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Green synthesis and physicochemical characterization of Cu(II) and Ni(II) Schiff base complexes derived from 2,3-dihydroxybenzaldehyde

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Article information **Abstract**

Key words

Green chemistry; Schiff base complexes; Copper(II); Nickel(II); Mechanochemical synthesis; Spectral characterization

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Green chemistry, which focuses on the creation of ecologically friendly synthetic techniques, has emerged as a crucial strategy in contemporary coordination chemistry. This study used sustainable methods to manufacture Schiff base ligands from aminopyridine derivatives and 2,3-dihydroxybenzaldehyde. Their copper(II) and nickel(II) complexes were then made using green synthetic methods that minimized the use of solvents and energy, such as mechanochemical grinding and microwave-assisted synthesis.Using a variety of physicochemical and spectroscopic methods, including elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), Mass spectrum, magnetic susceptibility measurements, molar conductivity, and thermal analysis, the synthesized metal complexes were isolated in high yields. Spectral measurements demonstrated chelation behavior by confirming the interaction of the Schiff base ligands to the metal centers via the azomethine nitrogen and phenolic oxygen atoms..

I. Introduction

Green chemistry, which tries to design chemical processes that decrease or eliminate the use of hazardous compounds while retaining efficiency and economic viability, has attracted a lot of attention due to the growing awareness of environmental degradation and the need for sustainable development(Anastas & Warner, 2000) (Sheldon, 2017) . The search for greener options in coordination chemistry is prompted by the fact that conventional synthetic approaches frequently rely on hazardous organic solvents, long reaction durations, and high energy consumption (James et al., 2012).

Mechanochemical and microwave-assisted technologies are two of the most promising green synthetic approaches(Kaupp, 2009). Mechanochemical synthesis, which offers benefits including decreased waste, quicker reaction times, and increased reaction efficiency, uses mechanical force to trigger chemical reactions, usually in solvent-free or minimal-solvent circumstances(Varma, 1999).Microwave-assisted synthesis, on the other hand, provides rapid and homogeneous heating, leading to improved yields and cleaner products compared to conventional thermal methods (Servi, Genc, Gür, & Koca, 2005).

Schiff bases, characterized by the azomethine (–C=N–) functional group, are an important class of ligands in coordination chemistry due to their ease of synthesis, structural versatility, and strong metal-binding ability (Servi, Genc, Gür, & Koca, 2005).These ligands readily form stable complexes with transition metal ions, particularly copper(II) and nickel(II), which are known for their diverse coordination geometries and rich electronic properties (Mary, Geetha, & Ramesh, 2023).Due to their intriguing physicochemical

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characteristics and numerous uses in materials science, bioinorganic chemistry, and catalysis, copper(II) and nickel(II) Schiff base complexes have been thoroughly investigated(Mary, Geetha, & Ramesh, 2023) . Nitrogen and oxygen donor atoms are frequently involved in the coordination behavior of Schiff base ligands with these metal ions, resulting in chelated complexes with improved stability(Mary, Geetha, & Ramesh, 2023).

This work focuses on the environmentally friendly synthesis of Cu(II) and Ni(II) Schiff base complexes from 2,3-dihydroxybenzaldehyde by means of microwave irradiation and mechanochemical grinding. In order to clarify their coordination modes and structural characteristics, the produced complexes were extensively studied using a variety of spectroscopic and analytical techniques, proving the feasibility of green approaches in the synthesis of coordination molecules.

