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Synthesis And Spectroscopic Analysis Of Schiff Base Chelators For Transition Metal Ions

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ABSTRACT

Schiff bases, due to their ease of synthesis, structural versatility, and strong metal-binding properties, have gained attention in coordination chemistry, catalysis, and medicinal applications. This study presents the synthesis of Schiff base ligands through condensation reactions of aromatic aldehydes with primary amines and investigates their coordination behavior with transition metal ions such as Cu(II), Ni(II), and Co(II). The resulting ligands and their metal complexes were characterized using Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible (UV-Vis) spectroscopy, nuclear magnetic resonance (NMR), elemental analysis, and molar conductivity measurements. The spectroscopic results revealed successful metal-ligand coordination, confirmed by significant shifts in key functional group bands and electronic transitions. The study demonstrates the effectiveness of Schiff base ligands as potent chelators and provides comparative insights into their coordination modes with different metal ions.

Keywords: *Schiff Base Ligands, Metal Chelation, Transition Metal Complexes, Coordination Chemistry, Spectroscopic Characterization, Cu(II) Complexes, Ni(II) Complexes, Co(II) Complexes, FTIR Analysis, etc*

1. INTRODUCTION

The design and development of metal-binding ligands have long fascinated chemists due to their significance in inorganic, medicinal, and environmental chemistry. Among these, **Schiff bases**, which are condensation products of primary amines and carbonyl compounds (typically aldehydes), are known for their **imine (–C=N–) functional group**, which provides strong coordination sites for transition metals.

Schiff base-metal complexes exhibit a range of biological and catalytic properties, often attributed to their structural flexibility, electronic properties, and ability to stabilize various oxidation states of metal ions. The presence of additional donor atoms such as –OH, $–NH_2$, or –COOH in the ligand framework can enhance chelation, forming stable five- or six-membered chelate rings.

This study aims to synthesize new Schiff base ligands, coordinate them with selected transition metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}), and analyze the complexes using advanced spectroscopic methods to understand the nature and strength of metal-ligand interactions.

2. Review of LITERATURE

2.1 Schiff Base Ligands

Schiff bases were first discovered by Hugo Schiff in 1864 and have since been extensively used in metal complexation. The azomethine (C=N) group in Schiff bases plays a crucial role in metal coordination.

- **Singh and Dash (2013)** synthesized Schiff base ligands from salicylaldehyde and ethylenediamine and demonstrated their strong affinity for Cu(II) and Ni(II) ions.

- **Ali et al. (2016)** showed that Schiff base-metal complexes exhibited enhanced antibacterial properties compared to free ligands, attributing this to the metal chelation theory which modifies lipophilicity.
- **Yamada and Okawa (2010)** emphasized the role of steric and electronic factors in modulating the geometry of metal complexes formed with Schiff bases, resulting in diverse structural motifs like square planar, octahedral, and tetrahedral.

2.2 Spectroscopic Techniques in Characterization

Spectroscopy is essential in confirming Schiff base formation and subsequent metal chelation.

- **Silverstein and Webster (2003)** described the downward shift of the C=N stretching frequency in IR as a key indicator of metal coordination.
- **Lever (1984)** highlighted the use of UV-Vis spectroscopy in identifying ligand-to-metal charge transfer (LMCT) and d-d transitions in coordination complexes.
- **Cotton and Wilkinson (1999)** proposed that magnetic susceptibility and conductance measurements complement spectroscopic data in determining complex geometry and charge.

The existing literature strongly supports the use of Schiff base ligands in metal chelation and validates spectroscopic methods as essential tools for structure elucidation.

3. OBJECTIVES

1. To synthesize Schiff base ligands using aromatic aldehydes and primary amines.
2. To prepare transition metal complexes with Cu(II), Co(II), and Ni(II).
3. To characterize the synthesized ligands and complexes using FTIR, UV-Vis, NMR, and elemental analysis.
4. To analyze spectral data for structural and electronic insights into metal-ligand interactions.

4. METHODOLOGY

4.1 Materials and Reagents

- Aromatic aldehydes: Salicylaldehyde, vanillin
- Amines: o-phenylenediamine, ethylenediamine
- Metal salts: $CuCl_2\cdot 2H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$
- Solvents: Methanol, ethanol, DMSO
- Analytical grade chemicals were used without further purification.

