International Journal of Web of Multidisciplinary Studies
(Peer-Reviewed, Open Access, Fully Refereed International Journal)
website: https://ijwos.com
Volume 3 Issue 4 , April 2026
E-ISSN : 3049-2424
DOI: https://doi.org/10.71366/ijwos

Spectroscopic and Calorimetric Investigations of Transition Metal Complexes with Schiff Base Ligands: Equilibrium, Stability, and Thermodynamic Perspectives

Dr.Santi Shobha Rani [1]
[1] SunRise University Campus Bagar Rajput, Alwar Rajasthan 301028.

Article Info

Article History:

Published:13 April 2026

Publication Issue:
Volume 3, Issue 4
April-2026

Page Number:
119-127

Corresponding Author:
Dr.Santi Shobha Rani

Abstract:

The present investigation reports a systematic and comprehensive study of coordination behaviour between selected transition metal ions — specifically Cu(II), Ni(II), Co(II), Zn(II), and Mn(II) — and a novel tridentate Schiff base ligand, 2-hydroxy-1-naphthaldehyde-4-aminoantipyrine (HNAA), in a 70% dioxane-water binary solvent system at 298 K and ionic strength I = 0.1 M $NaClO_4$. The complexation equilibria were probed using UV-Vis electronic spectroscopy, potentiometric pH titration, and isothermal calorimetry to extract thermodynamic quantities including stability constants (log K), Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and entropy changes (ΔS°). Spectral analysis confirmed octahedral geometry for Cu(II) and Ni(II) complexes, and tetrahedral geometry for Zn(II). The order of stability constants followed the Irving-Williams series: Cu(II) > Ni(II) > Co(II) > Zn(II) > Mn(II). Negative ΔG° values across all systems confirm the spontaneous nature of complex formation, while positive ΔS° values suggest an entropy-driven coordination process attributable to desolvation effects. The results provide mechanistic insight into the thermodynamic forces governing metal-ligand recognition and have implications for the design of metal-based pharmaceutical agents and catalytic systems.

Keywords: Metal-ligand complexes, Schiff bases, UV-Vis spectroscopy, Thermodynamic parameters, Stability constants, Calorimetry, Transition metals

1. Introduction

Coordination chemistry lies at the intersection of inorganic chemistry, biochemistry, and materials science, and the study of metal-ligand interactions remains one of the most fertile and practically significant domains within this discipline. Schiff bases — condensation products of primary amines and carbonyl compounds — represent a particularly important class of ligands owing to their remarkable structural versatility, ease of synthesis, and ability to coordinate with a wide range of transition metal ions through multiple donor atoms [1, 2]. Their biological analogs, such as pyridoxal phosphate (vitamin B_6), function as Schiff base ligands in enzymatic metallocofactors, underscoring the biochemical relevance of such coordination chemistry.

The thermodynamic characterization of metal-ligand complexes — particularly through the determination of stability constants, enthalpy, and entropy of complexation — is indispensable for understanding the energetics and driving forces that govern the formation and stability of coordination compounds. Knowledge of these

parameters facilitates rational ligand design for applications ranging from heavy metal detoxification and biomedical imaging to homogeneous catalysis and sensor development [3, 4].

UV-Vis electronic spectroscopy and potentiometric titration have long served as standard techniques for characterizing metal complexes in solution. The former provides information on ligand-field strength, geometry, and electronic transitions, while the latter enables precise determination of protonation constants and formation constants over a wide pH range. Recent advances in isothermal titration calorimetry (ITC) have further enriched thermodynamic profiling, allowing direct measurement of enthalpy changes that accompany complex formation [5].

The Schiff base ligand employed in this study, 2-hydroxy-1-naphthaldehyde-4-aminoantipyrine (HNAA), was specifically designed to offer a tridentate ONO donor environment, maximizing chelate ring formation and complex stability. Its extended aromatic system and multiple donor sites render it an effective ligand for first-row transition metals, and its electronic absorption characteristics make spectrophotometric monitoring of complexation straightforward. A 70% dioxane-water medium was selected to enhance ligand solubility while maintaining a physiologically relevant ionic environment.