II. Experimental

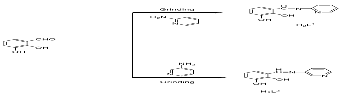
A.Synthesis of Schiff Base Ligands

In this work, a green, straightforward, and eco-friendly mechanochemical grinding approach was used to manufacture two Schiff base ligands. The prepared ligands are:

N-(2,3-dihydroxybenzylidene)pyridin-2-amine (H_2L_4)

N-(2,3-dihydroxybenzylidene)pyridin-3-amine (H_2L_2)

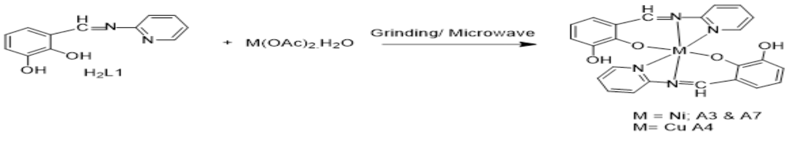
Solvent-free condensation processes involving 2,3-dihydroxybenzaldehyde and the corresponding aminopyridine derivatives were used to create both ligands. In particular, H_2L_1 was prepared using 2-aminopyridine, whereas H_2L_2 was synthesized using 3-aminopyridine. In compliance with green chemistry principles, the reactions were mechanically ground using a mortar and pestle in ambient settings.



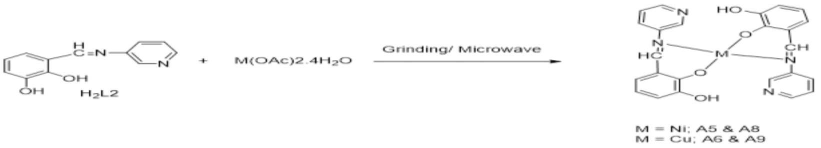
Scheme (2-1): Preparation of ligands H_2L_1 and H_2L_2

B.Metal Complex Synthesis

Green chemistry techniques were used to create nickel(II) and copper(II) complexes of the Schiff base ligands H_2L_1 and H_2L_2, utilizing both mechanochemical grinding and microwave-assisted techniques. Schemes 2-2 and 2-3 show that the metal-to-ligand molar ratio was kept at 1:2 in every production.Elemental analysis and spectroscopic methods such as FT-IR, , and mass spectrometry were used to ascertain the suggested molecular formulae of the produced metal complexes. The findings show that all complexes produced using both techniques have the generic formula [$M(HL)_2$], where HL stands for the mono-deprotonated Schiff base ligand (H_2L_1 or H_2L_2) and M = Ni(II) or Cu(II).Every created metal complex is a colorful solid with good stability in the presence of moisture and air. The copper(II) complex produced from copper acetate and ligand H_2L_4 using the microwave-assisted technique was an exception, as it immediately degraded from green to black upon synthesis.



Scheme (2-2): Preparation of complexes A3, A4, A7



Scheme (2-3): Preparation of complexes A5, A6, A8, A9

Qualitative proof of effective coordination between the metal ions and the Schiff base ligands is provided by the color changes that were seen during the complexes' formation employing both preparation techniques. The complexes' molar conductance was measured at room temperature in DMSO at a concentration of 1 × 10^{-3} M. All complexes are non-electrolytic due to their low conductivity values, which confirm their neutral nature and imply the absence of counterions outside the coordination sphere.

C.Infrared Spectral Analysis

Infrared Spectra of the H_2L_1 Ligand and Its Metal Complexes

Figures(2-1)(2-2) show the infrared spectra of complexes A3, A4, and A7. There are notable spectral differences between the infrared spectra of the free ligand H_2L_4 and those of its metal complexes, suggesting coordination to the metal ions.

The azomethine group's (vC=N) distinctive stretching vibration can be seen in the free H_2L_4 ligand at 1620 cm^{-1}. This band shifts to lower frequencies upon complexation, showing up in complexes A3, A4, and A7 at about 1590 cm^{-1}. The azomethine nitrogen atom's coordination with both copper (II) and nickel (II) ions is confirmed by this shift (İnci, Aydın, & Zorlu, 2021).

