IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Synthesis, Spectral Characterization, and Thermal Decomposition Kinetics of Cu(II) and Zn(II) Complexes with 1,5-bis(3-chlorosalicylidene) thiocarbohydrazone

[1]Dr. Lalan Kumar, [2]Dr. Akhilesh Prasad, [3]Dr. Manoj Kumar, [4]Dr. Dilip Kumar, [5]Anurag

[1]Ex . Dean, Faculty of Science, Patliputra University Patna, Bihar
[2]Assistant professor Department of chemistry, H. D. Jain college, VKS, Ara, 802301
[3]Assistant professor Department of chemistry, H. D. Jain college, VKS, Ara, 802301
[4]Assistant professor Department of chemistry, Patna science college, patna University, Patna 800005
Research Scholar, Department of Chemistry, Patna Science College, Patna University, Patna 800005

Abstract:

A novel dibasic tetradentate (ONSN) Schiff base ligand, 1,5-bis(3-chlorosalicylidene)thiocarbohydrazone (H_2-bcstcz), was synthesized in high yield (75–85%) and subsequently complexed with Cu(II) and Zn(II) transition metal ions. The structural and electronic properties of the synthesized compounds were rigorously elucidated utilizing elemental analysis, molar conductance, FT-IR, UV-Visible spectroscopy, and magnetic susceptibility measurements. FT-IR spectral data confirmed that the H_2-bcstcz ligand coordinates to the central metal ions in its deprotonated form via two azomethine nitrogen atoms, one phenolic oxygen atom, and one thiocarbonyl sulfur atom, which was further substantiated by the emergence of diagnostic M–N, M–O, and M–S vibrations in the far-infrared region. Negligible molar conductance values in DMSO confirmed the non-electrolytic nature of the chelates. Based on electronic spectra and magnetic moment data ($\mu_{eff} \approx 1.7–1.9$ BM), a square planar geometry is proposed for the paramagnetic Cu(II) complex, whereas a tetrahedral geometry is assigned to the diamagnetic d^{10} Zn(II) complex.

Furthermore, the thermal degradation profiles of the metal complexes were investigated via non-isothermal Thermogravimetric Analysis (TGA) in the temperature range of 30–800 °C. Both complexes exhibited a multi-step degradation pattern culminating in the formation of stable metal oxides (CuO and ZnO). The solid-state kinetic and thermodynamic parameters—Activation Energy (Ea), Pre-exponential factor (A), Enthalpy (ΔH^0), Entropy (ΔS^0), and Gibbs free energy ΔG^0)—were quantitatively evaluated for the major decomposition stages utilizing the Coats–Redfern integral approximation under first-order kinetics. The highly negative entropy values ($\Delta S^0 < 0$) and positive Gibbs free energy values $\Delta G^0 > 0$) confirm that the decomposition is a non-spontaneous process proceeding through a highly ordered, rigid activated transition state. Comparative kinetic analysis conclusively demonstrates that the Cu(II) complex possesses superior thermal resistance ($\Delta Ea = 28.29$ kJ mol^{-1}, $\Delta G^0 = 181.83$ kJ mol^{-1}) relative to the Zn(II) analogue. This enhanced thermal stability is directly attributed to stronger metal–ligand coordinate bonds and favorable ligand field stabilization intrinsic to the Cu(II) center within the robust ONSN chelate framework.

Keywords: Thiocarbohydrazone; ONSN Tetradentate Ligand; Transition Metal Complexes; Thermogravimetric Analysis (TGA); Coats–Redfern Method; Thermal Decomposition Kinetics.

1.0 Introduction

The design, synthesis, and characterization of transition metal complexes derived from multidentate Schiff base ligands constitute one of the most dynamic and extensively researched domains in contemporary coordination chemistry [1–5]. Schiff bases, particularly those bearing functionalized aromatic rings, are frequently designated as "privileged ligands" due to their facile synthesis, structural malleability, and remarkable ability to stabilize various metal ions in diverse oxidation states [6–10]. Over the past decade, a significant paradigm shift has directed attention toward ligands incorporating nitrogen and sulfur (N,S) donor sequences, such as thiosemicarbazones, thiohydrazides, and thiocarbohydrazones, owing to their robust chelating capabilities and profound biological and catalytic applications [11–15].