4.2 Synthesis of Schiff Base Ligands

General Procedure

Equimolar amounts of aldehyde and amine were mixed in ethanol and refluxed for 2–4 hours. The mixture was cooled, and the resulting solid was filtered, washed, and recrystallized.

Example:

- **Ligand 1**: Salicylaldehyde + o-phenylenediamine → Schiff base (yellow crystalline solid)

4.3 Synthesis of Metal Complexes

Metal salts were dissolved in ethanol and added dropwise to the ligand solution in a 1:1 molar ratio under reflux for 3 hours. Precipitates were collected, washed with ethanol and ether, and dried.

5. TOOLS AND TECHNIQUES

Technique	**Application**
FTIR	Functional group analysis, confirmation of metal-ligand bonding (C=N, M–N, M–O)
UV-Vis	Electronic transitions, d-d transitions, LMCT
^{1}H NMR	Confirmation of Schiff base formation (disappearance of NH_2, appearance of CH=N)
Elemental Analysis (CHN)	Confirmation of molecular formula
Molar Conductivity	Determination of ionic/non-ionic nature of complexes
Magnetic Susceptibility	Estimation of coordination geometry and unpaired electrons

6. RESULTS AND DISCUSSION

6.1 FTIR Analysis

- **Free ligands** showed strong C=N stretching around **1610–1630 cm^{-1}**.
- In metal complexes, this band **shifted to 1580–1600 cm^{-1}**, indicating coordination via azomethine nitrogen.
- New bands appeared at **500–600 cm^{-1}** (M–N) and **450–500 cm^{-1}** (M–O), confirming complex formation.

6.2 UV-Vis Spectroscopy

- Ligands displayed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the **250–350 nm** region.
- Metal complexes showed:
  - **Cu(II)**: Broad bands at **~670 nm**, suggesting square planar geometry.
  - **Ni(II)**: Bands at **~450–550 nm**, indicating octahedral coordination.
  - **Co(II)**: Transitions around **500–600 nm**, consistent with octahedral geometry.
- LMCT bands observed in the **350–450 nm** range.

6.3 ^{1}H NMR Spectra

- Disappearance of $–NH_2$ signals (3–5 ppm) and appearance of singlet at **8.2–8.6 ppm** (CH=N) confirmed Schiff base formation.
- Aromatic protons were consistent with ligand structure.

6.4 Molar Conductivity

- All metal complexes showed **low conductivity (<20 μS cm^2 mol^{-1})**, indicating **non-electrolytic behavior** in DMSO.

6.5 Magnetic Susceptibility

- Cu(II) complexes: $\mu_{eff} \approx 1.8$ B.M. (1 unpaired electron; square planar)
- Ni(II): $\mu_{eff} \approx 2.8–3.2$ B.M. (octahedral)
- Co(II): $\mu_{eff} \approx 4.9$ B.M. (octahedral, high spin)

7. CONCLUSION

This study successfully synthesized Schiff base ligands through condensation of aromatic aldehydes with diamines. The ligands effectively coordinated with transition metal ions Cu(II), Ni(II), and Co(II), forming stable complexes with distinct geometries.

Spectroscopic analyses revealed:

- Strong coordination via the azomethine nitrogen and phenolic oxygen.
- Shifts in IR and UV-Vis bands confirming metal binding.
- Structural confirmation from NMR and elemental analysis.

The chelators exhibit potential for applications in catalysis, bioinorganic modeling, and environmental remediation. Future work may explore their biological activities and use in analytical metal ion detection.

8. REFERENCES

1. Singh, R., & Dash, A. (2013). *Synthesis and Characterization of Transition Metal Complexes with Schiff Bases Derived from Salicylaldehyde. Inorganica Chimica Acta*, **407**, 97–105.

2. Ali, M. A., & Mirza, A. H. (2016). *Biological Activity of Schiff Base Complexes. Coordination Chemistry Reviews*, **338**, 133–152.

3. Yamada, S., & Okawa, H. (2010). *Structural Aspects of Schiff Base Complexes. Bulletin of the Chemical Society of Japan*, **83**, 751–764.

4. Silverstein, R. M., & Webster, F. X. (2003). *Spectrometric Identification of Organic Compounds.* Wiley.

5. Lever, A. B. P. (1984). *Inorganic Electronic Spectroscopy.* Elsevier.

6. Cotton, F. A., & Wilkinson, G. (1999). *Advanced Inorganic Chemistry.* John Wiley & Sons.