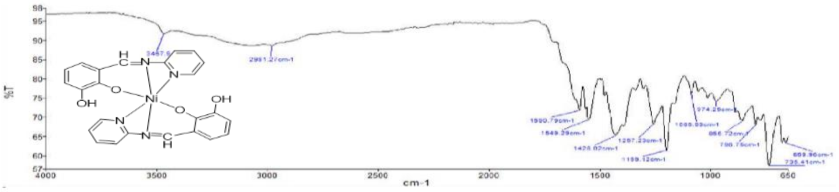


Figure (2-1): Infrared spectrum of complex (A3) [Ni(HL1)2]

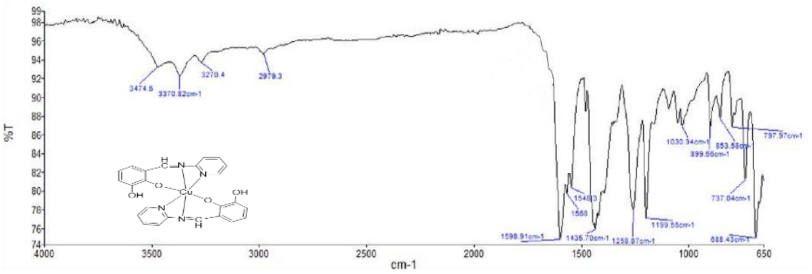


Figure (2-2) Infrared spectrum of complex (A7)

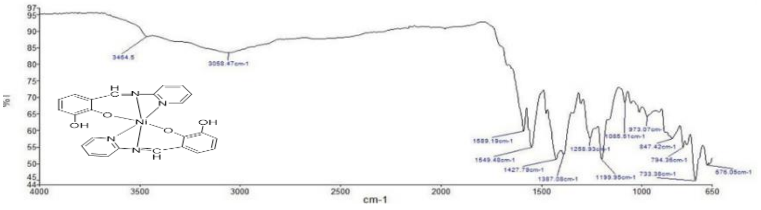


Figure (2-3): Infrared spectrum of complex (A4)

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Furthermore, in the corresponding complexes, the stretching vibration linked to the pyridine ring (vC=N), which was detected at 1557 cm⁻¹ in the free ligand, is moved to a lower frequency of roughly 1549 cm⁻¹. This behavior suggests that the pyridine nitrogen atom is involved in coordinating with the metal centers(Lever & Rice, 1969). Additionally, compared to the free ligand, the IR spectra of the produced complexes exhibit a discernible shift of the phenolic C–O stretching vibration toward lower frequencies. This change offers compelling proof that the phenolic oxygen atom is involved in metal–ligand coordination (Pradhan, Sinha, Verma, Kumar, & Sharma, 2018). The stretching vibration of the remaining uncoordinated phenolic –OH group is responsible for the notable broad absorption band that all complexes show about 3470 cm⁻¹.

The H_2L_2 Ligand and Its Metal Complexes' Infrared Spectra

Figures (2-4) (2-5)(2-6) (2-7)display the infrared spectra of complexes A5, A6, A8, and A9. These complexes' IR spectra show clear coordination-induced alterations as compared to the free H_2L_2 ligand.

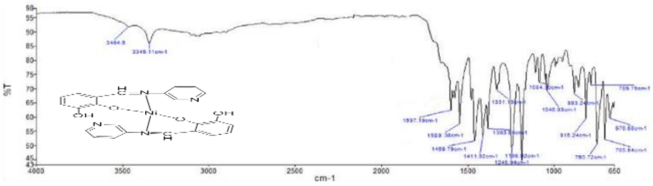


Figure (2-4): Infrared spectrum of complex (A5)

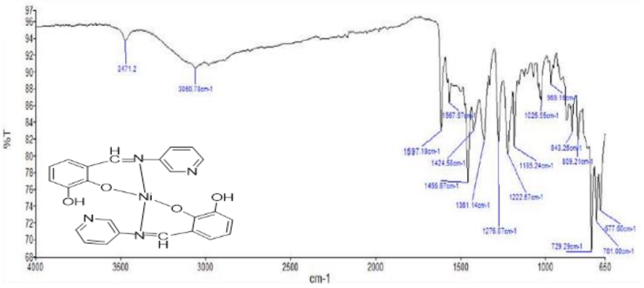


Figure (2-5): Infrared spectrum of complex (A8)