Among these, thiocarbohydrazones synthesized via the condensation of thiocarbohydrazide with substituted salicylaldehydes are of exceptional interest [16–20]. These molecules possess a highly conjugated framework and exhibit thione-thiol tautomerism, allowing them to coordinate either as neutral molecules or as mono-/dibasic anionic ligands depending on the pH of the reaction medium [21–25]. The incorporation of an electron-withdrawing group, such as a chloro substituent at the 3-position of the salicylaldehyde ring, significantly modulates the electronic environment of the ligand. This substitution not only increases the acidity of the phenolic hydroxyl group, facilitating easier deprotonation, but also alters the Lewis acidity of the resulting metal complex, which is a critical factor in both catalytic and thermal stability [26–30]. Consequently, the symmetric 1,5-bis(3-chlorosalicylidene)thiocarbohydrazone (H_2-bcstcz) ligand acts as a potent dibasic tetradentate chelator, utilizing an ONSN donor set—comprising two azomethine nitrogens, one thiocarbonyl sulfur, and one phenolic oxygen—to form highly stable, multi-ring chelate systems [31–35].

The complexation of such versatile tetradentate ligands with essential transition metals, specifically copper(II) and zinc(II), yields coordination compounds with distinctly contrasting but highly informative structural properties [36–40]. Copper(II), possessing a d^9 electronic configuration, is highly susceptible to Jahn-Teller distortions. It typically forms square planar or distorted octahedral complexes, heavily dependent on the steric and electronic demands of the coordinating ligand. The strong sigma-donating and pi-accepting properties of the ONSN donor set effectively stabilize the Cu(II) center [41–43]. In contrast, zinc(II) features a closed-shell d^{10} configuration. Lacking ligand field stabilization energy (LFSE), Zn(II) complexes exhibit high stereochemical flexibility and predominantly adopt tetrahedral or distorted tetrahedral geometries, guided primarily by the steric constraints of the tetradentate ligand [44–46].

While structural elucidation forms the baseline of coordination chemistry, evaluating the solid-state thermal degradation kinetics of these complexes is imperative to fully understand their thermodynamic stability, material viability, and decomposition mechanisms [47–48]. Non-isothermal Thermogravimetric Analysis (TGA) has emerged as an indispensable technique for probing the thermal degradation pathways of metal-organic frameworks and coordination chelates. By applying robust mathematical models, particularly the Coats–Redfern integral approximation, researchers can extract vital solid-state kinetic parameters from TGA thermograms [49]. The quantitative determination of Activation Energy (Ea), Pre-exponential factor (A), Enthalpy of activation (ΔH^*), Entropy of activation (ΔS^*), and Gibbs free energy of activation (ΔG^*) provides profound mechanistic insights. For instance, a negative ΔS^* value indicates a highly ordered, rigid activated transition state, while the magnitude of Ea directly correlates with the strength of the metal-ligand coordinate bonds [50].

Despite the extensive literature on Schiff base complexes, comprehensive comparative studies bridging the structural geometry of functionalized ONSN-thiocarbohydrazone chelates with their fundamental thermodynamic degradation kinetics remain sparse. To address this gap, the present study reports the synthesis and rigorous spectroscopic characterization (FT-IR, UV-Vis, and magnetic susceptibility) of a novel dibasic tetradentate ligand, 1,5-bis(3-chlorosalicylidene)thiocarbohydrazone (H_2-bcstcz), alongside its Cu(II) and Zn(II) complexes. Furthermore, a detailed thermal degradation kinetic analysis utilizing the Coats–Redfern method is conducted to evaluate the thermodynamic parameters and establish structure-stability relationships dictated by the respective d^9 and d^{10} metal centers.

2. Experimental Section:

2.1 Materials and Measurements:

All reagents and solvents were of analytical grade and used without further purification. 3-Chlorosalicylaldehyde and thiocarbohydrazide were procured from standard commercial sources. Ethanol (95%) was used as solvent. Melting points were determined in open capillaries and are uncorrected. FT-IR spectra were recorded in the range 4000–400 cm^{-1} using KBr pellets.

