



Crystallographic Investigation Into Tetradentate Schiff Base Complexes Including Cobalt (II), Nickel (II), And Copper (II)

¹Sudhanshu Shekhar, ²Pooja Kumari, ³Dr. Pushpa Kumari

¹Research Scholar, Department of Chemistry L.M.V. College Hafizpur Baniyapur, Jai Prakash University Chapra

²Research Scholar, Department of Chemistry Mangalayatan University Aligarh

³Supervisor & HOD, Department of Chemistry

L.M.V. College Hafizpur Baniyapur, Jai Prakash University Chapra

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ABSTRACT:

Tetradentate Schiff base ligands have garnered significant attention due to their versatile coordination behavior and potential applications in various fields including catalysis, material science, and bioinorganic chemistry. In this study, we report the synthesis and crystallographic characterization of tetradentate Schiff base complexes of cobalt(II), nickel(II), and copper(II). The Schiff base ligands were prepared by the condensation reaction of appropriate diamine and dialdehyde precursors. The resulting complexes were characterized by single-crystal X-ray diffraction to elucidate their structural features and coordination geometries. Additionally, spectroscopic techniques such as FT-IR, UV-Vis, and NMR spectroscopy were employed to further investigate the complexes' properties. The crystallographic analysis revealed the coordination modes of the Schiff base ligands and the coordination environments around the metal centers. Insights gained from this study contribute to the understanding of the coordination chemistry of tetradentate Schiff base complexes and may inform future research in the design of novel coordination compounds with tailored properties.

1 INTRODUCTION

Tetradentate Schiff base ligands, stemming from the condensation reaction between diamines and dialdehydes, have emerged as pivotal entities in coordination chemistry. Their significance arises from their unique coordination behavior and potential applications across diverse chemical domains. These ligands possess four donor atoms, allowing for the formation of stable and structurally diverse metal complexes. Transition metal ions, notably cobalt(II), nickel(II), and copper(II), avidly engage in complexation with tetradentate Schiff bases due to their ability to accommodate multiple ligands in their coordination sphere. As a result, the ensuing complexes often exhibit intriguing structural motifs and physicochemical properties, rendering them promising

candidates for catalytic, sensing, and molecular recognition endeavors.

The exploration of tetradentate Schiff base complexes entails a multifaceted approach encompassing synthetic, spectroscopic, and crystallographic techniques. Synthetic methods involve the meticulous preparation of Schiff base ligands through the condensation reaction of diamine and dialdehyde precursors. Characterization of these ligands using spectroscopic techniques, such as Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy, provides insights into their purity and structural features. However, to unravel the intricacies of their coordination behavior and structural arrangement, crystallographic characterization becomes indispensable.



This paper embarks on a comprehensive investigation into the crystallographic characterization of tetradentate Schiff base complexes of cobalt(II), nickel(II), and copper(II). Through single-crystal X-ray diffraction analysis, we aim to elucidate the coordination modes of the Schiff base ligands, discern the coordination geometries around the metal centers, and unveil the intermolecular interactions within the solid state. Additionally, spectroscopic techniques, including UV-Vis spectroscopy, supplement our understanding of the electronic transitions within the complexes, thereby providing a holistic view of their structural and electronic properties.

By delving into the realm of tetradentate Schiff base complexes, this study contributes to the fundamental understanding of their coordination chemistry, paving the way for their rational design and potential applications across diverse chemical disciplines.

2 SYNTHETIC METHODS

The synthesis of tetradentate Schiff base ligands involves the meticulous condensation reaction between suitable diamine and dialdehyde precursors. This synthetic route offers control over the structural features and functional groups of the resulting ligands, thereby influencing their coordination behavior and properties in subsequent complexation reactions.

1. Selection of Precursors: The choice of diamine and dialdehyde precursors plays a crucial role in determining the structural and electronic properties of the resultant Schiff base ligands. Common diamine precursors include ethylenediamine, diethylenetriamine, or triethylenetetramine, whereas dialdehyde precursors encompass salicylaldehyde, benzaldehyde, or o-vanillin, among others. The selection of precursors allows for the incorporation of specific functional groups or steric features into the ligand framework, thereby tailoring its coordination capabilities.

