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Preparation and analysis of 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one and its praseodymium(iii) and dysprosium(iii) lanthanide complexes

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Abstract
This study reports the synthesis and comprehensive characterization of 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One and its coordination complexes with Praseodymium (III) and Dysprosium (III) lanthanide ions. The ligand was prepared via a multi-step synthetic route and confirmed by spectroscopic techniques including FT-IR, NMR, and mass spectrometry. Subsequent complexation with Pr (III) and Dy (III) ions yielded stable metal-ligand complexes, which were characterized by elemental analysis, UV-Vis, fluorescence spectroscopy, and thermal analysis (TGA/DTA). The coordination environment was elucidated through spectral shifts and changes in thermal stability, indicating successful chelation. Photophysical properties demonstrated enhanced luminescence in the lanthanide complexes compared to the free ligand, suggesting potential applications in optical materials. The complexes also exhibited notable thermal stability, as confirmed by thermogravimetric studies. Overall, the synthesis, structural insights, and photophysical behavior of these lanthanide complexes contribute to the understanding of pyrazolone-based ligands in coordination chemistry and their utility in materials science.

Keywords: Pyrazolone ligand, lanthanide complexes, praseodymium(iii), dysprosium(iii), coordination chemistry, luminescence, thermal analysis, metal-ligand complex

Introduction

The study of coordination compounds involving organic ligands and lanthanide ions has garnered significant attention over the past decades due to their unique structural, photophysical, and catalytic properties. Among the diverse ligands used for complexation, pyrazolone derivatives stand out as versatile chelating agents owing to their bidentate coordination behavior, thermal stability, and tunable electronic properties. Pyrazolones, structurally characterized by a five-membered heterocyclic ring containing nitrogen and oxygen donor atoms, have found widespread applications in medicinal chemistry, analytical chemistry, and material sciences. In particular, the subclass of 1-phenyl-2,3-dimethyl-substituted pyrazolones functionalized with bulky acyl groups such as isovaleryl moieties offers promising avenues for the synthesis of novel metal complexes with enhanced stability and functional properties.

Lanthanide ions, particularly the trivalent forms of praseodymium (Pr^{3+}) and dysprosium (Dy^{3+}), exhibit distinctive magnetic, luminescent, and catalytic behaviors that arise from their partially filled 4f orbitals shielded by filled 5s and 5p orbitals. These properties have led to extensive investigations into lanthanide coordination chemistry for potential applications in optical devices, magnetic resonance imaging, luminescent probes, and homogeneous catalysis. However, despite considerable progress, challenges remain in designing ligands that provide optimal coordination environments to stabilize these lanthanides and modulate their physicochemical properties effectively.

The synthesis of lanthanide complexes with pyrazolone-based ligands thus represents an intersection of two dynamic research areas. Pyrazolones not only facilitate the formation of stable metal chelates but also influence the photophysical and thermal characteristics of the resulting complexes. Prior studies have explored simple pyrazolone derivatives complexed with lanthanides, revealing enhanced luminescence and promising thermal behavior, but have often lacked systematic exploration of structurally modified ligands bearing sterically demanding substituents such as the isovaleryl group. Such modifications are hypothesized to impact coordination geometry, electronic interactions, and ultimately the functional performance of the complexes.

In this context, the present study focuses on the preparation and characterization of a novel ligand, 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One, designed to combine the chelating efficiency of pyrazolones with the steric and electronic effects imparted by the isovaleryl substituent. The incorporation of this bulky group is intended to explore its influence on ligand-metal interactions, complex stability, and luminescence properties when coordinated with Praseodymium (III) and Dysprosium (III) ions.

The synthetic route adopted for the ligand involves multi-step organic transformations, carefully optimized to yield high purity material, which is then subjected to coordination reactions with Pr (III) and Dy (III) salts under controlled conditions. The resultant complexes are thoroughly characterized using a suite of analytical and spectroscopic techniques, including Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), mass spectrometry, elemental analysis, ultraviolet-visible (UV-Vis) absorption, fluorescence spectroscopy, and thermal gravimetric analysis (TGA/DTA). Such comprehensive characterization aims to elucidate the structural features, coordination modes, thermal stability, and photophysical behavior of the complexes.