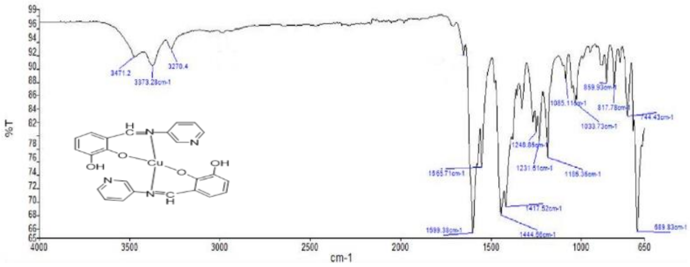


Figure (2-6): Infrared spectrum of complex (A6)

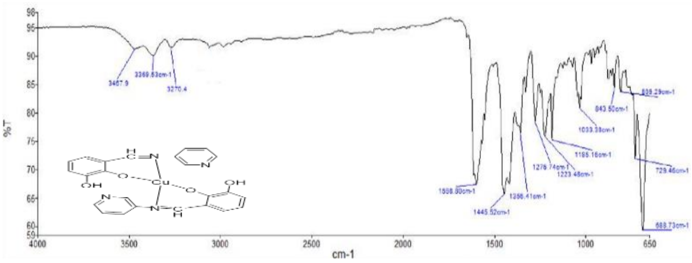


Figure (2-7): Infrared spectrum of complex (A9)

In all related metal complexes, the azomethine stretching vibration (νC=N), which was detected at 1614 cm^{-1} in the free H_2L_2 ligand, is moved to roughly 1598 cm^{-1}. This change demonstrates that the azomethine nitrogen atom is coordinated with both nickel (II) and copper (II) ions (Lever & Rice, 1969).

The participation of the phenolic oxygen atom in interaction with the metal ions is also shown by the shift of the phenolic C–O stretching band in the free ligand to lower frequencies in the complexes(İnci, Aydın, & Zorlu, 2021).

On the other hand, the stretching vibration of the pyridine ring (νC=N), which is present in the free ligand at 1567 cm^{-1}, is nearly unaltered in the complexes' spectra (around 1569 cm^{-1}). This finding implies that the pyridine nitrogen atom in H_2L_2 is not involved in coordination with the metal ions (Pradhan, Sinha, Verma, Kumar, & Sharma, 2018).

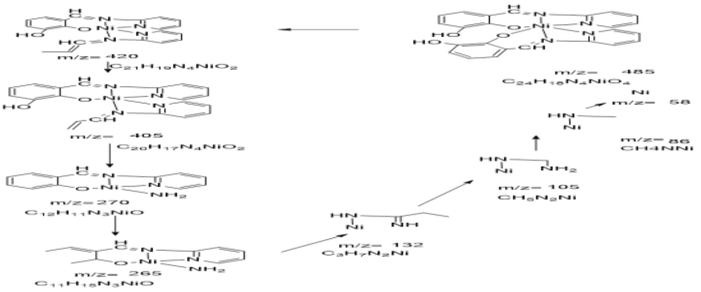
The Schiff base ligand H_2L_1, which is derived from 2-aminopyridine, acts as a tridentate chelating ligand, coordinating to Cu(II) and Ni(II) ions through the azomethine nitrogen atom, the phenolic oxygen atom, and the pyridine ring nitrogen atom, according to the infrared spectral data.

On the other hand, the Schiff base ligand H_2L_2, which is generated from 3-aminopyridine, functions as a bidentate ligand, coordinating through the phenolic oxygen atom and the azomethine nitrogen atom while leaving the pyridine nitrogen uncoordinated.

D.The mass spectrum

The mass spectrum of the complex (A3) $[Ni(HL1)_2]$

was recorded. The mass spectrum of the nickel complex with the ligand H_2L_1 gave a set of peaks, as shown in Figure (2-8). Scheme (2-4) shows the proposed mass fractions of the complex, where it gave a major peak at m/z = 484.95, which corresponds to the molecular weight of the nickel complex C24H18N4NiO4, which has a molecular weight of 485. This supports the proposed structure of the nickel(II) complex, where the mass spectrum showed a peak at m/z = 405.9, which corresponds to C20H17N4NiO2, while a peak at m/z = 265.3 appeared, which corresponds to C11H15N3NiO. A peak also appeared at m/z = 132.2, which is C3H7N2Ni, while it gave a value at m/z = 105 CH5N2Ni, and also gave a clear value at m/z = 86, which is CH4NNi.



