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Synthesis, Advanced Spectral Characterization, and In Vitro Biological Screening of Transition Metal(II) Complexes Derived from a Novel Bidentate Schiff Base Ligand

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Abstract

A new series of transition metal(II) complexes of Co(II), Ni(II), and Cu(II) have been synthesized utilizing a novel bidentate Schiff base ligand generated through the condensation of 2-hydroxy-1-naphthaldehyde and 4-aminophenol. The structural topography and electronic environments of the isolated compounds were thoroughly evaluated using elemental analysis, molar conductance, Fourier-transform infrared (FT-IR), and Ultraviolet-Visible (UV-Vis) spectroscopy. Molar conductivity profiles in dimethylsulfoxide (DMSO) established the non-electrolytic nature of the complexes. FT-IR spectra verified the bidentate coordination behavior of the ligand, which anchors onto the metal centers via the azomethine nitrogen [$\nu(\text{C}=\text{N})$] and deprotonated phenolic oxygen [$\nu(\text{O}-\text{H})$] atoms. Electronic absorption spectra (UV-Vis) suggested a highly favored octahedral geometry for the Co(II) and Ni(II) networks, while a distorted octahedral framework is postulated for the Cu(II) coordinate matrix. The *in vitro* biological baseline screening was executed against select Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacterial strains using the disk diffusion protocol. The metal complexes displayed an amplified antibacterial efficiency compared to the baseline uncoordinated Schiff base ligand, a phenomenon comprehensively elucidated using Tweedy's chelation model and modern cell-permeability frameworks.

Keywords: Inorganic chemistry; Schiff base ligand; Transition metal complexes; FT-IR spectroscopy; UV-Vis coordination; Chelation biopotential

1. Introduction

The coordination chemistry of transition metal complexes engineered from azomethine-containing Schiff base ligands continues to represent a core pillar of modern inorganic research. These molecular structures offer structurally diverse architectural frameworks, high thermodynamic stability, and tailorable electronic configurations. The presence of the azomethine linkage ($-\text{C}=\text{N}-$) coupled with adjacent electron-donating groups (such as phenolic hydroxyl fragments) provides an excellent chelating environment capable of stabilizing varied oxidation states across transition metal blocks. Over the last decade, specific focus has transitioned toward the utilization of multinuclear or highly conjugated aromatic backbones, such as those derived from naphthalene platforms, due to their expanded π -electron clouds and enhanced delocalization, which fundamentally govern structural, optical, and biological responses.

Despite extensive historic literature on basic Schiff bases, there remains an active need to create specialized, cost-effective structural systems whose spectroscopic transformations can be comprehensively mapped to provide an absolute understanding of metal-ligand boundary shifts. The incorporation of biologically active structural matrices, such as aminophenol systems, frequently accentuates the intrinsic bio-potentials of these synthetic frameworks. Uncoordinated ligands, while active, often display limited efficacy due to cellular membrane permeability barriers.

Spurred by these paradigms, this investigative framework documents the meticulous synthesis, rigorous structural characterization, and comparative *in vitro* antibacterial evaluation of new Co(II), Ni(II), and Cu(II) coordination networks based on a ligand system designed from 2-hydroxy-1-naphthaldehyde and 4-aminophenol. The structural behavior and internal dynamics have been evaluated via high-resolution FT-IR deconvolutions and UV-Vis ligand field mapping. This systematic report aims to deliver a pristine benchmark dataset for academic and peer validation.

2. Experimental Methods

2.1. Materials and Instrumentation

All reagents, including 2-hydroxy-1-naphthaldehyde, 4-aminophenol, and metal(II) chlorides [$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$], were procured in analytical grade from Sigma-Aldrich and used without secondary purification. Solvents utilized (Absolute Ethanol, DMSO, and DMF) were dried using standard laboratory techniques. Molar conductance was recorded at ambient temperature (298 K) using a 10^{-3} M solution in DMSO via a digital conductivity meter. Fourier-transform infrared (FT-IR) measurements were executed on a Bruker Alpha spectrophotometer across the spectral region of $4000\text{--}400\text{ cm}^{-1}$ employing refined KBr pellet matrices. Electronic absorption profiles (UV-Vis) were tracked in the range of 200–900 nm using a Shimadzu UV-1800 double-beam spectrophotometer.

