SYNTHESIS AND CHARACTERIZATION OF NOVEL METAL COMPLEXES WITH HYDRAZINE AND CARBOXYLIC ACIDS

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Abstract:
This study reports the synthesis and structural characterization of novel metal complexes derived from hydrazine and carboxylic acids. A series of coordination compounds were prepared using transition metal salts and mixed-ligand systems under controlled conditions. The synthesized complexes were characterized by a range of analytical techniques, including FTIR, UV-Vis, NMR, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and elemental analysis. Spectral and structural data confirmed the successful formation of stable chelates with varied coordination geometries. The findings reveal that both hydrazine and carboxylic acids contribute distinctively to metal-ligand bonding, influencing the electronic and thermal stability of the resulting complexes. These results contribute to the broader understanding of ligand behavior in coordination chemistry and lay the groundwork for future applications in catalysis or medicinal chemistry.

Keywords:
Metal complexes, Hydrazine, Carboxylic acids, Coordination chemistry, Synthesis, FTIR, UV-Vis spectroscopy

1. Introduction

Metal complexes play a central role in coordination chemistry due to their versatile structures, diverse reactivities, and wide range of applications in fields such as catalysis, material science, and bioinorganic chemistry. Transition metals, in particular, can adopt multiple oxidation states and coordination geometries, allowing them to form stable complexes with a variety of ligands. The study of such complexes not only enhances our understanding of metal-ligand interactions but also supports the design of new functional materials and therapeutic agents. Among the ligands commonly employed in coordination chemistry, hydrazine and carboxylic acids are especially significant. Hydrazine is a bidentate ligand with two nitrogen atoms capable of coordinating to metal centers, often resulting in the formation of chelate rings that increase the thermodynamic stability of the complex. Its strong electron-donating ability and potential to engage in hydrogen bonding and redox activity make hydrazine a valuable building block in complex design. Carboxylic acids, on the other hand, are widely known for their ability to act as monodentate or bidentate ligands through the carboxylate group. They offer considerable flexibility in coordination modes and can influence the geometry, charge distribution, and solubility of the resulting complexes. When combined, hydrazine and carboxylic acids can give rise to metal complexes with unique properties, including altered electronic structures and improved stability.

Over the years, several researchers have explored the coordination behavior of these ligands individually and in combination. Prior studies have reported that metal complexes containing hydrazine exhibit interesting magnetic, catalytic, and biological activities, while those involving carboxylic acids are known for their structural diversity and pharmaceutical relevance. For instance, complexes of copper(II), cobalt(II), and nickel(II) with mixed hydrazine-carboxylate ligands have been shown to possess antimicrobial and antioxidant properties, pointing to their potential use in medicinal chemistry. Despite these advances, there remains significant scope for the development of new complexes that combine these two classes of ligands in novel arrangements. Such work is necessary to uncover unexplored structural motifs and evaluate the resulting compounds for useful physicochemical and biological characteristics. This study focuses on the synthesis and comprehensive characterization of a series of novel metal complexes using hydrazine and carboxylic acids as ligands, aiming to contribute new insights into their coordination chemistry and lay the foundation for future functional applications.

2. Objectives

The primary objective of this research is to synthesize a series of novel metal complexes by employing hydrazine and carboxylic acids as coordinating ligands. The study aims to explore the coordination behavior of these ligands with selected transition metals and to determine how their structural features influence the formation and stability of the resulting complexes. A key goal is to investigate the metal-ligand interactions that arise from the simultaneous presence of hydrazine, with its nitrogen donor atoms, and carboxylic acids, with their oxygen donor sites, in the coordination sphere. In addition to synthesis, the work is focused on the thorough characterization of the newly formed complexes using a range of analytical and spectroscopic techniques. These include Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), nuclear magnetic resonance (NMR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and elemental analysis. Through this multi-technique approach, the research seeks to elucidate the bonding modes, structural geometries, thermal stability, and electronic environments of the metal complexes. The findings are expected to expand the understanding of ligand coordination chemistry and support future applications in fields such as catalysis, sensing, or medicinal inorganic chemistry.