Scheme (2-4) Mass segmentation (A3)

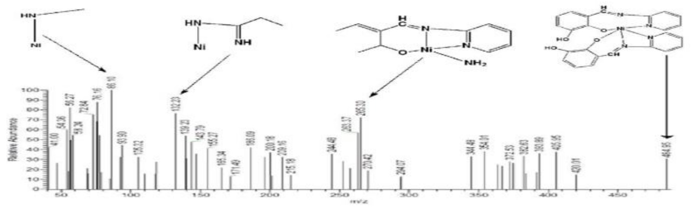
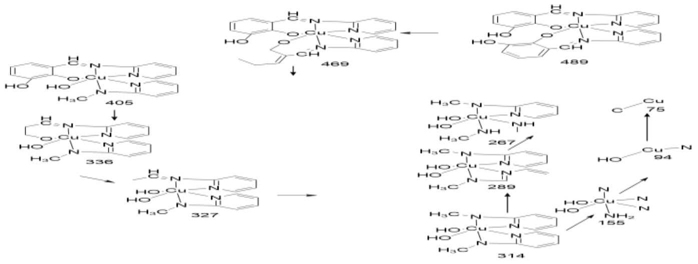


Figure (2-8): Mass spectrum of complex (A3)

Mass Spectrum of Complex [Cu(HL1)2] (A4)

The mass spectrum of the copper complex with the H2L1 ligand was recorded and yielded a series of peaks, as shown in Figure (2-9). The proposed mass fractions of the complex are shown in Scheme (2-5). The figure shows a major peak at m/z = 489.31 corresponding to the molecular weight of complex C24H18CuN4O4, which supports the proposed structure of the copper complex Cu(II). The mass spectrum showed a peak at m/z = 469 corresponding to C23H22CuN4O3, while a peak at m/z = 409 corresponding to C18H25CuN4O3, and a significant peak at m/z = 327.1 corresponding to $C_{13}H_{17}CuN_4O_2$. Also, an atom appeared at m/z = 155 and m/z = 94 belonging to $CuH_4N_4O_2$ and CuHNO respectively.



Scheme (2-5) Block partitions of complex (A4)

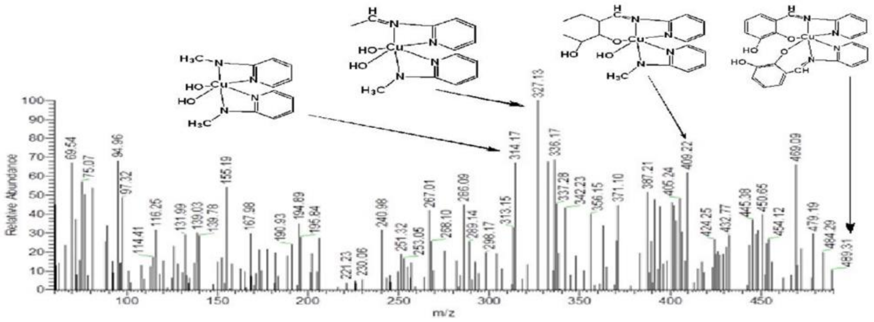
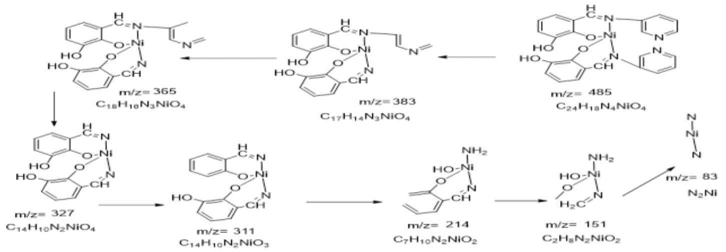