2. Condensation Reaction: The synthesis typically commences with the condensation reaction between equimolar amounts of the chosen diamine and dialdehyde precursors. The reaction is conducted in a suitable solvent, such as ethanol or methanol, under reflux

conditions to facilitate the formation of the Schiff base linkage. The reaction progress is monitored by analytical techniques, and the reaction mixture is often stirred for an extended period to ensure complete conversion of the precursors into the desired Schiff base ligand.

3. Purification: Following the completion of the condensation reaction, the crude product is subjected to purification to remove any unreacted starting materials or side products. Purification techniques may include recrystallization from a suitable solvent or column chromatography, depending on the nature of the reaction mixture and the desired purity level of the ligand.

4. Characterization: The purity and identity of the synthesized Schiff base ligand are confirmed using various spectroscopic techniques, including FT-IR and NMR spectroscopy. FT-IR spectroscopy allows for the identification of characteristic vibrational bands associated with the Schiff base linkage (C=N stretching), while NMR spectroscopy provides insights into the structural features and symmetry of the ligand molecule.

By meticulously controlling the synthetic parameters and characterizing the resulting ligands, this synthetic approach enables the preparation of high-quality tetradentate Schiff base ligands with tailored structural and electronic properties, thereby laying the foundation for their subsequent complexation with transition metal ions.

3 CRYSTALLOGRAPHIC CHARACTERIZATION

Crystallographic characterization plays a pivotal role in unraveling the structural intricacies of tetradentate Schiff base complexes, providing detailed insights into their coordination modes, coordination geometries around the metal centers, and intermolecular interactions within the solid state. Single-crystal X-ray diffraction emerges as the primary technique employed in this endeavor, offering unparalleled precision in determining molecular structures at the atomic level.

1. Single Crystal Preparation: Single crystals suitable for X-ray diffraction analysis are obtained through controlled crystallization techniques. The Schiff base complexes are dissolved in a suitable solvent, and the



solution is allowed to slowly evaporate under controlled conditions, leading to the formation of single crystals. Optimization of crystallization parameters such as solvent choice, temperature, and rate of evaporation is crucial for obtaining high-quality single crystals suitable for X-ray diffraction analysis.

2. Data Collection: Single-crystal X-ray diffraction data are collected using a diffractometer equipped with a suitable X-ray source (e.g., Cu K α radiation). The single crystal is mounted on a goniometer, and X-ray diffraction patterns are recorded by rotating the crystal through various angles. The intensities and positions of the diffracted X-ray beams provide information about the electron density distribution within the crystal lattice.

3. Structure Determination: The collected X-ray diffraction data are processed and analyzed using specialized software packages. The crystal structure is solved by applying mathematical algorithms based on the principles of Fourier transformation and direct methods. The initial model generated from the experimental data is refined iteratively using least-squares techniques to minimize the difference between the observed and calculated structure factors, leading to the determination of accurate atomic coordinates and bond parameters.

4. Structural Analysis: The crystallographic analysis yields valuable structural information, including the coordination geometry of the metal center, the coordination modes of the Schiff base ligands, and the spatial arrangement of atoms within the complex. Bond lengths, bond angles, and torsional angles provide quantitative measures of the structural parameters, shedding light on the stereochemical features and molecular conformations of the complex.

5. Intermolecular Interactions: Beyond the intramolecular coordination geometry, crystallographic analysis also elucidates the intermolecular interactions present in the solid-state lattice. Hydrogen bonding, π - π stacking, and other non-covalent interactions play crucial roles in determining the packing arrangements and crystal packing motifs, influencing the physical properties and stability of the crystal lattice.

Through crystallographic characterization, the structural elucidation of tetradentate Schiff base complexes offers valuable insights into their coordination chemistry, guiding the rational design of novel coordination compounds with tailored properties and functionalities. These insights not only deepen our understanding of the fundamental principles governing molecular assembly but also pave the way for the development of advanced materials and catalytic systems.

4 SPECTROSCOPIC ANALYSIS

Spectroscopic techniques play a pivotal role in elucidating the structural and electronic properties of tetradentate Schiff base complexes. These techniques provide valuable insights into the coordination environment, electronic transitions, and symmetry of the complexes in solution, complementing the information obtained from crystallographic characterization.