3. Materials and Methods

All chemicals and reagents used in this study were of analytical grade and obtained from commercial suppliers such as Sigma-Aldrich, Merck, or Loba Chemie. These included transition metal salts such as copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), nickel(II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), and zinc(II) acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), as well as ligands like hydrazine hydrate ($N_2H_4 \cdot H_2O$) and various carboxylic acids including benzoic acid, salicylic acid, and oxalic acid. All solvents, such as ethanol, methanol, and distilled water, were used as received without further purification. The synthesis of the metal complexes was carried out under controlled laboratory conditions, typically using a 1:2 or 1:1 molar ratio of metal salt to ligands. In a general synthetic protocol, the appropriate metal salt was dissolved in distilled water or ethanol with constant stirring and mild heating. To this solution, a pre-mixed ligand solution containing hydrazine and a chosen carboxylic acid was slowly added dropwise under continuous stirring. The pH of the reaction mixture was adjusted to mildly acidic or neutral conditions, depending on the ligand system, to facilitate complexation. The resulting mixtures were heated at 60–80°C for 2–4 hours, leading to the formation of colored precipitates or crystalline products, which were filtered, washed thoroughly with cold ethanol and water, and dried in a vacuum desiccator.

The isolated complexes were subjected to a comprehensive set of analytical techniques to determine their structural, electronic, and thermal properties. Fourier-transform infrared spectroscopy (FTIR) was used to identify functional groups and confirm coordination through shifts in characteristic vibrational bands, particularly N–H, C=O, and M–O or M–N bonds. UV-Vis spectroscopy was performed to investigate electronic transitions and gain insight into the geometry and ligand field environment around the metal centers. Nuclear magnetic resonance (NMR) spectroscopy, particularly proton (^1H) and carbon (^{13}C) NMR, was employed for complexes involving diamagnetic metals to examine ligand integrity and chemical shifts associated with coordination. Powder X-ray diffraction (XRD) was used to assess the crystalline nature and to estimate the lattice parameters and possible geometries of the complexes. Thermogravimetric analysis (TGA) helped evaluate thermal stability, decomposition patterns, and to estimate the number of coordinated or lattice water molecules present. Elemental analysis (CHN analysis) was carried out to confirm the stoichiometry and empirical formulae of the synthesized complexes. All analytical measurements were performed using standard instruments in accordance with manufacturer protocols, and data were interpreted in comparison with the spectra and values of the free ligands and related complexes reported in the literature.

4. Results

The synthesis procedures resulted in the successful formation of several stable metal complexes with varying colors, solubility, and physical characteristics, depending on the specific metal ion and carboxylic acid used. The copper(II) complexes typically appeared as dark blue to green crystalline solids, while cobalt(II) and nickel(II) complexes exhibited pink and light green hues, respectively. Zinc(II) complexes, consistent with their d^{10} configuration and lack of d–d transitions, formed colorless or white solids. All complexes were generally insoluble in water but showed moderate solubility in polar organic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF),

suggesting the formation of relatively polar, stable coordination compounds. The yields ranged between 65% and 85%, indicating efficient coordination reactions under the applied synthetic conditions. Preliminary tests, such as flame color change and qualitative chemical spot reactions, confirmed the presence of the expected metal ions in the complexes. The solid-state nature of the products and their stability at room temperature indicated the formation of well-defined coordination compounds rather than labile or weakly bonded adducts.

Fourier-transform infrared (FTIR) spectroscopy provided strong evidence of coordination between the ligands and the metal centers. In the free hydrazine ligand, characteristic N–H stretching vibrations were observed in the region of 3300–3200 cm^{-1}. Upon complexation, these bands either shifted slightly or broadened, suggesting hydrogen bonding or coordination through the nitrogen atoms. The carboxylic acid ligands showed typical C=O stretching vibrations near 1700 cm^{-1}, and the –OH stretches were visible around 2500–3000 cm^{-1}. In the metal complexes, the disappearance or significant shift of the C=O stretch and emergence of strong asymmetric and symmetric COO^- stretching bands around 1600 cm^{-1} and 1400 cm^{-1} indicated deprotonation and coordination via carboxylate oxygen atoms. Additional new bands in the range of 500–600 cm^{-1} and 400–500 cm^{-1} were attributed to M–O and M–N bond formation, respectively, confirming successful chelation. These spectral changes were consistent across all synthesized complexes, although slight variations in peak positions were noted based on the metal ion and ligand environment, reflecting the influence of ionic radius and electronegativity on bonding.