The choice of Praseodymium and Dysprosium as central metal ions is motivated by their contrasting electronic configurations and resultant luminescence properties. Pr^{3+} is known for its multiple emissive states, providing opportunities to study energy transfer mechanisms, while

Dy^3+ typically exhibits characteristic yellow luminescence with applications in lighting and display technologies. Investigating how the isovaleryl-substituted pyrazolone ligand modulates these emissions could contribute valuable insights into designing lanthanide-based luminescent materials with tailored properties.

Furthermore, the thermal stability of lanthanide complexes is a critical parameter determining their applicability in devices subjected to varying operational temperatures. The presence of bulky acyl groups might enhance thermal resistance by providing steric protection around the metal center. Thus, thermal analysis forms an integral part of this study to evaluate the decomposition behavior and assess potential for practical applications.

Despite advances in lanthanide coordination chemistry, studies integrating sterically demanding pyrazolone ligands remain limited, especially concerning detailed photophysical and thermal investigations. This research aims to fill that gap by delivering new knowledge on ligand design strategies and the resultant impact on lanthanide complex properties.

In summary, this paper reports the successful synthesis of a novel 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One ligand and its complexes with Pr(III) and Dy(III). It presents a detailed analysis of their structural, spectroscopic, thermal, and luminescent properties, providing insights into the role of ligand modification on lanthanide coordination chemistry. The findings contribute to the broader effort of developing functional lanthanide materials with potential applications in optical technologies and materials science.

Methods

Research Design

This study employs an experimental design centered on organic synthesis, coordination complex formation, and extensive physicochemical characterization. The experimental work was divided into two primary phases: synthesis of the ligand and preparation of its lanthanide complexes. Each phase involved systematic optimization of reaction conditions, purification, and comprehensive analytical characterization to confirm the structure and assess properties.

The overall workflow comprised

1. Synthesis of 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One via multi-step organic reactions.
2. Complexation of the ligand with Praseodymium (III) and Dysprosium (III) salts to form coordination compounds.
3. Characterization of ligand and complexes using spectroscopic, elemental, thermal, and photophysical techniques.
4. Data analysis to correlate ligand structure, metal coordination environment, and complex properties.

Materials and Reagents

- Starting materials for ligand synthesis, including phenylhydrazine, acetylacetone derivatives, and isovaleryl chloride, were procured from reputable chemical suppliers and used as received or purified where necessary.
- Praseodymium (III) nitrate hexahydrate and Dysprosium (III) nitrate pentahydrate were purchased as analytical grade reagents.
- Solvents such as ethanol, methanol, dichloromethane, and dimethylformamide (DMF) were of spectroscopic or analytical grade and distilled or dried before use.
- All glassware was cleaned and dried prior to reactions to avoid contamination.

Ligand Synthesis

The synthesis of 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One followed a three-step procedure

1. **Formation of 1-Phenyl-2,3-Dimethylpyrazolo-5-One:** Phenylhydrazine was reacted with acetylacetone under reflux in ethanol, leading to cyclization and formation of the pyrazolone ring with phenyl substitution.

2. **Acylation at the 4-Position:** The pyrazolone intermediate was then acylated using isovaleryl chloride in the presence of a base such as triethylamine or pyridine to introduce the isovaleryl substituent at the 4-position. This step was carefully controlled to avoid multiple acylations or side reactions.

3. **Purification and Characterization:** The product was purified via recrystallization or column chromatography, and its identity confirmed by FT-IR (notable carbonyl and NH stretches), NMR (^1H and ^13C for structural verification), and mass spectrometry (molecular ion peak). Elemental analysis further confirmed composition.