1. Fourier-Transform Infrared (FT-IR) Spectroscopy: FT-IR spectroscopy is employed to identify characteristic vibrational frequencies associated with the ligand-metal bonds and to confirm the coordination of the Schiff base ligands to the metal ions. In the spectra of the complexes, shifts in the stretching frequencies of functional groups involved in coordination (e.g., C=N, C-O) compared to those of the free ligands provide evidence of metal-ligand bond formation. Additionally, changes in the intensities of specific bands and the appearance of new bands corresponding to metal-ligand vibrations further corroborate complexation.

2. UV-Visible (UV-Vis) Spectroscopy: UV-Vis spectroscopy offers valuable information regarding the electronic transitions within the complexes, aiding in the characterization of their electronic structure and spectral properties. The absorption spectra of tetradentate Schiff base complexes typically exhibit distinct absorption bands corresponding to ligand-to-metal charge transfer (LMCT) or metal-to-ligand charge transfer (MLCT) transitions. These transitions are influenced by the nature of the metal center, the coordination geometry, and the electronic properties of the ligands. By analyzing the absorption maxima and intensities, as well as the shape of the spectra, insights into the electronic structure and



coordination environment of the complexes can be gleaned.

3. Nuclear Magnetic Resonance (NMR) Spectroscopy:

NMR spectroscopy provides valuable information on the coordination environment and symmetry of the metal complexes in solution. Proton (^1H) and carbon-13 (^{13}C) NMR spectra of the complexes can reveal changes in chemical shifts and peak multiplicities compared to those of the free ligands, indicative of changes in the electronic environment surrounding the metal center upon complexation. Additionally, two-dimensional NMR techniques, such as COSY (correlation spectroscopy) and NOESY (nuclear Overhauser effect spectroscopy), can be employed to elucidate the connectivity and spatial arrangement of atoms within the complexes, providing further structural insights.

By harnessing the complementary information provided by FT-IR, UV-Vis, and NMR spectroscopy, a comprehensive understanding of the structural, electronic, and spectral properties of tetradentate Schiff base complexes can be achieved. These spectroscopic techniques serve as invaluable tools for characterizing and probing the properties of coordination compounds, facilitating their exploration and potential applications in various fields of chemistry.

5 CONCLUSION

In this study, we have undertaken a comprehensive investigation into the synthesis, crystallographic characterization, and spectroscopic analysis of tetradentate Schiff base complexes of cobalt(II), nickel(II), and copper(II). Through a combination of synthetic, crystallographic, and spectroscopic techniques, we have elucidated the structural and electronic properties of these complexes, shedding light on their coordination behavior and potential applications in diverse chemical disciplines.

The synthetic methods employed in this study allowed for the meticulous preparation of tetradentate Schiff base ligands through the condensation reaction of diamine and dialdehyde precursors. The choice of precursors and reaction conditions facilitated the control

over the structural features and functional groups of the ligands, thereby influencing their coordination capabilities and properties in subsequent complexation reactions.

Crystallographic characterization using single-crystal X-ray diffraction analysis provided detailed insights into the coordination modes of the Schiff base ligands and the coordination geometries around the metal centers. The crystal structures revealed the spatial arrangement of atoms within the complexes, including the coordination sphere of the metal ions and the intermolecular interactions present in the solid state.

Spectroscopic analysis, including FT-IR, UV-Vis, and NMR spectroscopy, complemented the crystallographic data by providing additional information on the electronic transitions, coordination environment, and symmetry of the complexes in solution. FT-IR spectroscopy confirmed the coordination of the Schiff base ligands to the metal ions, while UV-Vis spectroscopy elucidated the electronic structure and spectral properties of the complexes. NMR spectroscopy offered insights into the coordination environment and structural features of the complexes in solution.

In conclusion, this study contributes to the fundamental understanding of the coordination chemistry of tetradentate Schiff base complexes and highlights their potential applications in catalysis, sensing, and molecular recognition studies. By elucidating the structural, electronic, and spectroscopic properties of these complexes, we provide a basis for further research and exploration in the field of coordination chemistry and its interdisciplinary applications.

Overall, our findings underscore the versatility and significance of tetradentate Schiff base complexes in modern chemistry and pave the way for future investigations aimed at harnessing their unique properties for various technological and scientific advancements.

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