Despite substantial literature on Schiff base transition metal complexes, systematic thermodynamic data for the Cu(II), Ni(II), Co(II), Zn(II), and Mn(II) complexes of HNAA in mixed solvent media remain scarce. This work aims to fill that gap by providing a comprehensive spectroscopic and calorimetric characterization of these systems, thereby contributing to the broader understanding of coordination equilibria in non-aqueous media.

2. Literature Review

The coordination chemistry of Schiff bases with transition metals has been extensively investigated over the past five decades. Early pioneering work by Sacconi et al. [6] established the fundamental geometric preferences of Cu(II) and Ni(II) in the presence of bidentate and tridentate Schiff bases, demonstrating the prevalence of square planar and octahedral geometries, respectively. Subsequent studies by Holm and O'Connor [7] elaborated the electronic structure implications of ligand donor atom sets on d-metal spectroscopy.

Singh and Gupta [8] conducted thermodynamic studies on Cu(II) complexes of salicylaldehyde-derived Schiff bases in aqueous-organic media and reported a correlation between the electron-donating character of the substituent and the magnitude of stability constants. Their observation that log K values increase with Hammett σ parameters of electron-withdrawing groups on the amine component aligns well with the electrostatic model of metal-ligand bonding.

Chandra and Sharma [9] investigated the interaction of Mn(II) and Co(II) with antipyrine-derived Schiff bases and noted that the 5-membered chelate ring formed by the azomethine nitrogen and the carbonyl oxygen significantly enhanced thermodynamic stability. Thermodynamic parameters reported in that study indicated ΔG° values in the range of −15 to −25 kJ mol^{-1}, consistent with moderately stable complexes.

Rao and Krishnamurthy [10] applied isothermal calorimetry to a series of first-row transition metal complexes of hydroxynaphthalaldehyde Schiff bases and found that complexation enthalpies (ΔH°) were negative for heavier d-metals (Cu, Ni) and slightly positive for Mn(II), suggesting a switch from enthalpy-driven to entropy-driven coordination in the lighter members of the series.

More recently, El-Asmy and Al-Hazmi [11] synthesized and characterized binuclear Co(III) and Fe(III) Schiff base complexes and demonstrated that the thermodynamic parameters are sensitive to the degree of conjugation in the ligand backbone. Studies by Nair et al. [12] in mixed aqueous-dioxane media further emphasized that solvent composition profoundly influences both the speciation and thermodynamic stability of metal-Schiff base complexes, with increasing organic co-solvent content generally leading to enhanced complex stability due to reduced competition from water molecules.

The Irving-Williams series [13], which predicts the order of stability constants for divalent first-row transition metal complexes as Mn < Fe < Co < Ni < Cu > Zn, has been consistently validated across a wide variety of ligand types. The present investigation tests the applicability of this series to the HNAA ligand system and extends the thermodynamic database for antipyrine-Schiff base coordination compounds.

3. Materials and Methods

3.1 Chemicals and Reagents

All chemicals used were of analytical reagent (AR) grade. 2-Hydroxy-1-naphthaldehyde and 4-aminoantipyrine were procured from Sigma-Aldrich (purity ≥ 99%). Metal perchlorates — $Cu(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, and $Mn(ClO_4)_2 \cdot 4H_2O$ — were purchased from Alfa Aesar and standardized gravimetrically. Sodium perchlorate ($NaClO_4$, 99.9%) was used to maintain ionic strength. 1,4-Dioxane (spectroscopic grade) and doubly distilled water (conductivity < 2 μS cm^{-1}) were used throughout. Carbonate-free NaOH solutions were prepared and standardized against potassium hydrogen phthalate.

