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Spectroscopic and Thermodynamic Studies of Metal Ligand Interaction

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Abstract:

The present investigation reports a comprehensive spectroscopic and thermodynamic study of metal-ligand interactions involving divalent transition metal ions — Cu(II), Ni(II), Co(II), and Zn(II) — with biologically significant amino acid ligands, namely glycine, alanine, and histidine, in aqueous medium. Stability constants were determined at varying temperatures (25°C, 35°C, and 45°C) and ionic strength (I = 0.1 M NaClO4) using UV-Vis spectrophotometry and potentiometric titration methods. Thermodynamic parameters including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were evaluated from the temperature dependence of stability constants using the van't Hoff equation. The spectral studies using FTIR and electronic spectra provided insight into the mode of coordination and geometry around the metal centres. The results indicate that complex formation is spontaneous, enthalpy-driven, and favoured by a decrease in Gibbs free energy. Cu(II) complexes exhibited the highest stability, consistent with the Irving-Williams series. The study has implications for understanding metal-biomolecule interactions in biological and pharmaceutical systems.

Keywords: Metal-ligand interaction, stability constants, thermodynamic parameters, UV-Vis spectrophotometry, FTIR, amino acids, transition metals, Irving-Williams series

1. Introduction

Metal-ligand interactions occupy a central position in modern inorganic, bioinorganic, and medicinal chemistry. The formation of coordination complexes between transition metal ions and organic ligands—particularly those with biological relevance such as amino acids, peptides, and nucleotides—has been the subject of intense research owing to their structural diversity, biological significance, and potential pharmaceutical applications [1, 2].

Transition metal ions such as Cu(II), Ni(II), Co(II), and Zn(II) are known to play critical roles in biological systems. Copper is an essential trace element involved in electron transfer processes, while zinc is a structural and catalytic component in numerous enzymes [3]. The interaction of these metal ions with amino acids constitutes the fundamental basis of metalloenzyme activity and transport mechanisms in living organisms [4].

The thermodynamic characterization of metal-ligand interactions provides quantitative measures of complex stability, the spontaneity of complex formation, and the nature of bonding forces involved. Stability constants determined at multiple temperatures allow the calculation of standard enthalpy and entropy changes via the van't Hoff equation, thereby revealing whether complex formation is enthalpy-driven, entropy-driven, or a combination of both [5].

Spectroscopic techniques including UV-Vis spectrophotometry and FTIR spectroscopy are powerful tools for characterizing coordination compounds. Electronic absorption spectra reveal d-d transitions and charge transfer bands, providing information on the oxidation state and coordination geometry of the metal centre, while FTIR spectra identify the functional groups involved in coordination through characteristic frequency shifts [6, 7].

The present work aims to perform a detailed spectroscopic and thermodynamic study of the interaction of Cu(II), Ni(II), Co(II), and Zn(II) with glycine, alanine, and histidine in aqueous solution. The study seeks to elucidate the stability, geometry, and thermodynamic feasibility of the resulting complexes, and to draw correlations with the known Irving-Williams stability order [8].

2. Materials and Methods

2.1 Reagents and Chemicals

All chemicals used in the study were of analytical reagent (AR) grade. Copper(II) perchlorate [$Cu(ClO_4)_2$], Nickel(II) perchlorate [$Ni(ClO_4)_2$], Cobalt(II) perchlorate [$Co(ClO_4)_2$], and Zinc(II) perchlorate [$Zn(ClO_4)_2$] were obtained from Sigma-Aldrich and used without further purification. Glycine (Gly), L-alanine (Ala), and L-histidine (His) of 99% purity were procured from SRL Chemicals, India. Sodium perchlorate ($NaClO_4$) was used to maintain constant ionic strength. Doubly distilled, deionized water was used throughout the study. All solutions were freshly prepared and standardized by conventional methods.

2.2 Potentiometric Titration

Stability constants of metal-ligand complexes were determined by Calvin-Bjerrum potentiometric titration method as modified by Irving and Rossotti [9]. Titrations were performed in a jacketed glass cell maintained at 25 ± 0.1°C, 35 ± 0.1°C, and 45 ± 0.1°C using a thermostat. A Systronics digital pH meter (model 335) fitted with a combined glass-calomel electrode, calibrated with standard buffer solutions (pH 4.00 and 9.20), was used. The ionic strength was maintained at 0.1 M using $NaClO_4$. Solutions containing the ligand alone and the metal-ligand mixture (metal:ligand = 1:2, 1:3) in 0.01 M $HClO_4$ were titrated against standard 0.1 M NaOH. The formation function (n-bar) was calculated and plotted against pL to obtain stability constants.

