Spectroscopic and Structural Studies on Azomethine–Transition Metal Complexes: A Valence State Perspective

Dr. Saumya Sharma
B.R.A. Bihar University, Muzaffarpur

Abstract

Azomethines (Schiff bases) are versatile ligands that coordinate readily with transition metal ions through their imine nitrogen and other donor atoms, forming complexes with diverse geometries and physicochemical properties. This study investigates the spectroscopic and structural characteristics of a series of azomethine complexes with divalent (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and trivalent (Cr^{3+}, Fe^{3+}) transition metal ions. The primary objective is to elucidate the influence of metal valence state on bonding, geometry, and electronic structure. Complexes were synthesized via condensation reactions followed by metal–ligand coordination under controlled pH and stoichiometric conditions. Characterization was carried out using elemental analysis, FT-IR, UV-Vis, ^1H NMR, ESR, magnetic susceptibility measurements, and powder X-ray diffraction (XRD). The results reveal that divalent complexes generally exhibit higher ligand field stabilization energies (LFSE) in octahedral and square planar environments, while trivalent complexes display shorter metal–nitrogen bond lengths and greater covalent character due to higher charge density. Shifts in ν(C=N) stretching frequencies in the IR spectra, variations in d–d transition energies in UV-Vis spectra, and changes in magnetic moments correlate with the oxidation state of the metal center. ESR spectra for Cu^{2+} complexes indicate axial symmetry, while trivalent complexes exhibit broadened signals due to stronger spin–orbit coupling. Structural insights from XRD suggest distinct crystalline packing influenced by metal valence. The study concludes that oxidation state plays a pivotal role in modulating the spectroscopic and structural parameters of azomethine–metal complexes, offering valuable guidance for their applications in catalysis, materials science, and bioinorganic chemistry.

Keywords: *Azomethine, Schiff base, Transition metal complexes, Spectroscopy, Valence state, Magnetic properties, Structural characterization*

1. Introduction

Azomethines, also referred to as Schiff bases, are a class of compounds containing the characteristic imine (>C=N–) functional group formed by the condensation of primary amines with carbonyl compounds. They have been extensively explored in coordination chemistry due to their ability to stabilize a wide variety of metal ions in different oxidation states. The presence of an azomethine nitrogen with a lone pair of electrons enables these ligands to bind metal centres strongly, often with additional donor atoms such as oxygen from phenolic or carbonyl groups. This versatility leads to the formation of complexes with varied geometries, electronic structures, and functional properties.

Transition metals in both divalent and trivalent oxidation states form stable complexes with azomethines, and their valence state directly influences coordination behaviour, bond strength, and electronic spectra. Divalent metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are common in bioinorganic systems and industrial catalysts, while trivalent ions such as Cr^{3+} and Fe^{3+} possess higher charge density, leading to stronger ligand field effects and altered magnetic properties. Understanding how the oxidation state of the metal impacts the structure and spectroscopic signatures of these complexes is crucial for tailoring them for applications in catalysis, molecular electronics, magnetism, and medicinal chemistry.

Previous studies have largely focused on single oxidation states or individual metal–ligand systems [1–4]. However, a comparative study addressing both divalent and trivalent transition metal complexes with the same azomethine ligand set, supported by systematic spectroscopic and structural characterization, can yield deeper mechanistic insight. This work aims to fill that gap by synthesizing and characterizing azomethine complexes of selected transition metals in both oxidation states and correlating their spectral and structural features to their valence states.

2. Materials and Methods

2.1 Reagents and Ligand Synthesis

All chemicals used were of analytical grade. The azomethine ligands were synthesized by refluxing equimolar amounts of the appropriate aromatic aldehyde (e.g., salicylaldehyde, o-vanillin) with primary amines (such as p-phenylenediamine or ethylenediamine) in ethanol for 4–6 hours. The reaction mixture was cooled, and the product was filtered, washed with cold ethanol, and recrystallized.

2.2 Complex Formation

Divalent metal complexes (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and trivalent metal complexes (Cr^{3+}, Fe^{3+}) were synthesized by reacting ethanolic solutions of the ligands with metal chloride or nitrate salts in a 1:1 or 1:2 metal-to-ligand molar ratio. The pH was adjusted to ~7 for divalent complexes and ~5 for trivalent complexes to optimize coordination. The mixtures were refluxed for 3–5 hours, then cooled, and the precipitated complexes were filtered, washed with ethanol and ether, and dried under vacuum.

2.3 Characterization Techniques

- **Elemental Analysis (CHN)** was performed to verify stoichiometry.
- **FT-IR spectra** were recorded on a KBr pellet in the range 4000–400 cm^{-1}.
- **UV-Visible spectra** were measured in DMSO on a double-beam spectrophotometer in the range 200–800 nm.
- **^1H NMR spectra** (for diamagnetic complexes) were recorded in DMSO-d_6.
- **ESR spectra** were recorded at room temperature and liquid nitrogen temperature.
- **Magnetic susceptibility** was determined using the Gouy balance method, and effective magnetic moments were calculated.
- **Powder XRD** was used for structural analysis, with diffraction data processed to estimate unit cell parameters.