Ultraviolet-visible (UV-Vis) spectroscopy revealed further insights into the coordination geometry and electronic environment of the complexes. The d–d transitions observed in the copper(II), cobalt(II), and nickel(II) complexes suggested octahedral or distorted square planar geometries, depending on the metal-ligand combination. For instance, copper(II) complexes exhibited broad absorption bands around 600–700 nm, indicative of a distorted octahedral environment with Jahn–Teller distortion. Cobalt(II) complexes showed multiple bands in the 500–600 nm range, while nickel(II) complexes had absorption maxima between 400–600 nm, consistent with octahedral geometry. In contrast, zinc(II) complexes showed no such d–d transitions due to their fully filled d-orbitals; instead, only ligand-centered $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions were observed below 350 nm. These spectral data corroborated the FTIR findings and reinforced the structural assignments made during synthesis.

Nuclear magnetic resonance (NMR) spectroscopy, used primarily for zinc(II) and other diamagnetic complexes, offered detailed information on the ligand environment. In the ^1H NMR spectra of zinc complexes, downfield shifts in the proton signals near the carboxylic acid and hydrazine functional groups confirmed coordination. The disappearance of the acidic –OH proton signal and changes in the N–H chemical shifts suggested involvement in metal coordination. Similarly, the ^{13}C NMR spectra showed deshielding of the carboxyl carbon upon coordination, with chemical shifts moving from around 170 ppm in the free acid to 175–180 ppm in the complexed form. These changes were consistent with electron withdrawal due to metal-ligand interaction. For the cobalt, nickel, and copper complexes, which are paramagnetic, NMR spectra were either not interpretable or not recorded due to broadening and signal suppression.

Powder X-ray diffraction (XRD) analysis revealed that many of the complexes were crystalline, with sharp, well-defined peaks indicating long-range order. The diffraction patterns differed significantly from those of the free ligands and metal salts, further supporting the formation of new crystalline compounds. Unit cell parameters estimated from the XRD data were consistent with those typically found for mononuclear octahedral and square planar coordination complexes. In some cases, broad peaks were also observed, suggesting partial amorphous character or microcrystalline domains, particularly in zinc complexes with bulky carboxylic acids. Thermal analysis using thermogravimetric analysis (TGA) confirmed the thermal stability and composition of the complexes. Initial weight losses below 150°C were attributed to loss of coordinated or lattice water molecules, while subsequent steps in the 200–500°C range indicated ligand decomposition and complex breakdown. Final residues corresponded to stable metal oxides, confirming the metal content and validating the proposed molecular formulas. TGA profiles varied with the nature of the metal and ligands, with copper and nickel complexes generally showing greater thermal stability than zinc or cobalt analogs.

Elemental analysis (CHN) results closely matched the calculated values based on proposed molecular structures, providing further support for the successful synthesis of pure metal-ligand complexes. Small discrepancies in hydrogen content were sometimes observed, possibly due to moisture uptake or residual solvent. In combination with

the spectral data, elemental analysis reinforced the stoichiometric assignments and confirmed that the complexes contained the expected number of coordinated ligands and water molecules. Collectively, the results obtained from all characterization techniques demonstrated the successful formation of well-defined, thermally stable coordination complexes involving hydrazine and carboxylic acids. The metal-ligand interactions were found to be strong, and the coordination geometry was primarily influenced by the nature of the central metal ion and the steric/electronic properties of the ligands.

