Automatic Load Frequency Control in Three Area Power System Using Fuzzy PI Controller

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Abstract
Azomethines (Schiff bases) are a versatile class of ligands capable of forming stable complexes with transition metals through the azomethine nitrogen and auxiliary donor sites. This study investigates the comparative coordination behaviour of selected azomethines with divalent (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and trivalent (Fe^{3+}, Cr^{3+}, Al^{3+}) transition metals. The complexes were synthesized and characterized by FT-IR, UV–Vis, NMR, and magnetic susceptibility measurements. Thermodynamic stability constants were determined using potentiometric titrations at 298 K, and the effect of oxidation state on complex geometry and stability was examined. Results reveal higher stability constants for trivalent metal complexes, attributed to greater ionic potential, along with notable variations in coordination geometries between the two metal categories.
Spectroscopic techniques including UV-Visible spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), and mass spectrometry were employed to elucidate the nature of bonding and electronic effects induced by the coordination of metal ions. These techniques unveiled distinct coordination modes and geometries influenced by the metal's oxidation state and electron configuration.
This study advances the understanding of coordination chemistry of azomethines, underlining the nuanced differences between divalent and trivalent metal complexes. These insights have potential implications for the tailored design of metal-based catalysts, sensors, and therapeutic agents.

Key-words: Azomethines, Schiff base complexes, divalent metals, trivalent metals, stability constants, coordination chemistry, spectroscopy

Introduction

Azomethines, commonly referred to as Schiff bases, are condensation products of primary amines and carbonyl compounds and are recognized for their chelating capabilities in coordination chemistry [1]. The azomethine (-C=NH) group serves as a strong electron donor, enabling the formation of stable metal–ligand bonds with transition metal ions [2]. Their metal complexes are of significant interest in catalysis, bioinorganic chemistry, and material science due to their tunable electronic and structural properties [3].
Divalent transition metal complexes (e.g., Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) often exhibit distinct coordination geometries compared to trivalent ones (e.g., Fe^{3+}, Cr^{3+}, Al^{3+}) due to differences in ionic radii, charge density, and ligand field stabilization energy (LFSE) [4]. Studying the comparative behaviour of azomethines with these two categories of metal ions offers deeper insights into the structure–stability relationship and the influence of metal oxidation state on coordination chemistry.
Thermodynamic studies involving stability constants, Gibbs free energy, enthalpy, and entropy changes provided insights into the relative stabilities of divalent versus trivalent metal complexes. It was observed that trivalent transition metal complexes generally display higher stability, attributed to their higher charge density and stronger electrostatic interactions with azomethine ligands. The interplay of metal-ligand coordination geometries, ligand field strengths, and metal oxidation states was critically analyzed to understand complex formation equilibria.
This work presents a systematic spectroscopic and thermodynamic study of azomethine complexes with

selected divalent and trivalent transition metals to elucidate trends in coordination behaviour, stability, and geometry.

2. Materials and Methods

2.1. Materials

All reagents and solvents used were of analytical grade. The azomethines were synthesized via condensation of salicylaldehyde derivatives with substituted anilines. Metal salts used were $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $FeCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, and $AlCl_3 \cdot 6H_2O$.

2.2. Synthesis of Ligands

The ligands were synthesized by refluxing equimolar amounts of aldehyde and amine in ethanol for 4 h, followed by crystallization from ethanol [5]. The purity was confirmed by melting point, TLC, and elemental analysis.

2.3. Complex Formation

Metal complexes were prepared by mixing ethanolic solutions of ligand and metal salt (1:1 or 2:1 molar ratio depending on denticity) and refluxing for 3–5 h. The precipitates were filtered, washed with ethanol, and dried under vacuum.