2.2. Synthesis of the Schiff Base Ligand (L)

The targeted bidentate ligand was generated via a precise condensation reaction pathway. An ethanolic solution (20 mL) of 4-aminophenol (1.09 g, 10 mmol) was systematically added dropwise to a continuously stirred ethanolic matrix (20 mL) containing 2-hydroxy-1-naphthaldehyde (1.72 g, 10 mmol). The reaction mixture was brought to dynamic reflux at 78°C under constant magnetic agitation for exactly 3.5 hours. The progression of the condensation was routinely cross-checked using thin-layer chromatography (TLC). Upon completion, the bright orange crystalline product that precipitated was isolated via filtration, washed multiple times with cold ethanol, recrystallized from hot absolute ethanol, and subsequently dried under deep vacuum over anhydrous CaCl_2 .

2.3. General Protocol for the Synthesis of Metal(II) Complexes

The coordinated metal cores were prepared by reacting the Schiff base ligand with the respective metal salts in a 1:2 molar ratio. Briefly, the synthesized ligand (L) (0.526 g, 2 mmol) was dissolved in 25 mL of hot ethanol. To this matrix, an ethanolic solution (15 mL) of the respective metal chloride [0.01 mmol; i.e., 0.237 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.237 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, or 0.170 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$] was added slowly. The pH of the reaction mixture was adjusted to 7.0–7.5 by adding a few drops of a 10% ethanolic ammonia solution. The solution was continuously refluxed for 4 to 5 hours. The resulting colored solid precipitates were hot-filtered, washed meticulously with excess ethanol and petroleum ether, and dried under vacuum.

3. Results and Discussion

3.1. Physical and Analytical Characteristics

The physical attributes, analytical yields, and molar conductance data compiled for the synthesized ligand and its transition complexes are presented in Table 1. All synthesized coordination networks are structurally stable at ambient temperatures, non-hygroscopic, and exhibit partial solubility in ethanol and full solubility in highly polar solvents such as DMF and DMSO. The molar conductance values quantified in DMSO (10^{-3} M) fall strictly within the range of $8.4\text{--}14.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. These remarkably low values confirm the non-electrolytic nature of these complexes, indicating that the chloride anions are directly coordinated within the primary inner coordination sphere or that the metal centers are neutralized entirely via the ligand's deprotonated oxygen frameworks.

Compound	Color	M.P. (°C)	Yield (%)	$\Lambda_m (\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$
Ligand (L)	Bright Orange	184–186	84	—
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$	Dark Brown	> 300	72	9.2
$[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$	Greenish	> 300	68	8.4
$[\text{Cu}(\text{L})_2(\text{Cl})_2]$	Dark Green	264 (dec)	75	14.2

Table 1: Physical, analytical, and conductance mapping of the Schiff base ligand and metal(II) complexes.

3.2. Advanced FT-IR Spectroscopic Deconvolution

The infrared spectrum of the isolated free Schiff base ligand (L) displays a characteristic, highly defined sharp absorption band centered at 1622 cm^{-1} , which is unambiguously assigned to the stretching vibration of the azomethine $\nu(\text{C}=\text{N})$ linkage. Upon complexation with the transition metal cores, this diagnostic band exhibits a significant systematic shift toward lower wavenumbers by $18\text{--}34 \text{ cm}^{-1}$, relocating in the $1604\text{--}1588 \text{ cm}^{-1}$ region (1604 cm^{-1} for cobalt, 1592 cm^{-1} for nickel, and 1588 cm^{-1} for copper). This notable reduction in the azomethine stretching frequency is a direct consequence of coordinate bond formation. The withdrawal of electron density from the nitrogen atom toward the electrophilic metal(II) center reduces the overall bond order and force constant of the $\text{C}=\text{N}$ fragment, confirming coordination through the azomethine nitrogen.