Figure (2-9) Mass spectrum of complex (A4)

The mass spectrum of the complex (A5) [Ni(HL2)2]

was recorded. The mass spectrum of the nickel complex with the ligand H2L2 gave a set of peaks, as shown in Figure (2-10). The proposed mass fractions of the complex are shown in Scheme (2-6). The figure shows a major peak at m/z = 485.7, which corresponds to the molecular weight of the complex $C_{24}H_{18}N_4NiO_2$, which has a molecular weight of 485.71. This supports the proposed structure of the nickel complex Ni(II), where the mass spectrum showed a peak at m/z = 373, which corresponds to $C_{23}H_{19}N_4NiO_4$, while it gave a clear peak at m/z = 368.4, which corresponds to $C_{17}H_{15}N_3NiO_4$, while it gave another clear peak at m/z = 83.3, which corresponds to N_2Ni. It also gave a peak at m/z = 311.3 that goes back to $C_{14}H_{10}N_2NiO_3$ and a peak at m/z = 269 that goes back to $C_{12}H_{10}N_2NiO_2$.



Scheme (2-6): Proposed block partitions for complex (A5)

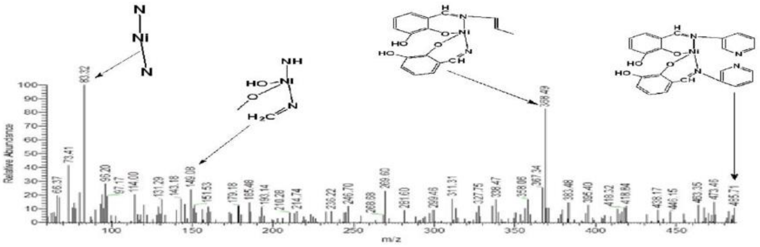
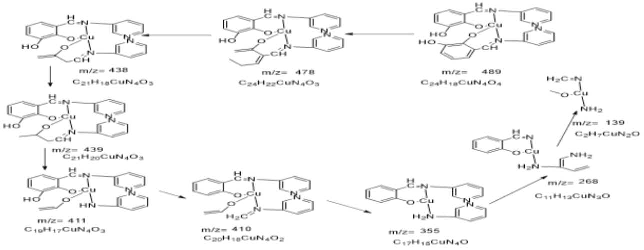


Figure (2-10): Mass spectrum of complex (A5)

The mass spectrum of complex (A6) [Cu(HL2)2]
showed the mass of complex (A6) in Figure (2-11) with a peak at m/z = 489.99, which corresponds to the molecular weight of complex C24H18CuN4O. This supports the proposed structure of the Cu(II) complex with a molecular weight of 489. The mass fractions shown in Scheme (2-7) show a peak at 478 m/z = C24H22CuN4O3, a peak at 438.7 m/z = 3C21H18CuN4O, while a clear peak at 410 m/z = C20H18CuN4O2 is observed, while a peak at 355 m/z = C17H15CuN4O, which undergoes several fissiones of 268 m/z =, 226 m/z =, and 139 m/z = C11H13CuN3O, C9H10CuN2O, and C2H7CuN2O respectively.



Scheme (2-7): Block partitions of complex (A6)

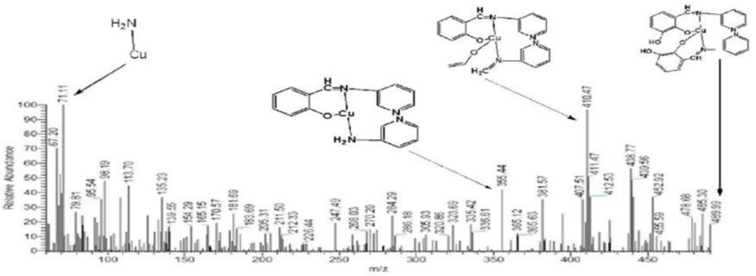
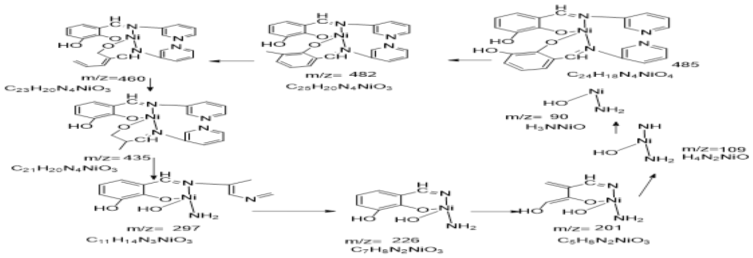