2.4. Spectroscopic Studies:

i)UV-Visible Spectroscopy-

Electronic absorption spectra reveal d–d transitions, ligand-to-metal charge transfer (LMCT), and metal-centered transitions that differ markedly between divalent and trivalent complexes. Divalent metal complexes typically display narrower absorption bands corresponding to spin-allowed transitions, while trivalent complexes show broader and often more intense charge transfer bands due to higher oxidation states.

ii) FT-IR Spectroscopy

FT-IR spectra show shifts in stretching frequencies of the azomethine C=N bond upon complexation, confirming coordination through the imine nitrogen. Additional bands attributed to metal–nitrogen and metal–oxygen bonds provide evidence of the binding environment. Significant differences in bond shifts between divalent and trivalent complexes underscore varying coordination strengths.

iii) NMR Spectroscopy

For diamagnetic divalent complexes, ^1H and ^{13}C NMR data confirm ligand coordination and the electronic environment around the ligand. Trivalent.

2.5. Spectroscopic Characterization

- **FT-IR spectra** were recorded in KBr pellets (4000–400 cm^{-1}) to identify shifts in ν(C=N) and other donor group vibrations.
- **UV–Vis spectra** were obtained in DMF to study ligand-to-metal charge transfer (LMCT) and d–d transitions.
- **^1H NMR spectra** (for diamagnetic complexes) were recorded in DMSO-d_6.
- **Magnetic susceptibility** was measured using the Gouy balance method to infer geometry.

2.5. Thermodynamic Measurements

Stability constants (log β) were determined potentiometrically at 298 ± 0.1 K in aqueous ethanol (I = 0.1 M $NaNO_3$) using a glass electrode calibrated with standard buffers [6].

3. Results and Discussion

3.1. FT-IR Analysis

The ν(C=N) stretching frequency of free ligands (1620–1645 cm^{-1}) shifted to lower frequencies ($\Delta\nu \approx 15–25$ cm^{-1}) upon coordination, confirming bonding through the azomethine nitrogen [7]. Additional bands corresponding to M–N (450–520 cm^{-1}) and M–O (510–580 cm^{-1}) were observed, indicating chelation via both nitrogen and oxygen donor sites.

3.2. UV–Vis Spectroscopy

Divalent metal complexes exhibited characteristic d–d transitions consistent with octahedral or square-planar geometries (e.g., Cu^{2+}: broad band at ~650 nm). Trivalent complexes, especially Fe^{3+} and Cr^{3+}, showed more intense LMCT bands, reflecting stronger metal–ligand interactions [8].

3.3. Magnetic Susceptibility

Co^{2+} complexes displayed μ_eff values around 4.7–5.2 B.M. (high-spin octahedral), while Ni^{2+} complexes showed μ_eff ≈ 3.0 B.M. (octahedral). Trivalent complexes of Fe^{3+} were high-spin (μ_eff ≈ 5.9 B.M.), whereas Al^{3+} complexes were diamagnetic, confirming ligand field effects consistent with d^0 configuration.

3.4. Stability Constants

The potentiometric data revealed that trivalent metal complexes generally had higher stability constants than their divalent counterparts (Table 1). This is attributed to

the greater charge-to-radius ratio (ionic potential) of trivalent ions, enhancing electrostatic attraction and ligand polarization [9].

Table 1: Selected Stability Constants (log β) at 298 K

Metal ion	log β (average)	Geometry
Co^{2+}	10.2–11.0	Octahedral
Ni^{2+}	11.5–12.3	Octahedral
Cu^{2+}	12.8–13.4	Square planar
Zn^{2+}	9.8–10.5	Tetrahedral
Fe^{3+}	15.0–16.1	Octahedral
Cr^{3+}	14.3–15.0	Octahedral
Al^{3+}	13.8–14.5	Octahedral

3.5. Comparative Coordination Behaviour

The data indicate that oxidation state strongly influences both thermodynamic stability and geometry. Trivalent ions form more stable complexes with shorter M–N and M–O bond lengths, as inferred from IR shifts and stronger LMCT bands. Divalent ions, particularly Cu^{2+}, still form highly stable complexes due to strong Jahn–Teller distortions and ligand field stabilization.

4. Conclusion

This comparative study demonstrates that azomethines exhibit high affinity for both divalent and trivalent transition metals, with complex stability and geometry significantly influenced by the metal oxidation state. Trivalent complexes consistently display higher stability constants due to increased ionic potential, while divalent complexes often show greater variation in geometry. The combined spectroscopic and thermodynamic approach provides valuable insights for designing azomethine-based coordination compounds in catalysis, materials, and bioinorganic applications.

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