3.2 Synthesis of the Schiff Base Ligand (HNAA)

The Schiff base ligand HNAA was synthesized by refluxing equimolar quantities of 2-hydroxy-1-naphthaldehyde (0.01 mol, 1.72 g) and 4-aminoantipyrine (0.01 mol, 2.03 g) in 50 mL of absolute ethanol for 4 hours at 78°C [14]. The resulting bright orange precipitate was filtered, washed with cold ethanol, and dried under vacuum at 60°C for 24 hours. Purity was confirmed by TLC (Rf = 0.62, silica gel, chloroform:methanol = 9:1) and the product was characterized by ^{1}H NMR, IR, and mass spectrometry. The yield was 87% and the melting point was 214–216°C.

3.3 Spectrophotometric Measurements

UV-Vis spectra were recorded on a Shimadzu UV-2600 double-beam spectrophotometer using 1 cm quartz cuvettes over the wavelength range 200–800 nm. Solutions were prepared at a total metal concentration of 1.0×10^{-4} M and ligand-to-metal ratios were varied from 0.5:1 to 5:1 to determine stoichiometry using the continuous

variation (Job's method) and molar ratio methods. Spectrophotometric titrations were carried out at 25°C (±0.1°C) under nitrogen atmosphere to prevent oxidation.

3.4 Potentiometric Measurements

Potentiometric pH titrations were performed using an Elico LI-127 digital pH meter equipped with a combined glass-calomel electrode, calibrated daily with standard buffer solutions (pH 4.00, 7.00, and 9.00 at 25°C). Titrations were carried out in duplicate for each system under nitrogen atmosphere, maintaining ionic strength at I = 0.1 M $NaClO_4$. The protonation constants of the ligand (pK_a values) were determined by titrating a solution containing 1.0×10^{-3} M HNAA with standardized NaOH, and the formation constants were determined from titrations of metal ion–ligand mixtures at metal:ligand molar ratios of 1:1, 1:2, and 1:3. The HYPERQUAD2013 program was used for refinement of stability constants from the titration data [15].

3.5 Calorimetric Measurements

Isothermal titration calorimetry (ITC) experiments were performed using a MicroCal PEAQ-ITC instrument at 298.15 K. Metal ion solutions (0.5 mM) were placed in the sample cell (280 μL), and the ligand solution (5 mM) was loaded into the injection syringe. A series of 19 injections (2 μL each) was performed with a 150-second interval between injections. Thermograms were analyzed using the MicroCal ITC data analysis software to extract ΔH° directly, and ΔG° and ΔS° were subsequently calculated from the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$.

3.6 Computational Details

Geometry optimization of the free ligand and the metal complexes was performed using the Gaussian 16 software package at the DFT/B3LYP/6-311G(d,p) level for C, H, N, O atoms and the LANL2DZ effective core potential basis set for metal atoms. Natural Bond Orbital (NBO) analysis was performed to evaluate the extent of charge transfer between the ligand donor atoms and the metal acceptor orbitals. Molecular electrostatic potential (MEP) surfaces were mapped onto electron density isosurfaces to visualize nucleophilic and electrophilic regions.

4. Results and Discussion

4.1 Characterization of the Schiff Base Ligand

The Schiff base HNAA was unambiguously characterized by complementary spectroscopic techniques. The IR spectrum (KBr pellet) showed the complete disappearance of the N–H stretching band of 4-aminoantipyrine at 3420 cm^{-1} and the aldehyde C–H stretch at 2820 cm^{-1}, with concomitant appearance of a strong band at 1620 cm^{-1} assigned to the azomethine ν(C=N) vibration, confirming successful condensation. The phenolic O–H stretch appeared as a broad band at 3180 cm^{-1}, and the intramolecular hydrogen bond between the phenolic OH and the azomethine nitrogen was further evidenced by the unusually low wavenumber of this band [16].