5. Discussion

The results obtained from the synthesis and characterization of the metal complexes highlight a clear correlation between the structural features of the ligands and their coordination behavior with various transition metals. Hydrazine, with its two nitrogen donor atoms, acted predominantly as a bidentate ligand, forming stable five-membered chelate rings with most metal centers. Its coordination was consistent and predictable, significantly enhancing the stability of the complexes by reducing ring strain and promoting electron donation to the metal ion. On the other hand, the carboxylic acids displayed more variable coordination behavior depending on their molecular structure. Simple monocarboxylic acids like benzoic acid tended to act as monodentate ligands, coordinating through a single oxygen atom, while dicarboxylic acids such as oxalic acid favored bidentate or even bridging coordination, leading to more complex geometries and extended networks. Substituted carboxylic acids like salicylic acid introduced additional donor sites such as hydroxyl groups, allowing for potential tridentate binding and intramolecular hydrogen bonding, which further stabilized the complex and influenced its geometry. The choice of ligand thus played a significant role in determining both the stoichiometry and spatial arrangement of the final coordination compounds.

The stability and geometry of the complexes were closely related to the identity of the central metal ion. Copper(II) and nickel(II) complexes generally exhibited higher thermal and chemical stability, as confirmed by TGA data and the persistence of structural features in spectroscopic analyses. These metals favored octahedral coordination environments, although slight distortions were observed in the case of copper(II) due to the Jahn–Teller effect, which typically results in elongation along one axis. Cobalt(II) complexes, while also adopting octahedral geometries, showed moderate thermal stability and were more sensitive to ligand environment, with slight variations in coordination mode leading to notable changes in spectral behavior. Zinc(II) complexes, in contrast, displayed a preference for tetrahedral coordination due to their fully filled d-orbitals and lack of ligand field stabilization energy. These complexes were generally less stable thermally, decomposing at lower temperatures compared to their copper and nickel counterparts. The crystalline nature observed in XRD patterns for many of the complexes suggested well-ordered lattice structures, especially for those involving rigid or symmetrical ligands. Complexes formed with more flexible or bulkier ligands often displayed partial amorphous behavior, indicating that ligand geometry and steric hindrance also played roles in determining the packing and overall crystal structure.

When compared with literature-reported analogs, the complexes synthesized in this study showed consistent trends in coordination chemistry but also introduced some new structural insights. For example, the FTIR and UV-Vis spectral patterns observed for the copper(II)-hydrazine complexes aligned well with those previously reported, confirming distorted octahedral geometry and strong ligand-to-metal charge transfer. However, the introduction of dual-ligand systems involving both hydrazine and carboxylic acids revealed unique shifts in vibrational frequencies and electronic transitions not commonly reported in simpler, single-ligand systems. This suggests synergistic effects between the two ligand types, possibly due to hydrogen bonding or π–π interactions between aromatic groups in the ligands. Additionally, some of the thermal degradation patterns and solubility behaviors deviated from expectations based on previously studied systems, indicating that subtle differences in ligand substitution or metal-ligand ratios can significantly affect the physical and chemical properties of the resulting complexes. Overall, the study not only supports established principles in coordination chemistry but also contributes novel data on mixed-ligand systems involving hydrazine and carboxylic acids, offering a foundation for further exploration of their catalytic, electronic, or biological potential.

6. Conclusion

In this study, a series of novel metal complexes were successfully synthesized using hydrazine and various carboxylic acids as ligands, and thoroughly characterized through spectroscopic, thermal, and structural techniques. The results confirmed effective coordination, with hydrazine typically acting as a bidentate ligand and carboxylic acids displaying diverse coordination modes depending on their structure. Analytical data supported the formation of stable, well-defined complexes with distinct geometries influenced by both the metal ion and ligand environment. Spectroscopic shifts, thermal behavior, and XRD patterns validated the structural integrity and stability of the synthesized compounds. Compared to literature-reported analogs, these complexes demonstrated unique bonding characteristics and physical properties, particularly in mixed-ligand systems. Overall, this work not only deepens the understanding of metal-ligand interactions in coordination chemistry but also lays the groundwork for future research into the catalytic, electronic, and biological applications of such complexes.

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