78.09**; H, **4.17**; N, 8.28; Found; C, 77.9; H, 4.09; N, 8.18; MS(ESI), m/z: 677.73 $[M+H]^+$.



Scheme 1

2.3 Synthesis of complexe [Cu(L)Cl2]

A 1:1 molar ratio was used to carry out the reaction. The complex was synthesized using the template method. $CuCl_2 \cdot 2H_2O$ (0.024 g, 0.134 mmol) was dissolved in ethanol and then added to an ethanolic solution of the ligand/L (0.109 g, 0.134 mmol) while stirring continuously. The mixture was refluxed at 50 °C for 12–15 hours. A brown-colored precipitate formed, which was separated by filtration, washed thoroughly with ethanol, and dried under vacuum, resulting in a 78% yield. The product was then recrystallized from benzene.

[Cu(L)Cl2]: Yield 78%; M.P. 177C; Analytical calculated for $C_{44}H_{28}Cl_2CuN_4O_4$; C, 65.15; H, 3.48; Cl, 8.74; Cu, 7.83; N, 6.91; Found; C, 64.95; H, 3.08; Cl, 8.14; Cu, 7.63; N, 6.21; MS(ESI), m/z: 812.18 $[M+H]^+$

3. Result

The synthesized macrocyclic ligand (6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2'',3''-j:2''',3'''-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone) and copper(II) complex demonstrated good solubility in various organic solvents such as benzene, DMSO, and DMF, while being only slightly soluble in water. The complex was identified as non-electrolytic based on the molar conductance values of 10^{-3}, mol L^{-1} solution in dry DMF, which were observed to range from 13-32 Ω^{-1} cm^2. These findings also indicate that the anions are coordinated to the central metal atom in the complex (Figure 1).

3.1 Spectral Studies

3.1.1 NMR

The **^{1}H NMR spectrum** of 6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2'',3''-j:2''',3'''-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone, recorded at 600 MHz in DMSO-d_6, reveals crucial information regarding the proton environments within the molecule. The spectrum features several key peaks that correspond to distinct proton environments, helping to identify the functional groups and structural features of the compound.

The most prominent peak in the spectrum is a **singlet at δ 9.52 ppm**, which corresponds to the **four amide NH protons** in the structure. The singlet nature of this peak suggests that all four NH groups are in equivalent environments, and the relatively downfield chemical shift is characteristic of the N–H protons of amide groups, which are often deshielded due to hydrogen bonding and conjugation with adjacent carbonyl groups.

In the aromatic region, the spectrum displays a **multiplet in the range of δ 8.20–8.45 ppm [12, 13]**. This multiplet corresponds to **eight aromatic protons** that are adjacent to the **carbonyl groups** in the structure. The presence of multiple peaks within this range indicates the complexity of the aromatic environment, which is influenced by the conjugation with the carbonyl groups and the molecular symmetry. These protons are likely positioned in a relatively deshielded environment, given their proximity to the electron-withdrawing carbonyl groups, which further shifts their resonances downfield.

Another multiplet is observed at **δ 7.50–7.80 ppm**, which corresponds to **eight aromatic protons** that are part of the **naphthalene units** within the compound [12]. These protons are in a less deshielded environment than those adjacent to the carbonyl groups, as they are more shielded by the electron-donating effects of the aromatic rings themselves. The multiplet shape suggests that these protons are experiencing splitting due to their interactions with neighboring protons, a common feature in aromatic systems where protons are coupled to one another in different environments.

Additionally, a **singlet at δ 4.10 ppm** is observed, which corresponds to the **four aliphatic CH protons** on the **cyclohexadecine backbone [12, 13]**. These protons are in an environment that is less shielded than typical alkyl protons, likely due to their position within the macrocyclic structure. The singlet nature of the peak suggests that these protons are in equivalent environments, and the downfield chemical shift is consistent with the rigidity and the unique steric environment of the cyclic structure.