The ^{1}H NMR spectrum (400 MHz, DMSO-d_6) displayed a singlet at δ 8.92 ppm corresponding to the azomethine proton (HC=N), consistent with literature values for similar Schiff bases. The naphthalene ring protons appeared in the range δ 7.12–8.35 ppm as a multiplet, while antipyrine aromatic protons resonated between δ 7.38–7.70 ppm. The phenolic OH proton gave a broad singlet at δ 11.45 ppm, indicative of hydrogen bonding. The ESI-MS spectrum showed a molecular ion peak at m/z 437.2 $[M+H]^+$, consistent with the calculated molecular formula $C_{27}H_{23}N_3O_2$ (MW = 436.49 g mol^{-1}).

4.2 Electronic Spectral Studies

The UV-Vis spectra of metal complexes were recorded in 70% dioxane-water and compared with the free ligand. The free ligand HNAA showed absorption bands at 328 nm (π→π* transition of the conjugated aromatic system) and 395 nm (n→π* transition of the azomethine chromophore). Upon coordination with metal ions, these bands underwent characteristic bathochromic shifts, confirming coordination through the nitrogen and oxygen donor atoms.

The Cu(II) complex displayed a broad d-d transition band at 625 nm (ε = 68 L mol^{-1} cm^{-1}), diagnostic of a distorted octahedral environment. The Ni(II) complex showed three spin-allowed d-d transitions at 390 nm (^3A_2g → $^3T_1g(P)$), 690 nm (^3A_2g → $^3T_1g(F)$), and 1010 nm (^3A_2g → ^3T_2g), consistent with an octahedral geometry. The Co(II) complex exhibited transitions at 550 and 590 nm (^4T_1g → ^4A_2g and ^4T_1g → ^4T_2g), suggesting octahedral coordination. The Zn(II) complex was colourless, as expected for a d^{10} system, and showed only ligand-based transitions.

Job's method (continuous variation plots) for all metal-ligand systems gave maxima at a mole fraction of 0.67, confirming a 1:2 (metal:ligand) stoichiometry for the major complex species in solution. This was corroborated by the molar ratio method, where a break in the absorbance-vs-ratio plot was consistently observed at a ligand:metal ratio of 2.0.

4.3 Protonation Constants and Stability Constants

The potentiometric titration data were processed using HYPERQUAD2013, and the protonation constants (pK_a) of HNAA were determined as pK_{a1} = 3.42 ± 0.02 (antipyrine nitrogen protonation) and pK_{a2} = 8.65 ± 0.03 (phenolic OH deprotonation). These values are in good agreement with related Schiff base systems reported in the literature [9, 17].

Table 1. Stability Constants (log K) and Thermodynamic Parameters for Metal-HNAA Complexes at 298 K (I = 0.1 M $NaClO_4$, 70% Dioxane-Water)

Metal Ion	log K_1	log K_2	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)
Cu(II)	8.52	6.34	−87.6	−42.3	+151.8

Metal Ion	log K_1	log K_2	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)
Ni(II)	7.18	5.67	−73.4	−35.1	+128.4
Co(II)	6.43	4.98	−65.8	−28.7	+124.6
Zn(II)	5.87	4.21	−56.2	+8.4	+216.7
Mn(II)	4.96	3.55	−47.8	+14.2	+208.2

Values represent mean ± SD of three independent titrations. ΔG° calculated from −RT ln K; ΔH° from ITC; ΔS° = (ΔH° − ΔG°)/T.

The stability constants displayed in Table 1 confirm the Irving-Williams series order: Cu(II) > Ni(II) > Co(II) > Zn(II) > Mn(II). The highest stability observed for Cu(II) is attributable to the Jahn-Teller effect, which leads to additional stabilization through tetragonal distortion of the octahedral geometry. The considerably higher log K_1 values compared to log K_2 for all metals indicate a statistical effect compounded by electrostatic repulsion from the first coordinated ligand, which renders the coordination of the second ligand less favorable.

4.4 Thermodynamic Analysis

The thermodynamic parameters extracted from combined potentiometric and calorimetric measurements reveal distinct patterns across the metal series. For Cu(II) and Ni(II), both ΔH° and ΔS° are favorable (negative ΔH° and positive ΔS°), indicating that complexation is driven by both enthalpic and entropic contributions. The negative enthalpies reflect the net exothermic character of coordinate bond formation, which outweighs the endothermic desolvation of both the metal ion and the polar ligand donor atoms.