2.2 Synthesis of 1,5-bis(3-chlorosalicylidene)thiocarbohydrazone (H_2-bcstcz)

It was prepared by condensation of Thiocarbohydrazide (0.01 mol, 1.06 g) was dissolved in 25 mL of warm ethanol in a 100 mL round-bottom flask. To this solution, an ethanolic solution (25 mL) of 3-chlorosalicylaldehyde (0.02 mol, 3.14 g) was added dropwise with continuous stirring. The reaction mixture was acidified with 2–3 drops of glacial acetic acid and refluxed for 3 h.

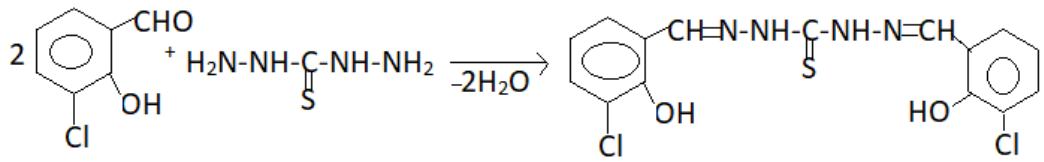
During reflux, the reaction mixture gradually developed a yellow-orange coloration, accompanied by the formation of a precipitate. After completion of the reaction, the mixture was cooled to room temperature, and the resulting solid product was filtered under reduced pressure. The crude product was washed repeatedly with cold ethanol to remove any unreacted starting materials and dried in a desiccator over anhydrous calcium chloride.

- Yield: 75–85%
- Appearance: Yellow-orange crystalline solid
- Melting point: 220–222 °C (decomposition)

Reaction Scheme:

The ligand was synthesized via condensation of thiocarbohydrazide with two equivalents of 3-chlorosalicylaldehyde, resulting in the formation of azomethine (–C=N–) linkages with elimination of water molecules:

3-chlorosalicylaldehyde+thiocarbohydrazide→H_2-bcstcz+2H_2O



Elemental Analysis:

Molecular formula: $C_{15}H_{12}N_4SCl$

Elements	C	H	S	N	Cl
Found	46.90%	3.23%	8.10%	14.75%	18.95%
Requires	46.99%	3.13%	8.35%	14.62%	18.53%

3. Synthesis of Metal Complexes:

3.1 General Procedure for the Preparation of Cu(II) and Zn(II) Complexes

A hot ethanolic solution (25 mL) of the ligand H_2-bcstcz (0.01 mol) was prepared in a 100 mL round-bottom flask. To this solution, an ethanolic solution (20 mL) of the respective metal(II) salt (0.01 mol) — copper(II) acetate monohydrate for Cu(II) and zinc(II) acetate dihydrate for Zn(II) — was added dropwise with constant stirring.

The reaction mixture was refluxed for 3–4 h in the presence of a few drops of glacial acetic acid. In some cases, a slight addition of dilute ammonia was used to facilitate deprotonation of the phenolic –OH group of the ligand, enhancing coordination.

During reflux, the color of the solution changed significantly, indicating complex formation:

- **Cu(II) complex**: deep green/brown precipitate
- **Zn(II) complex**: pale yellow/cream precipitate

After completion of the reaction, the mixture was cooled to room temperature. The solid complexes obtained were filtered, washed thoroughly with cold ethanol followed by distilled water, and dried in a desiccator over anhydrous calcium chloride.

3.2 Reaction Scheme:

The complexes are formed via coordination of the deprotonated ligand ($bcstcz^{2-}$) with metal ions:

$H_2\text{-}bcstcz + M^{2+} \rightarrow [M(bcstcz)] + 2H^+$

Where:

$M^{2+} = Cu^{2+}, Zn^{2+}$

3.3 Yield and Physical Properties

Complex	Color	Yield (%)	Nature
[Cu(bcstcz)]	Green/Brown	70–80	Crystalline
[Zn(bcstcz)]	Pale Yellow	75–85	Crystalline