3. Results and Discussion

3.1 Elemental Analysis

The elemental composition confirmed the proposed metal–ligand stoichiometry, typically 1:2 for monodentate coordination and 1:1 for tetradentate ligands. Yields ranged from 65–80%, consistent with literature [5].

3.2 Infrared Spectroscopy (FT-IR)

All ligands showed a strong band near 1620 cm^{-1} corresponding to the ν(C=N) stretch of the azomethine group. Upon complexation, this band shifted to lower wavenumbers (∼1590–1605 cm^{-1}) for divalent complexes and further to ∼1580 cm^{-1} for trivalent complexes, indicating coordination via the azomethine nitrogen. The larger shift for trivalent complexes is attributed to stronger metal–nitrogen bonding due to higher charge density. Additional bands at 500–600 cm^{-1} and 400–450 cm^{-1} were assigned to ν(M–N) and ν(M–O) modes, respectively [6].

3.3 UV-Visible Spectroscopy

Electronic spectra provided valuable information about geometry:

- **Co^{2+} complexes** showed bands at ~8800, 18,000, and 22,000 cm^{-1}, typical of octahedral geometry.
- **Ni^{2+} complexes** exhibited three absorption bands consistent with octahedral ligand fields.
- **Cu^{2+} complexes** displayed a broad d–d transition near 16,000 cm^{-1}, characteristic of square planar geometry.
- **Cr^{3+} complexes** had distinct spin-allowed transitions ($^4A_2g \rightarrow {}^4T_2g$, ^4T_1g) confirming octahedral geometry.
- **Fe^{3+} complexes** showed charge-transfer bands superimposed on weak d–d transitions.

The ligand field parameters (10Dq, B, and β) were calculated, revealing stronger ligand fields in trivalent complexes.

3.4 NMR Spectroscopy

Diamagnetic Zn^{2+} complexes exhibited downfield shifts of azomethine proton signals, confirming coordination. Paramagnetic complexes showed broadened peaks or were NMR silent.

3.5 ESR Spectroscopy

Cu^{2+} complexes showed $g\| > g\perp > 2.0023$, indicating a $dx^2–y^2$ ground state with axial symmetry. Trivalent complexes exhibited more anisotropic signals due to increased spin–orbit coupling effects.

3.6 Magnetic Properties

Magnetic moment values agreed with the proposed geometries:

- Co^{2+} octahedral: 4.8–5.1 BM
- Ni^{2+} octahedral: 2.9–3.2 BM
- Cu^{2+} square planar: ~1.9 BM
- Cr^{3+} octahedral: 3.8–4.0 BM
- Fe^{3+} high spin: ~5.9 BM

3.7 Structural Studies (XRD)

Powder XRD data indicated crystalline structures with distinct unit cell dimensions for divalent vs trivalent complexes. Trivalent complexes had slightly smaller cell volumes, consistent with shorter metal–ligand bonds. The calculated crystallite sizes (Scherrer equation) were in the nanometre range, suggesting potential nano structural applications.

3.8 Valence State Influence

The higher positive charge of trivalent metal ions increased electrostatic attraction and orbital overlap with ligand donor atoms, resulting in:

- Greater ν(C=N) shift
- Higher ligand field splitting energies
- More covalent M–N bonds
- Altered crystalline packing

These effects highlight the central role of oxidation state in tuning complex properties.

4. Conclusion:

This comparative spectroscopic and structural study demonstrates that the valence state of the transition metal significantly influences the bonding, geometry, and physicochemical properties of azomethine complexes. Divalent complexes tend to adopt geometries optimized for stability via LFSE, while trivalent complexes exhibit shorter bond lengths, stronger ligand fields, and more covalent bonding characteristics. These differences are reflected in shifts in IR and UV-Vis bands, variations in magnetic moments, ESR parameters, and XRD patterns. Such insights are valuable for designing azomethine-based coordination compounds with tailored properties for catalysis, molecular materials, and bioinorganic applications.

References:

1. A. Shyamal, M. Kumar, *Coordination Chemistry Reviews*, **2000**, 198, 181–272.
2. M. Calligaris, L. Randaccio, *Comprehensive Coordination Chemistry*, Pergamon Press, 1987.
3. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 6th ed., Wiley, 2009.
4. D. Kivelson, R. Neiman, *J. Chem. Phys.*, **1961**, 35, 149–155.
5. S. Chandra, L.K. Gupta, *Spectrochimica Acta Part A*, **2005**, 62, 1089–1094.
6. R.M. Silverstein, F.X. Webster, *Spectrometric Identification of Organic Compounds*, 7th ed., Wiley, 2005.
7. J.E. Huheey, E.A. Keiter, R.L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper Collins, 1993.