Figure (2-11): Mass spectrum of complex (A6)

The mass spectrum of the complex (A8) [Ni(HL2)2]

is shown in Figure (2-12). A series of peaks yielded the proposed mass fractions for the complex, as illustrated in Scheme (2-8). The figure shows a major peak at m/z = 485.08, corresponding to the molecular weight of the complex C24H18N4NiO4, and supporting the proposed structure of the binary nickel(II) complex, where the mass peak at m/z = 482.9 corresponds to [C25H20N4NiO3].

We observe two peaks at m/z = 460 and m/z = 449, corresponding to the cleavage of C23H20N4NiO3 and C22H20N4NiO3, respectively.
The appearance of distinct peaks at m/z = 297 and m/z = 226 is attributed to the fission of C11H14N3NiO3 and C7H8N2NiO3, respectively. A distinct peak at m/z = 201 is also observed, attributed to the fission of C5H8N2NiO3, and another peak at m/z = 109 is attributed to H4N2NiO.



Scheme (2-8): Proposed block partitions for complex (A8)

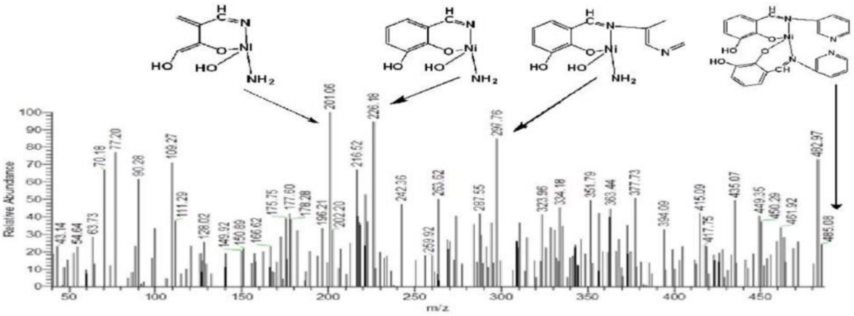
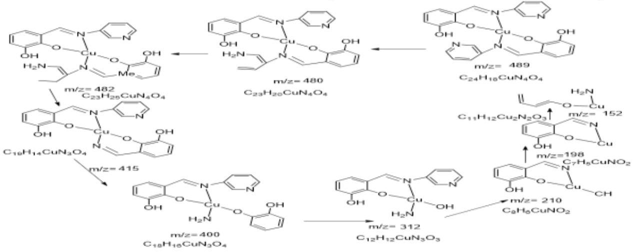


Figure (2-12): Mass spectrum of complex (A8)

The mass spectrum of complex (A9) [Cu(HL2)2]

was recorded for the copper-ligand complex (H_2L_2), yielding a series of peaks as shown in Figure (2-13). The proposed mass fractions for the complex are shown in Scheme (2-9). The figure shows a major peak at m/z = 489, corresponding to the molecular weight of the complex, which is 489. This supports the proposed structure of the copper complex Cu(II), where the mass spectrum showed a peak at m/z = 459. It also showed a peak at m/z = 210, corresponding to C8H6CuNO2, and a distinct peak at m/z = 152, corresponding to C4H7CuNO.