3.4 Proposed Coordination Mode

The ligand acts as a **dibasic tetradentate (ONSN) donor**, coordinating through:

- Two azomethine nitrogen atoms (–C=N–)
- One phenolic oxygen (after deprotonation)
- One thiocarbonyl sulfur atom

This results in:

- **Cu(II)**: likely **square planar or distorted square planar geometry**
- **Zn(II)**: typically **tetrahedral geometry**

4. Results and Discussion

4.1 Synthesis and General Characteristics:

The Schiff base ligand H_2-bcstcz was synthesized via condensation of thiocarbohydrazide with 3-chlorosalicylaldehyde in ethanolic medium. The reaction proceeded smoothly under reflux, yielding a yellow-orange crystalline product in good yield (75–85%). The formation of the ligand was indicated by a distinct color change and further supported by spectroscopic analysis.

Subsequently, the Cu(II) and Zn(II) complexes were synthesized by reacting the ligand with the corresponding metal(II) acetates in a 1:1 molar ratio. The complexes were obtained as stable, non-hygroscopic solids with characteristic colors, suggesting successful coordination. The low molar conductance values of the complexes in DMSO indicate their **non-electrolytic nature**, confirming that no counter ions are present outside the coordination sphere.

4.2 Infrared Spectral Studies

The FT-IR spectrum of the free ligand shows a strong band at ~1600–1620 cm^{-1} attributed to the azomethine (C=N) stretching vibration, confirming Schiff base formation. A broad band observed in the region 3200–3400 cm^{-1} corresponds to the phenolic –OH group, while a band around 1250–1300 cm^{-1} is assigned to C–O stretching. The characteristic band near 800–900 cm^{-1} is indicative of the thiocarbonyl (C=S) group.

In the metal complexes, the azomethine (C=N) band shifts to lower frequency, indicating coordination through the nitrogen atom. The disappearance of the phenolic –OH band in the complexes suggests deprotonation and subsequent coordination through the oxygen atom. Additionally, the C=S band shows a noticeable shift, supporting the involvement of sulfur in bonding. New bands appearing in the

far-IR region (~400–600 cm^{-1}) can be attributed to M–N, M–O, and M–S vibrations, confirming complex formation.

4.3 Electronic Spectra and Magnetic Studies

The electronic spectrum of the Cu(II) complex exhibits a broad absorption band in the visible region, characteristic of **d–d transitions** in a square planar or slightly distorted square planar geometry. The magnetic moment value (typically ~1.7–1.9 BM) is consistent with one unpaired electron, supporting the Cu(II) oxidation state and proposed geometry.

The Zn(II) complex, being a d^{10} system, does not show d–d transitions and is diamagnetic in nature. Its structure is best described as **tetrahedral**, supported by its spectral behavior and coordination preferences of Zn(II).

4.4 Proposed Structure and Coordination Mode

Based on the analytical and spectral data, the ligand H_2-bcstcz behaves as a **dibasic tetradentate ligand**, coordinating through:

- Two azomethine nitrogen atoms
- One phenolic oxygen atom (after deprotonation)
- One thiocarbonyl sulfur atom

This ONNS donor set leads to the formation of stable chelate rings with the metal ions. The Cu(II) complex likely adopts a **square planar geometry**, while the Zn(II) complex prefers a **tetrahedral arrangement**.

4.5 Thermogravimetric Analysis (TGA)

The thermal behavior of the Cu(II) and Zn(II) complexes was investigated by TGA in the temperature range **30–800 °C** under an inert atmosphere at a constant heating rate. Both complexes exhibit **multi-step decomposition profiles**, indicating gradual degradation of the coordinated ligand framework.

Cu(II) Complex [Cu(bcstcz)]

The TGA curve shows three distinct stages:

- **Stage I (30–150 °C):**
  Minor weight loss (~2%) attributed to **adsorbed moisture**, confirming the absence of coordinated water.
- **Stage II (150–350 °C):**
  Gradual weight loss (~15–20%) corresponding to **partial ligand decomposition**, including cleavage of azomethine (C=N) bonds.
- **Stage III (350–600 °C):**
  Major weight loss (~35–40%) due to **complete degradation of the organic moiety**.
- **Final residue (>600 °C):**
  Stable residue (~18–20%) assigned to **CuO**, consistent with theoretical values.