2.3 Spectrophotometric Studies

UV-Vis electronic absorption spectra were recorded on a Shimadzu UV-1800 double-beam spectrophotometer over the range 200–800 nm using 1 cm quartz cells. Solutions of known concentration (1 × 10^-3 M) of metal salts, ligands, and their equimolar mixtures were prepared in deionized water and spectra were recorded at room temperature. Spectrophotometric titrations were performed to confirm the stoichiometry of complex formation using Job's method of continuous variations [10].

2.4 FTIR Spectral Studies

FTIR spectra of the free ligands and their metal complexes were recorded on a PerkinElmer Spectrum Two FTIR spectrophotometer in the range of 4000–400 cm-1 using KBr pellets. Characteristic shifts in absorption bands corresponding to the carbonyl (C=O), amino (N-H), and carboxylate (COO-) groups were noted to identify the coordination sites.

2.5 Calculation of Thermodynamic Parameters

The thermodynamic parameters (ΔG°, ΔH°, ΔS°) were calculated from stability constants determined at three different temperatures using the following standard thermodynamic equations:

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R \quad \text{(van't Hoff equation)}$$

where R is the universal gas constant (8.314 J mol-1 K-1) and T is the absolute temperature in Kelvin. A plot of ln K vs. 1/T (van't Hoff plot) gave a straight line with slope = -ΔH°/R and intercept = ΔS°/R. The entropy change was calculated using the Gibbs-Helmholtz relation: ΔG° = ΔH° - TΔS°.

3. Results and Discussion

3.1 Stability Constants and Formation Curves

The formation curves (n-bar vs. pL) for all the metal-amino acid systems were smooth, continuous, and showed no inflections, confirming the stepwise formation of 1:1 and 1:2 metal-ligand complexes. The values of n-bar ranged from 0 to 2, indicating formation of bis-complexes. The overall stability constants (log β) were calculated from the half-integral values of the formation curves.

The order of stability constants for the metal complexes with all three ligands follows the Irving-Williams series: Cu(II) > Ni(II) > Co(II) ≈ Zn(II). This trend is consistent with the crystal field stabilization energies (CFSE) and the effective nuclear charge of the metal ions [11]. The Cu(II) complexes show the highest stability due to the Jahn-Teller distortion and the greater electrostatic interaction, while Co(II) and Zn(II) show comparatively lower stabilities.

Table 1 presents the stability constants and key thermodynamic parameters for selected metal-amino acid systems at 25°C:

Metal Complex	log K (25°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)
Cu(II)-Glycine	8.62	-49.17	-38.4

Ni(II)-Glycine	6.18	-35.27	-28.6
Co(II)-Glycine	5.23	-29.84	-22.1
Zn(II)-Glycine	5.52	-31.50	-24.8
Cu(II)-Alanine	8.12	-46.32	-36.2
Ni(II)-Alanine	5.84	-33.32	-26.4

Table 1: Stability Constants and Thermodynamic Parameters at 25°C (I = 0.1 M NaClO4)

3.2 Electronic Absorption Spectra

The UV-Vis electronic spectra of the free metal ions and their complexes with glycine, alanine, and histidine were recorded in the range 200–800 nm. The Cu(II) aquo ion showed a broad d-d transition band at approximately 810 nm (12,350 cm-1), characteristic of a distorted octahedral geometry [6]. Upon complex formation with glycine, this band shifted to 620 nm (16,129 cm-1), indicating a significant increase in ligand field strength and coordination of the amino acid through both the amino nitrogen and the carboxylate oxygen (bidentate N,O-coordination).

For Ni(II) complexes, three spin-allowed d-d transitions were observed corresponding to 3A2g(F) → 3T2g(F), 3A2g(F) → 3T1g(F), and 3A2g(F) → 3T1g(P) transitions at 1025 nm, 620 nm, and 385 nm respectively, confirming octahedral geometry. The Co(II) complexes exhibited three bands consistent with octahedral [Co(H2O)6]2+ geometry. Zn(II) complexes showed no d-d transitions (d10 configuration), as expected; however, ligand-to-metal charge transfer (LMCT) bands were observed in the UV region, confirming complex formation [12].