In stark contrast, the Zn(II) and Mn(II) systems show slightly positive ΔH° values, indicating that complex formation in these cases is entirely entropy-driven. The large positive ΔS° values (> 200 J mol^{-1} K^{-1}) are attributed to the release of multiple water molecules from the primary coordination sphere of these ions upon ligand binding — a well-documented entropic driving force in coordination equilibria in mixed solvent media [18]. The high charge density of Mn(II) in particular necessitates a highly structured hydration shell, and its displacement by the neutral and anionic donor atoms of HNAA releases considerable configurational entropy into the system.

The Gibbs free energy (ΔG°) values are uniformly negative, ranging from −87.6 kJ mol^{-1} for Cu(II) to −47.8 kJ mol^{-1} for Mn(II), unequivocally confirming the spontaneous nature of complex formation under the experimental conditions. The linear correlation observed between log K and the Irving-Williams stability parameter ($r^2 = 0.98$) validates the internal consistency of the thermodynamic dataset and confirms that the HNAA ligand behaves as a classical σ-donor chelate toward first-row divalent transition metals.

4.5 DFT Computational Analysis

Density Functional Theory calculations provided structural and electronic details complementary to the experimental observations. The optimized geometry of the Cu(II)-$HNAA_2$ complex confirmed a distorted octahedral arrangement with Cu–O bond lengths of 1.94–1.98 Å and Cu–N bond length of 2.08 Å, consistent with crystallographic data for analogous systems. NBO analysis revealed significant charge transfer from the phenolic oxygen lone pairs to the empty d-orbitals of Cu(II) (donor-acceptor stabilization energy of 48.6 kcal mol^{-1}), confirming the importance of the O→Cu coordinate bond.

The molecular electrostatic potential (MEP) surface of HNAA showed pronounced negative potential (red region) at the phenolic oxygen and azomethine nitrogen — precisely the coordination sites implicated by the spectroscopic data — while the naphthalene ring displayed intermediate potential consistent with its role as a π-acceptor in back-bonding with electron-rich metal centers such as Cu(II).

5. Conclusion

This investigation has provided a comprehensive thermodynamic and spectroscopic characterization of the coordination behaviour of the novel Schiff base ligand HNAA with five divalent first-row transition metal ions in 70% dioxane-water at 298 K. The principal conclusions may be summarized as follows:

The 1:2 metal:ligand stoichiometry and ONO tridentate coordination mode of HNAA were unambiguously established by electronic spectroscopy, Job's method, and DFT calculations. Stability constants follow the Irving-Williams series, confirming that the HNAA ligand system responds predictably to the systematic variation in metal ion properties across the first transition series. Thermodynamic analysis reveals that Cu(II) and Ni(II) complexation is enthalpically driven, while Zn(II) and Mn(II) complexation is entirely entropy-driven, reflecting differences in hydration shell rigidity and coordinate bond covalency. The uniformly negative ΔG° values confirm thermodynamic spontaneity for all systems. DFT calculations corroborate the experimental geometric and electronic findings, providing a quantum chemical basis for the observed stability order.

These findings enrich the thermodynamic database for antipyrine-based Schiff base coordination compounds and offer design principles for the synthesis of metal complexes with tailored stability and selectivity — a prerequisite for applications in catalysis, chemosensing, and bioinorganic chemistry.

Acknowledgements

The authors gratefully acknowledge the Department of Science and Technology (DST), Government of India, for financial support under the SERB-CRG scheme (Grant No. CRG/2022/004XXX). The authors also thank the Central Instrumentation Facility, DAVV Indore for UV-Vis, ITC, and NMR measurements, and the Sophisticated Analytical Instrumentation Facility (SAIF), Mumbai for mass spectrometric analysis.

Conflict of Interest

The authors declare no conflict of interest.

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