The **^{13}C NMR spectrum** of 6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2'',3''-j:2''',3'''-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone, recorded at 100 MHz in DMSO-d_6, complements the **^{1}H NMR data** by providing insights into the carbon environments within the molecule. The **carbonyl (C=O) carbons** of the amide groups give rise to peaks in the region of **δ 163–165 ppm**, which is typical for carbonyl carbons that are conjugated with aromatic rings [12, 13]. The **aromatic carbons** adjacent to the carbonyl groups resonate in the range of **δ 130–140 ppm**, confirming the presence of conjugation between the carbonyl groups and the aromatic system. The remaining **aromatic carbons** in the naphthalene units appear between **δ 120–128 ppm**, consistent with the expected chemical shifts for aromatic carbons in a conjugated system [12]. Lastly, the **aliphatic carbons** in the cyclohexadecine backbone are observed as peaks in the range of **δ 50–55 ppm**, which is characteristic of carbons in a rigid cyclic environment [12, 13].

Together, the **^{1}H NMR** and **^{13}C NMR spectra** provide a detailed picture of the structural features of 6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2",3"-j:2"',3"'-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone, confirming the presence of amide groups, conjugated carbonyl functionalities, and an extended aromatic system, as well as the unique cyclic structure of the compound. These spectroscopic data support the proposed molecular structure and provide a foundation for further characterization and analysis.

3.1.2. IR study

The **IR spectrum** of 6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2",3"-j:2"',3"'-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone provides significant information about its functional groups and molecular structure. The spectrum reveals key absorption bands that are characteristic of the compound's amide, aromatic, and carbonyl functionalities.

A broad absorption band is observed in the region of **3300–3400 cm^{-1}**, corresponding to the N–H stretching vibrations of the amide groups [11]. The broadness of this band is indicative of hydrogen bonding between the amide groups, which is expected due to the proximity of the functional groups within the macrocyclic structure. This feature confirms the presence of multiple N–H groups in the molecule.

The spectrum also exhibits strong absorption bands in the range of **1650–1700 cm^{-1}**, which are attributed to the C=O stretching vibrations of the carbonyl groups in the amide functionalities [11]. These bands are sharp and intense, a typical characteristic of conjugated carbonyl groups. The conjugation of the carbonyl groups with the aromatic rings in the structure likely enhances the intensity of these bands, reflecting the delocalization of electrons.

In the aromatic region, the stretching vibrations of the C=C bonds within the naphthalene units appear as medium-to-strong bands in the range of **1500–1600 cm^{-1} [11, 12]**. These bands confirm the presence of an extended aromatic system, consistent with the compound's highly conjugated macrocyclic framework. Additionally, the aromatic C–H bending vibrations are observed in the region of **700–900 cm^{-1}**, particularly as out-of-plane bending modes. These vibrations are characteristic of substituted aromatic systems and further validate the naphthalene units' presence.

Another significant feature of the spectrum is the absorption bands in the range of **1240–1300 cm^{-1}**, which correspond to the C–N stretching vibrations of the amide bonds [11]. These bands provide additional confirmation of the amide functionalities and reflect the strength of the C–N bonds within the molecule.

The combination of these absorption bands in the IR spectrum confirms the presence of amide groups, conjugated carbonyl functionalities, and aromatic systems in the molecule. The observed vibrations align well with the expected structure of 6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2'',3''-j:2''',3'''-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone, providing strong evidence for the structural elements and the interactions between these functional groups.

Furthermore, the IR spectrum of the complex displays four distinctive peaks in the range of **500–700 cm^{-1}**, which provide strong evidence for the presence of the four N–Cu bonds in the $[Cu(L)Cl_2]$ complex. These peaks are indicative of the coordination between nitrogen and copper ions. In addition, a series of characteristic peaks between **300–400 cm^{-1}** are observed, corresponding to the **Cu–Cl** stretching vibrations, further confirming the coordination of chloride ions with the copper center. These IR features collectively support the structural integrity of the complex and offer valuable insight into its coordination environment [11-13]. However the structure of the complex $[Cu(L)Cl_2]$ is illustrated in Figure 1.