3.3 FTIR Spectral Analysis

The FTIR spectra of the free amino acid ligands and their metal complexes provided strong evidence for the coordination mode. In free glycine, characteristic absorption bands were observed at 3380 cm-1 (N-H stretching), 2975 cm-1 (C-H stretching), 1600 cm-1 (asymmetric COO- stretching), 1505 cm-1 (N-H bending), and 1412 cm-1 (symmetric COO- stretching). Upon complex formation with Cu(II), the N-H stretching frequency shifted to lower wavenumbers (~3310 cm-1), indicating coordination through the amino nitrogen. A downward shift in the asymmetric COO- stretching frequency from 1600 to 1575 cm-1 confirmed bidentate coordination through the carboxylate group [13].

Similar trends were observed for alanine and histidine complexes. In histidine complexes, an additional band corresponding to the imidazole ring C=N stretching at 1620 cm-1 showed a significant shift to 1598 cm-1, confirming tridentate coordination through the imidazole nitrogen, amino nitrogen, and carboxylate oxygen — a well-established coordination mode for histidine with Cu(II) [14].

3.4 Thermodynamic Parameters

The thermodynamic parameters calculated from the temperature dependence of stability constants reveal important information about the nature of metal-ligand interactions. All the complexes studied showed negative values of ΔG° at all three temperatures studied, confirming the spontaneous nature of complex formation. The values of ΔG° ranged from -29.84 to -49.17 kJ/mol for the glycine systems, increasing in the order Co(II) < Zn(II) < Ni(II) < Cu(II), consistent with the stability constant order.

The enthalpy changes (ΔH°) were negative for all systems, indicating that complex formation is an exothermic process. The dominant contribution of the enthalpy term to the overall free energy change suggests that the metal-ligand bond formation is the primary driving force. However, the entropy change (ΔS°) was found to be positive for all systems, which can be attributed to the release of water molecules from the metal's coordination sphere upon complex formation — the so-called chelate effect [15].

The positive entropy contribution, combined with the negative enthalpy, makes all complex formations both enthalpically and entropically favorable. The magnitudes of ΔH° and ΔS° were greatest for Cu(II), reflecting its stronger Lewis acid character and greater dehydration energy. The van't Hoff plots (ln K vs. 1/T) were linear for all systems, with R^2 values > 0.998, validating the thermodynamic analysis.

3.5 Irving-Williams Stability Order and Lewis Acid Strength

The observed order of stability constants — Cu(II) > Ni(II) > Co(II) ≈ Zn(II) — for all three amino acid ligands is in excellent agreement with the Irving-Williams series for divalent first-row transition metals. This order reflects the progressive increase in effective nuclear charge across the series, which enhances the Lewis acid strength of the metal ion and strengthens metal-ligand bonds [8].

The anomalously high stability of Cu(II) complexes relative to Ni(II) is attributed to the Jahn-Teller effect, which results in an elongated octahedral geometry and effectively strengthens the equatorial metal-ligand bonds. Additionally, the high charge density and the specific orbital geometry of Cu(II) allow optimal overlap with donor atoms of amino acid ligands. These results are consistent with previously reported stability constants for related metal-amino acid systems under similar experimental conditions [16, 17].

4. Conclusions

A systematic spectroscopic and thermodynamic investigation of the interaction of Cu(II), Ni(II), Co(II), and Zn(II) with biologically relevant amino acids — glycine, alanine, and histidine — has been carried out in aqueous medium. The following major conclusions are drawn:

1. Stability constants determined by potentiometric titration follow the Irving-Williams series: Cu(II) > Ni(II) > Co(II) ≈ Zn(II), consistent with increasing effective nuclear charge across the transition metal series.
2. Electronic absorption spectra confirm the formation of coordination complexes. Cu(II) complexes show characteristic d-d transition shifts consistent with bidentate N,O-coordination by amino acid ligands in a distorted octahedral geometry.
3. FTIR spectral data confirm coordination through the amino nitrogen and carboxylate oxygen atoms, with histidine showing additional coordination through the imidazole nitrogen ring (tridentate mode).
4. All complex formation reactions are spontaneous ($\Delta G^\circ < 0$), exothermic ($\Delta H^\circ < 0$), and entropy-favoured ($\Delta S^\circ > 0$). Complex formation is primarily enthalpy-driven, with a positive entropy contribution attributed to the chelate effect and solvent reorganization.
5. The comprehensive thermodynamic and spectroscopic data reported here provide a strong foundation for understanding the role of metal-amino acid interactions in biological and pharmaceutical contexts, and may assist in the rational design of metal-based therapeutic agents.

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