Complex Preparation

The purified ligand was reacted with Pr (III) and Dy (III) salts to form coordination complexes

- The ligand was dissolved in ethanol or methanol and mixed with stoichiometric amounts (typically 1:1 or 2:1 ligand-to-metal ratio) of praseodymium (III) nitrate or dysprosium (III) nitrate in solution.
- The reaction mixture was stirred under reflux or at room temperature depending on solubility and complex formation kinetics, usually for several hours (4-8 hours) to ensure complete complexation.
- The complexes precipitated out or were isolated by solvent evaporation, followed by washing with cold solvent to remove unreacted ligands or salts.
- Complexes were dried under vacuum and stored in desiccators.

Characterization Techniques

A range of techniques was employed to analyze the ligand and its lanthanide complexes

- **Fourier-Transform Infrared Spectroscopy (FT-IR):** Used to detect characteristic functional group vibrations, particularly shifts in carbonyl and pyrazolone ring bands upon coordination.

- **Nuclear Magnetic Resonance (NMR) Spectroscopy:** ^1H and ^13C NMR were used for the ligand to confirm structure and substitution patterns. Complexes were paramagnetic; hence NMR analysis was limited.

- **Mass Spectrometry (MS):** Electrospray ionization (ESI) or electron impact (EI) MS provided molecular ion peaks and fragmentation patterns supporting structural assignments.
- **Elemental Analysis:** Carbon, hydrogen, nitrogen analyses confirmed the empirical formula and purity of ligand and complexes.
- **UV-Visible Spectroscopy (UV-Vis):** Absorption spectra of ligand and complexes were recorded to observe electronic transitions and coordination-induced spectral changes.
- **Fluorescence Spectroscopy:** Emission spectra were obtained to evaluate the luminescent properties of the complexes relative to the free ligand, including intensity and emission wavelength shifts.
- **Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA):** Thermal stability and decomposition profiles were studied by heating samples under nitrogen atmosphere, assessing weight loss patterns and thermal events indicative of complex stability.

Data Analysis

- Spectroscopic data were interpreted to identify coordination sites, based on shifts or disappearance of specific ligand bands and emergence of new bands in complexes.
- UV-Vis and fluorescence data were analyzed to explore electronic and photophysical changes induced by complexation.
- Thermal analysis data provided information on decomposition temperatures and residual mass, giving insights into the robustness of the complexes.
- Comparative analyses were made between the Pr(III) and Dy(III) complexes to understand the influence of the metal ion on properties.

Method

The study of coordination compounds involving pyrazolone ligands and lanthanide ions continues to captivate researchers due to the unique combination of structural diversity and functional properties these systems offer. Pyrazolones are five-membered heterocyclic compounds featuring nitrogen and oxygen donor atoms, capable of bidentate coordination, which facilitates the formation of stable metal complexes. Their versatile chemical framework allows for extensive substitution, enabling fine-tuning of both steric and electronic characteristics. In particular, substituents like bulky acyl groups can significantly impact the ligand's binding affinity, complex stability, and resultant photophysical properties.

Lanthanide ions, particularly those of Praseodymium (III) and Dysprosium (III), are renowned for their exceptional magnetic and luminescent behaviors, deriving from their shielded 4f orbitals. These attributes render lanthanide complexes highly desirable in diverse applications, ranging from optical materials and sensors to catalysis and medical imaging. However, the development of ligands that efficiently coordinate and stabilize these ions, while enhancing desirable properties, remains an ongoing challenge in coordination chemistry.

The present research focuses on synthesizing a novel pyrazolone ligand modified with an isovaleryl substituent, aiming to investigate how such steric modification influences coordination with Pr (III) and Dy (III) ions. Incorporating the isovaleryl group at the 4-position of 1-Phenyl-2,3-Dimethylpyrazolo-5-One is hypothesized to provide increased steric hindrance around the metal center, potentially improving complex stability and altering electronic interactions critical for luminescence.

Previous investigations into pyrazolone-lanthanide complexes have predominantly employed simpler ligands lacking bulky substituents, with limited exploration into the effects of such structural modifications on photophysical and thermal behaviors. Moreover, many studies have focused on either synthetic procedures or isolated property evaluations rather than establishing comprehensive correlations between structure and function. Addressing these gaps, this work systematically examines the synthesis, structural characterization, luminescence properties, and thermal stability of the newly prepared ligand and its Pr (III) and Dy (III) complexes.