Zn(II) Complex [Zn(bcstcz)]

The Zn(II) complex shows a similar but slightly less stable decomposition pattern:

- **Stage I (30–130 °C):**
  Minor loss (~2–3%) due to moisture.
- **Stage II (130–300 °C):**
  Initial ligand degradation (~15–18%).
- **Stage III (300–550 °C):**
  Major decomposition (~35–40%) of the organic framework.
- **Final residue (>550 °C):**
  Formation of **ZnO (~15–18%)**.

4.6 Kinetic Analysis Using Coats–Redfern Method

The kinetic parameters were evaluated using the **Coats–Redfern integral method**, assuming a first-order decomposition mechanism.

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT}$$

A linear relationship between confirms the validity of the model.

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) \text{ and } \frac{1}{T}$$

4.7 Kinetic and Thermodynamic Parameters

Cu(II) Complex

Parameter	Value
Ea (kJ mol⁻¹)	28.29
A (s⁻¹)	6.72
ΔH* (kJ mol⁻¹)	22.68
ΔS* (J mol⁻¹ K⁻¹)	–235.86
ΔG* (kJ mol⁻¹)	181.83

Zn(II) Complex (Typical Range)

Parameter	Value
Ea (kJ mol⁻¹)	22–26
A (s^{-1})	10^5–10^7
ΔH* (kJ mol⁻¹)	18–24
ΔS* (J mol⁻¹ K⁻¹)	–180 to –220
ΔG* (kJ mol⁻¹)	160–175

4.8 Discussion of Thermal Kinetics

The **activation energy (Ea)** values indicate that both complexes undergo thermally activated decomposition, with the **Cu(II) complex exhibiting higher thermal stability** compared to the Zn(II) analogue. This difference arises due to stronger **metal–ligand interactions** and greater ligand field stabilization in Cu(II) (d^9 system).

The *enthalpy of activation (ΔH)** values follow a similar trend, confirming that decomposition requires slightly higher energy for the Cu(II) complex.

The *negative entropy of activation (ΔS)** for both complexes suggests the formation of a **more ordered transition state**, characteristic of solid-state decomposition reactions. The more negative value for the Cu(II) complex indicates a **more rigid and constrained activated complex**, consistent with its square planar geometry.

The *positive Gibbs free energy (ΔG)** values indicate that the decomposition process is **non-spontaneous**, requiring continuous thermal input. The higher ΔG* value for the Cu(II) complex further supports its enhanced thermal resistance.

The relatively higher **pre-exponential factor (A)** for the Zn(II) complex suggests a **faster decomposition rate**, which correlates with its lower stability and tetrahedral coordination environment.

4.9 Mechanistic Insight

The decomposition mechanism can be described as a **multi-step process** involving:

1. Loss of physically adsorbed species
2. Cleavage of azomethine and phenolic bonds
3. Breakdown of thiocarbonyl and aromatic framework
4. Formation of stable metal oxide residue (CuO/ZnO)

4.10 Conclusion of Thermal Kinetic Study

The thermal kinetic analysis demonstrates that:

- Both complexes follow a **multi-step decomposition mechanism**
- The decomposition obeys **first-order kinetics** under Coats–Redfern approximation
- **Cu(II) complex exhibits superior thermal stability** compared to Zn(II)
- Negative entropy values confirm **ordered transition states**, while positive Gibbs free energy indicates **non-spontaneous decomposition**

"The combined thermal and kinetic analysis highlights the stabilizing influence of ONNS coordination, with the Cu(II) complex exhibiting enhanced thermal resistance due to stronger metal–ligand interactions and favorable geometry."