Scheme (2-9): Proposed block partitions for complex (A9)

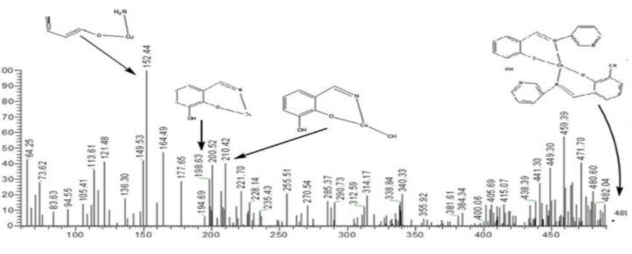


Figure (2-13): Mass spectrum of complex (A9)

IIIConclusion

In this study, environmentally friendly synthetic strategies were employed for the preparation of copper(II) and nickel(II) Schiff base complexes derived from 2,3-dihydroxybenzaldehyde and aminopyridine derivatives. The Schiff base ligands were synthesized via a solvent-free mechanochemical grinding method in accordance with green chemistry principles. Subsequently, their corresponding Cu(II) and Ni(II) complexes were prepared using both mechanochemical grinding and microwave-assisted techniques, minimizing solvent usage, reaction time, and energy consumption.

The synthesized ligands and metal complexes were characterized using elemental (C, H, N) analysis, Fourier-transform infrared (FT-IR) spectroscopy, , mass spectrometry. Infrared spectral data confirmed coordination through the azomethine nitrogen and phenolic oxygen atoms in all complexes. Additionally, the ligand derived from 2-aminopyridine exhibited tridentate coordination behavior involving the pyridine nitrogen atom, whereas the ligand derived from 3-aminopyridine acted as a bidentate chelator .The obtained results demonstrate that mechanochemical and microwave-assisted methods provide efficient, sustainable, and reliable routes for the synthesis of Cu(II) and Ni(II) Schiff base complexes, highlighting their potential as green alternatives to conventional solution-based synthetic approaches in coordination chemistry.

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Green synthesis and physicochemical characterization of Cu(II) and Ni(II) Schiff base complexes derived from 2,3-dihydroxybenzaldehyde

التخليق الأخضر والتوصيف الفيزيائي والكيميائي لمعقدات قواعد شيف للنحاس (II) والنيكل (II) المشتقة من 3،2-ثنائي هيدروكسي بنزالدهيد

فايزة فرج إسويسي هناء بشير شاويش
قسم الكيمياء، كلية العلوم، جامعة مصراتة

قسم الكيمياء، كلية العلوم، جامعة مصراتة

الملخص

استلمت الورقة بتاريخ 2026/01/08، وقبلت بتاريخ 2026/01/27، ونشرت بتاريخ 2026/01/27

الكلمات المفتاحية: الكيمياء الخضراء؛ معقدات قواعد شيف؛ النحاس (II)؛ النيكل (II)؛ التخليق الميكانيكي الكيميائي؛ التوصيف الطيفي

برزت الكيمياء الخضراء، التي تركز على ابتكار تقنيات تركيبية صديقة للبيئة، كاستراتيجية أساسية في كيمياء التناسق المعاصرة. استخدمت هذه الدراسة أساليب مستدامة لتصنيع روابط قاعدة شيف من مشتقات أمينوبيريدين و3،2-ثنائي هيدروكسي بنزالدهيد. ثم تم تحضير معقدات النحاس (**II**) والنيكل (**II**) باستخدام أساليب تركيبية خضراء تقلل من استخدام المذيبات والطاقة، مثل الطحن الميكانيكي الكيميائي والتخليق بمساعدة الموجات الدقيقة. وباستخدام مجموعة متنوعة من الأساليب الفيزيائية والكيميائية والطيفية، بما في ذلك التحليل العنصري، ومطيافية الأشعة تحت الحمراء بتحويل فورييه (**FT-IR**)، وطيف الكتلة، وقياسات القابلية المغناطيسية، والتوصيلية المولية، والتحليل الحراري، تم عزل المعقدات المعدنية المصنعة بنسب عالية. وأظهرت القياسات الطيفية سلوك التمخلب من خلال تأكيد تفاعل روابط قاعدة شيف مع المراكز المعدنية عبر ذرات نيتروجين الأزوميثين وأكسجين الفينول.