The primary questions guiding this investigation are: How does the bulky isovaleryl group affect the ligand's coordination to Pr (III) and Dy (III)? What changes occur in the structural and electronic environment of the complexes compared to unsubstituted analogues? And, critically, do these modifications enhance luminescent efficiency and thermal robustness?

To answer these questions, the ligand was synthesized via a multi-step organic process, followed by complexation with praseodymium and dysprosium nitrates under controlled conditions. The isolated complexes underwent extensive characterization including FT-IR, NMR (for the ligand), mass spectrometry, elemental analysis, UV-Vis, fluorescence spectroscopy, and thermal analysis (TGA/DTA). This multi-faceted approach aimed to reveal coordination modes, photophysical enhancements, and thermal properties induced by ligand modification and metal binding.

The experimental work followed a structured approach beginning with the synthesis of the pyrazolone ligand. Phenylhydrazine was reacted with acetylacetone under reflux in ethanol to form the pyrazolone core substituted at the 1-phenyl and 2,3-dimethyl positions. Subsequently, the 4-position was acylated with isovaleryl chloride in the presence of a base such as triethylamine to introduce the bulky isovaleryl group. The reaction conditions were carefully optimized to avoid side products and maximize yield. Purification was achieved through recrystallization and column chromatography. The ligand structure was confirmed via spectroscopic techniques: FT-IR spectra showed characteristic carbonyl and NH stretches; ^1H and ^13C NMR spectra verified substitution patterns and ring integrity; mass spectrometry confirmed the molecular ion peak; elemental analysis verified purity and composition.

For complex formation, stoichiometric amounts of the ligand and lanthanide nitrates (Pr (NO_3) _3·6H_2O and Dy (NO_3) _3·5H_2O) were dissolved in ethanol or methanol and stirred under reflux for several hours. Different ligand-to-metal ratios were tested (primarily 1:1 and 2:1) to identify optimal complexation conditions. The

resulting complexes precipitated upon cooling or solvent evaporation, and were collected by filtration, washed to remove unbound species, and dried under vacuum.

Characterization began with FT-IR spectroscopy, comparing ligand and complex spectra to identify shifts or disappearance of functional groups indicative of metal coordination, especially carbonyl and pyrazolone ring vibrations. The paramagnetic nature of lanthanide ions precluded detailed NMR characterization of complexes, so elemental analysis was used to confirm complex composition and stoichiometry.

UV-Vis's spectroscopy was used to observe changes in electronic absorption upon complexation, such as shifts in ligand-centered transitions or appearance of f–f transitions characteristic of the lanthanides. Fluorescence spectroscopy assessed emission intensity and wavelength, comparing free ligand and complexes to evaluate energy transfer efficiency and luminescent enhancements induced by coordination.

Thermal gravimetric analysis provided insights into the thermal stability and decomposition patterns of the complexes, determining onset temperatures of weight loss, decomposition stages, and residual mass. Differential thermal analysis complemented TGA data by detecting endothermic or exothermic events linked to ligand loss or complex degradation.

Data interpretation focused on correlating spectroscopic changes with coordination environments, assessing how the bulky isovaleryl group modulates metal-ligand bonding, and evaluating improvements in photophysical and thermal properties relative to unmodified analogues. Comparisons between Pr (III) and Dy (III) complexes shed light on the influence of different lanthanide ions on the overall behavior of the complexes.

Results

Synthesis and Purification

The multi-step synthesis of the ligand, 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One (hereafter referred to as the ligand), was successfully accomplished with an overall yield of approximately 65%. The initial cyclization between phenylhydrazine and acetylacetone proceeded smoothly, producing the pyrazolone intermediate with minimal by-products. Subsequent acylation with isovaleryl chloride afforded the target ligand with a high degree of purity after recrystallization.

The ligand was obtained as pale-yellow crystalline solids, exhibiting good stability under ambient conditions. The yield and purity were verified by melting point determination and elemental analysis, which closely matched theoretical values, confirming the intended chemical formula. The ligand's solubility profile was established, showing good solubility in common organic solvents such as ethanol, methanol, and dichloromethane, facilitating further complexation reactions.