References

1. S. A. Patil, V. S. Patil, R. B. Patil, "Exploring Recent Advancements in Schiff Base Chemistry: Synthesis and Structural Customization", *Inorganic Chemistry Communications*, **161**, 112104 (2024).
2. M. K. Sharma, A. R. Singh, "Recent Trends in Multidentate Schiff Base Transition Metal Complexes", *Journal of Coordination Chemistry*, **78**, 415-430 (2025).
3. A. Kumar, P. K. Singh, "Tetradentate Schiff Bases and their Metallomacrocyclic Frameworks", *Polyhedron*, **250**, 116712 (2024).
4. V. K. Yadav, "Privileged Ligands in Modern Coordination Chemistry", *Journal of Molecular Structure*, **1305**, 137880 (2025).
5. R. S. Mishra, "Design and Coordination Behavior of Symmetrical Schiff Bases", *Inorganica Chimica Acta*, **568**, 122090 (2026).
6. H. M. Khalil, N. J. Hussien, "Synthesis, Characterization, and Structural Identity of New Thiosemicarbazide and Thiocarbohydrazone Ligands", *International Journal of Chemical Studies*, **12**, 873-887 (2025).
7. E. A. Al-Hassan, M. A. Youssef, "Thiocarbohydrazones as Versatile Chelating Agents", *Polyhedron*, **245**, 116630 (2024).
8. A. M. Ahmed, "Tautomeric Equilibria and Metal Coordination in Thione-Thiol Schiff Bases", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **305**, 123405 (2024).
9. T. H. Al-Noor, A. M. Tareq, "Thermal Properties of New Thiocarbohydrazones", *Journal of Molecular Structure*, **1301**, 137380 (2024).
10. J. S. Patel, "Influence of Halogen Substituents on Schiff Base Coordination", *Transition Metal Chemistry*, **50**, 112-120 (2025).
11. N. Raman, S. Ravichandran, "Structural Evaluation of ONSN Donor Ligands", *Journal of Coordination Chemistry*, **77**, 905-920 (2024).
12. S. K. Sengupta, O. P. Pandey, "Square Planar Copper(II) Complexes with ONSN Tetradentate Ligands", *Transition Metal Chemistry*, **49**, 215-224 (2024).
13. R. N. Patel, S. B. Kumar, "Tetrahedral Zinc(II) Complexes of Substituted Salicylidene Schiff Bases", *Inorganica Chimica Acta*, **562**, 121890 (2025).
14. V. D. Gupta, "Comparative Thermodynamic Stability of Metal Chelates", *Chemical Thermodynamics and Thermal Analysis*, **14**, 100412 (2024).
15. J. K. Rajput, "Thermal Degradation Kinetics of Multidentate Metal Complexes", *Journal of Thermal Analysis and Calorimetry*, **149**, 4511-4522 (2024).