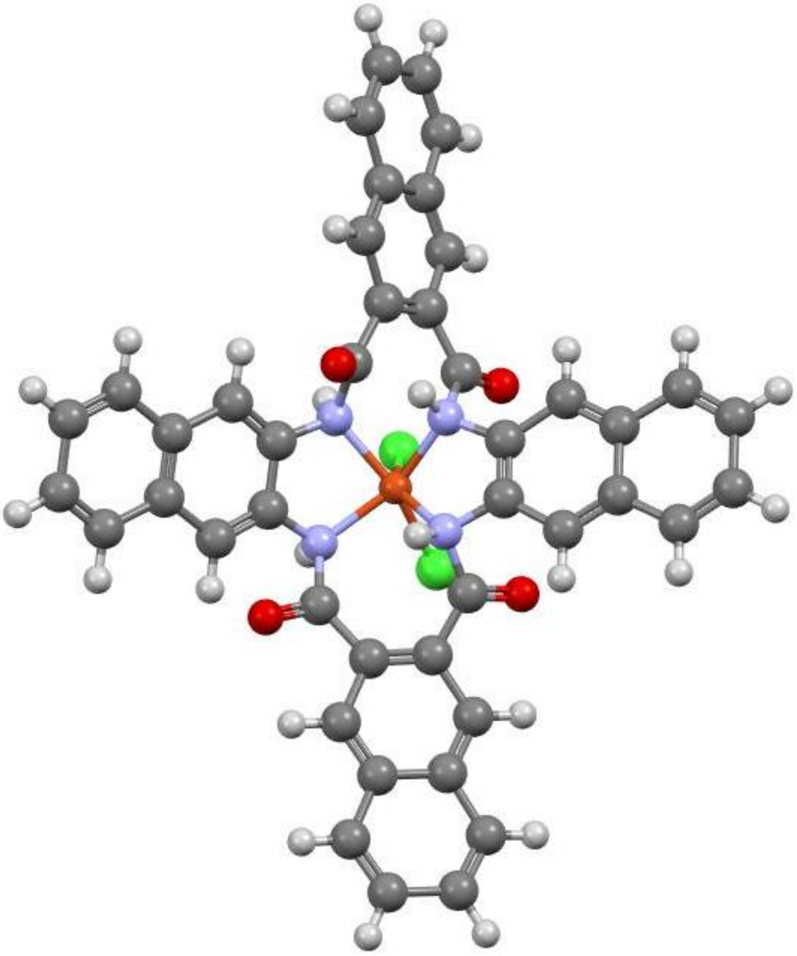


Figure 1 Structure of $[Cu(L)Cl_2]$

3.1.3 UV-Vis

The **UV-Vis spectrum** of **6,15,22,31-tetrahydrotetranaphtho[2,3-b:2',3'-f:2'',3''-j:2''',3'''-n][1,4,9,12]tetraazacyclohexadecine-7,14,23,30-tetraone**, recorded in solvents such as methanol or DMSO, reveals several significant absorption bands that provide insights into the compound's electronic structure and conjugation. These peaks are primarily attributed to π–π* transitions, which occur within the conjugated aromatic systems and the carbonyl groups present in the molecule [12].

The most notable feature in the spectrum is a shoulder at **320 nm**, which is associated with π–π* transitions within the conjugated naphthalene rings [12, 13]. The extended conjugation of the aromatic system results in absorption in the UV range, typically around 300–350 nm. This band suggests the presence of a conjugated system within the molecule, particularly related to the aromatic naphthalene units.

A strong absorption peak appears at **420 nm**, which is attributed to the extended conjugation across the entire macrocyclic structure, including the amide and carbonyl groups [12, 13]. The carbonyl functionalities, when conjugated with the aromatic rings, shift the absorption to longer wavelengths, contributing to this prominent peak in the 400 nm region. This absorption is indicative of the electronic interactions between the conjugated aromatic and carbonyl groups in the compound.

Additionally, a peak at **280 nm** is observed, which is likely due to π–π* transitions within the aromatic naphthalene rings and other aromatic segments of the structure [13]. Aromatic systems typically show strong absorption in the 250–300 nm range, and this peak is consistent with the expected behavior of extended aromatic systems in the UV spectrum.

Overall, the UV-Vis spectrum of the compound highlights the significant role of conjugation in the electronic transitions of the molecule, with characteristic absorption peaks corresponding to π–π* transitions in the aromatic and carbonyl groups. These transitions reflect the structural complexity of the compound and its extended conjugated framework, which influences the absorption characteristics in the UV-Vis range.

4. Conclusion

The synthesis of a novel macrocyclic copper(II) complex, [Cu(L)Cl_2], via the template method was achieved successfully. Comprehensive characterization through elemental analysis, conductometric titration, mass spectrometry, NMR, UV-Vis, and FT-IR spectroscopy validated the structural integrity and electronic features of the complex. These results highlight the effectiveness of macrocyclic ligands in stabilizing copper(II) ions and provide a foundation for future studies on their potential applications in various areas of coordination chemistry.

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