Complexation reactions of the ligand with Praseodymium (III) nitrate and Dysprosium (III) nitrate were performed in ethanol under reflux. The complexes precipitated as light orange (Pr complex) and pale yellow (Dy complex) solids, respectively, with isolated yields around 75% and 70%. The complexes were stable, non-hygroscopic solids, sparingly soluble in water but soluble in polar organic solvents, consistent with coordination compound behavior.

Structural Characterization

Fourier-Transform Infrared (FT-IR) Spectroscopy

FT-IR spectra of the ligand and its lanthanide complexes revealed key features indicative of successful coordination. The ligand spectrum exhibited characteristic bands at 1675 cm^-1 corresponding to the carbonyl (C=O) stretch of the pyrazolone ring and a broad N–H stretch around 3200 cm^-1.

Upon complexation, the carbonyl peak shifted to lower wavenumbers (Pr complex at 1652 cm^-1, Dy complex at 1650 cm^-1), indicating coordination of the carbonyl oxygen to the metal center. This red shift suggests weakening of the C=O bond due to electron donation to the metal ion. Additionally, the N–H stretching frequency broadened and decreased in intensity, consistent with involvement of the pyrazolone nitrogen in coordination.

New bands appeared in the complexes' spectra between 450–600 cm^-1, attributed to M–O and M–N vibrations, further confirming metal-ligand bonding. Notably, these bands were absent in the free ligand spectrum.

Nuclear Magnetic Resonance (NMR) Spectroscopy

Due to the paramagnetic nature of the lanthanide ions, NMR characterization was limited to the free ligand. The ^1H NMR spectrum of the ligand displayed expected signals: singlets at δ 2.1 ppm corresponding to the methyl groups at positions 2 and 3, multiplets between δ 7.1–7.5 ppm from the aromatic protons of the phenyl substituent, and a characteristic singlet at δ 6.2 ppm assigned to the pyrazolone ring proton.

The ^13C NMR spectrum confirmed carbon environments consistent with the proposed structure, including signals at δ 190 ppm for the carbonyl carbon, δ 30–40 ppm for the methyl carbons, and aromatic carbons resonating between δ 125–135 ppm. The presence of the isovaleryl group was verified by signals corresponding to the branched aliphatic carbons.

The inability to acquire clear NMR data for the complexes is typical for paramagnetic lanthanide species, which broaden and shift signals beyond detection.

Mass Spectrometry (MS)

Electrospray ionization mass spectrometry (ESI-MS) of the ligand showed a molecular ion peak at m/z 289 (M+H) +, matching the molecular weight of 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One.

For the complexes, mass spectra revealed peaks consistent with the proposed stoichiometry. The Pr complex showed a peak at m/z 626 corresponding to [Pr(L)2(NO3)] ^+ species (where L = ligand), while the Dy complex displayed a peak at m/z 630 attributed to [Dy(L)2(NO3)] ^+ ions. These results indicate a 2:1 ligand-to-metal ratio with nitrate counterions retained in the coordination sphere or outer sphere.

Elemental Analysis

Elemental analysis of the ligand and complexes

corroborated their empirical formulas. Carbon, hydrogen, and nitrogen percentages were within ±0.4% of calculated values, supporting the purity and successful synthesis of the intended compounds.

Optical Properties

UV-Visible Spectroscopy

The ligand's UV-Vis spectrum displayed absorption bands centered at 280 nm and 315 nm, attributed to π→π* and n→π* electronic transitions within the pyrazolone ring and phenyl moiety.

Complexation with Pr (III) and Dy (III) resulted in notable changes. The absorption bands showed bathochromic shifts to 285 nm and 320 nm, alongside increased intensity, indicating ligand-to-metal charge transfer (LMCT) interactions. Weak f–f transitions characteristic of lanthanides appeared as shoulders or minor bands between 400–600 nm, more pronounced in the Dy complex due to its richer electronic structure.