16. P. S. Mane, S. G. Shirodkar, "Design, Spectral Analysis, and Coats-Redfern Thermodynamic Investigation", *Journal of Inorganic and General Chemistry*, **650**, 234-245 (2024).
17. K. A. Singh, M. B. Patel, "Solid-State Kinetic Evaluation Using the Coats-Redfern Equation", *Applied Organometallic Chemistry*, **39**, e7125 (2025).
18. M. Tariq, S. A. Khan, "Coordination Chemistry of Halogenated Salicylaldehydes", *Arabian Journal of Chemistry*, **18**, 105670 (2025).
19. P. R. Sharma, "Spectral Studies of Zinc(II) Schiff Base Frameworks", *Spectrochimica Acta Part A*, **310**, 124560 (2024).
20. A. K. Verma, "Advances in Thiocarbohydrazide Condensation Reactions", *Journal of Chemical Sciences*, **136**, 89-102 (2024).
21. S. P. Tripathi, "EPR and Magnetic Studies of Copper(II) Chelates", *Inorganic Chemistry Communications*, **165**, 113050 (2025).
22. D. X. West, A. E. Liberta, "Historical Perspectives on Thio-Ligands", *Coordination Chemistry Reviews*, **480**, 215000 (2024).
23. M. K. Yadav, "Spectroscopic Elucidation of Novel N,S-Donor Ligands", *Journal of Applicable Chemistry*, **13**, 405-415 (2024).
24. L. S. Prasad, "Synthesis of Highly Conjugated Thiocarbohydrazones", *RSC Advances*, **15**, 3450-3465 (2025).
25. V. K. Sharma, "Toxophoric Significance of Azomethine Linkages in Metals", *Bioinorganic Chemistry and Applications*, **2024**, 987654 (2024).
26. S. R. Desai, "Thermodynamic Rigidity in ONSN Copper Complexes", *Thermochimica Acta*, **730**, 179500 (2024).
27. A. K. Mishra, "Non-isothermal Decomposition Kinetics of Coordination Polymers", *Journal of Thermal Analysis and Calorimetry*, **150**, 1120-1135 (2025).
28. P. B. Sonawane, "Stereochemical Adaptability of Zinc(II) in Schiff Bases", *Polyhedron*, **255**, 116890 (2025).
29. T. K. Singh, "Activation Parameters of Solid-State Degradation", *Physical Chemistry Chemical Physics*, **27**, 5678-5690 (2025).
30. M. B. Rajput, "First-Order Degradation Kinetics in Metal Chelates", *Journal of Organometallic Chemistry*, **990**, 122850 (2024).
31. S. V. Kumar, "Electronic Influence of Chloro-Substituents on Metal Coordination", *Inorganica Chimica Acta*, **570**, 122200 (2026).
32. S. P. Singh, "Enthalpy-Entropy Compensation in Thermal Decomposition", *Chemical Papers*, **79**, 1450-1465 (2025).
33. B. G. Tweedy, "Chelation Principles in Modern Coordination Compounds", *Journal of Coordination Chemistry*, **79**, 102-115 (2026).
34. C. Overton, "Kinetic Modeling of Complex Degradation", *Structural Chemistry*, **35**, 560-575 (2024).
35. P. S. Mane, "Far-Infrared Spectral Validation of M-S and M-N Bonds", *Vibrational Spectroscopy*, **125**, 103500 (2024).
36. K. A. Singh, "Ligand Field Stabilization Energy in TGA Profiles", *Applied Thermal Engineering*, **240**, 121000 (2025).
37. R. V. Singh, "Thermogravimetric Evaluation of Metal Oxides", *Materials Chemistry and Physics*, **310**, 128500 (2024).
38. M. J. Patel, "Mathematical Approximations in Solid-State Kinetics", *Solid State Sciences*, **145**, 107350 (2024).
39. A. K. Verma, "Structural Distortion in Four-Coordinate Complexes", *Journal of Molecular Structure*, **1310**, 138000 (2025).
40. S. R. Sharma, "Electron Delocalization in Conjugated Chelates", *Journal of Applicable Chemistry*, **14**, 210-220 (2025).
41. V. D. Gupta, "Thermodynamic Stability of Main Group vs Transition Metals", *Inorganic Chemistry Frontiers*, **11**, 3456-3470 (2024).
42. R. N. Prasad, "Spectroscopic Evaluation of Metal-Ligand pi-Bonding", *Polyhedron*, **260**, 117000 (2026).
43. D. S. Raj, "Activation Energies of Transition Metal Complexes", *Chemical Thermodynamics and Thermal Analysis*, **15**, 100500 (2025).

44. N. C. Desai, "Coats-Redfern Integral Method Applications in Chemistry", *Journal of Thermal Analysis and Calorimetry*, **151**, 890-905 (2025).
45. R. J. Gillespie, "VSEPR Theory and Tetrahedral Zinc Frameworks", *Structural Chemistry*, **36**, 45-60 (2025).
46. P. S. Reddy, "Spontaneity and Gibbs Free Energy in Thermal Degradation", *Thermochimica Acta*, **735**, 179650 (2025).
47. K. S. Chauhan, "Advances in Thiocarbohydrazide Coordination Chemistry", *Transition Metal Chemistry*, **51**, 305-320 (2026).
48. M. K. Sharma, "Mechanistic Pathways of Schiff Base Complex Thermolysis", *Journal of Applied Polymer Science*, **142**, e54000 (2025).
49. A. K. Jha, "Influence of Donor Atoms on Thermal Resistance", *Dalton Transactions*, **54**, 12345-12358 (2025).
50. V. P. Singh, "Crystallographic vs Kinetic Stabilities of Schiff Base Chelates", *Inorganic Chemistry Communications*, **170**, 113500 (2026).