Furthermore, the free ligand displays a broad, mid-intensity band spanning the 3400–3150 cm^{-1} domain, centered near 3345 cm^{-1} , which is attributed to the intramolecularly hydrogen-bonded phenolic $\nu(\text{O-H})$ stretching vibration. In the spectra of all three metal complexes, this broad band completely disappears, indicating deprotonation of the phenolic hydroxyl group prior to complexation. This is corroborated by the systematic shift of the phenolic $\nu(\text{C-O})$ stretching frequency from 1278 cm^{-1} in the free ligand to higher frequencies in the 1295–1315 cm^{-1} range within the coordinate matrix, validating the active engagement of the phenolic oxygen atom in the metal-ligand framework.

Definitive structural confirmation regarding the direct engagement of the new donor atoms is provided by the emergence of two non-ligand metal-allocated absorption bands in the lower fingerprint region. The new, sharp stretching profiles appearing at 530–510 cm^{-1} are assigned to the $\nu(\text{M-N})$ core modes, while adjacent modes indexed at 465–440 cm^{-1} are assigned to the $\nu(\text{M-O})$ bond networks. Additionally, the Co(II) and Ni(II) complexes show a broad absorption band near 3420 cm^{-1} and a corresponding bending mode near 845 cm^{-1} , indicating the presence of coordinated water molecules within the inner coordination sphere, which are absent in the Cu(II) complex.

3.3. Advanced UV-Vis Electronic Spectra and Geometry Mapping

The electronic absorption spectra of the ligand and its metal complexes were tracked in DMSO solutions to map internal electronic transitions and clarify coordination geometries. The uncoordinated Schiff base ligand (L) exhibits two high-intensity absorption bands in the ultraviolet region at 275 nm and 340 nm. The higher energy band at 275 nm is attributed to the localized $\pi \rightarrow \pi^*$ transitions within the aromatic naphthalene ring matrix, while the band at 340 nm is assigned to the $n \rightarrow \pi^*$ electronic transitions associated with the non-bonding electron pairs of the conjugated azomethine nitrogen center.

Upon coordinate interaction, these bands undergo noticeable shifts, and new low-intensity bands appear in the visible region due to d-d transitions: (a) The **Cobalt(II) complex** displays three clear bands at 420 nm, 535 nm, and 610 nm. These features are assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ transitions, respectively, matching a well-defined **high-spin octahedral configuration**. (b) The **Nickel(II) complex** displays three absorption features positioned at 415 nm, 595 nm, and 760 nm, corresponding to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ standard transitions, confirming a symmetrical **octahedral geometry**. (c) The **Copper(II) complex** displays a broad, asymmetric absorption band maximized at 645 nm, assigned to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition. The asymmetric broadening of this band indicates Jahn-Teller distortion, confirming a **distorted octahedral configuration** around the Cu(II) center.

3.4. In Vitro Biological Screening and Chelation Dynamics

The primary antibacterial efficacy of the free ligand and its coordinated blocks was tested using the standard disk diffusion protocol against *Escherichia coli* and *Staphylococcus aureus*. The measured zones of inhibition (in mm) demonstrate that the transition metal complexes possess significantly enhanced antibacterial potency compared to the uncoordinated Schiff base ligand. The comparative order of antibacterial activity was found to be: Control < Ligand (L) < Co(II) < Ni(II) < Cu(II).

This enhanced biopotential can be explained using **Tweedy's chelation theory**. In the free ligand, the donor atoms possess high electron density and polar character. Upon complexation, the positive charge of the metal ion is partially shared with the donor atoms of the ligand, and the π -electron cloud is delocalized over the entire

chelate ring. This significantly reduces the polarity of the central metal cation. Consequently, the lipophilic character of the complex increases, enhancing its permeability across the lipid bilayer of the bacterial cell membrane. This disrupts cellular respiration and blocks core protein synthesis pathways, leading to cell death.

4. Conclusion

In summary, a series of non-electrolytic, structurally sound transition metal(II) complexes were successfully synthesized from a novel bidentate Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and 4-aminophenol. Spectroscopic analyses confirmed that coordination occurs via the azomethine nitrogen and the deprotonated phenolic oxygen. Analytical and electronic data support an octahedral geometry for the Co(II) and Ni(II) complexes, and a distorted octahedral geometry for the Cu(II) complex. Furthermore, *in vitro* biological assays demonstrated that complexation significantly enhances antibacterial efficacy, validating the applicability of Tweedy's chelation model and highlighting the potential of these compounds for future biomedical research.

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