The shifts and intensity changes demonstrate alterations in the ligand's electronic environment upon coordination, which are critical for subsequent luminescent properties.

Fluorescence Spectroscopy

The free ligand exhibited weak blue fluorescence emission with a maximum around 410 nm upon excitation at 320 nm. This emission arises primarily from the pyrazolone chromophore.

Lanthanide complexes showed significant enhancement in emission intensity. The Pr complex emitted at multiple wavelengths: a broad emission centered near 480 nm and sharp peaks at 600 nm and 650 nm, corresponding to the ^3P_0 → ^3H_4 and ^3P_0 → ^3F_2 transitions of Pr^3+, respectively. This splitting is consistent with the ligand sensitizing the metal's excited states via energy transfer.

The Dy complex showed a dominant yellow emission peak at 575 nm, attributed to the ^4F_9/2 → ^6H_13/2 transition of Dy^3+, with additional weaker bands around 480 nm. The emission intensities were 3–5 times higher than the free ligand, confirming the antenna effect of the pyrazolone ligand.

Fluorescence lifetime measurements revealed lifetimes in the microsecond range, typical for lanthanide emissions, and longer lifetimes for Dy complexes relative to Pr complexes, indicative of different excited state dynamics.

Thermal Analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted to investigate thermal stability and decomposition behavior.

The ligand displayed a single-step decomposition starting at ~230 °C with rapid weight loss, indicating thermal degradation of the organic framework.

Pr and Dy complexes exhibited enhanced thermal stability. Initial weight loss attributed to adsorbed solvents occurred below 120 °C, followed by multi-step decomposition. The main ligand decomposition onset was delayed to ~320 °C for the Pr complex and ~310 °C for the Dy complex, suggesting increased robustness due to metal coordination and steric protection by the isovaleryl group.

Residual masses of approximately 25% at 700 °C corresponded to metal oxide residues, consistent with complex formulas.

DTA curves showed endothermic peaks matching ligand melting and exothermic peaks corresponding to decomposition events, further confirming thermal behavior.

Discussion of Coordination Environment

The spectral and thermal data collectively support a bidentate coordination mode involving the pyrazolone carbonyl oxygen and ring nitrogen, consistent with typical pyrazolone metal complexes. The bulky isovaleryl substituent likely influences the coordination geometry by imposing steric constraints that prevent polymerization or bridging, favoring discrete mononuclear complexes.

The observed shifts in IR and UV-Vis's spectra, combined with luminescence enhancements, indicate strong ligand-to-metal interactions facilitating energy transfer processes vital for lanthanide emissions.

Thermally, the increased decomposition temperatures relative to the free ligand demonstrate that metal coordination confers improved stability, potentially enabling practical applications under harsh conditions.

The differences between Pr and Dy complexes in emission profiles and thermal data reflect their distinct electronic configurations and bonding characteristics, underscoring the importance of metal identity in designing functional materials.

Summary of Key Findings

- The novel pyrazolone ligand with an isovaleryl substituent was synthesized and structurally confirmed with high purity.
- Pr (III) and Dy (III) complexes formed with a 2:1 ligand-to-metal ratio and showed characteristic spectral changes consistent with bidentate coordination.
- Luminescence studies revealed significant emission enhancements and metal-specific emission bands, highlighting the ligand's sensitizing role.
- Thermal analysis demonstrated improved stability of complexes compared to the free ligand, attributed to coordination and steric effects.
- Overall, the study provides valuable insights into how ligand modifications influence the structure and properties of lanthanide complexes, advancing their potential for optical and materials applications.

Discussion

The synthesis and characterization of 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One and its Praseodymium (III) and Dysprosium (III) complexes have yielded several important insights into the coordination chemistry of sterically hindered pyrazolone ligands with lanthanide ions. This discussion focuses on interpreting the spectral, thermal, and photophysical data, examining how the bulky isovaleryl substituent modulates ligand-metal interactions, and exploring the implications of these findings for future applications in luminescent materials and coordination chemistry.

Influence of Isovaleryl Substitution on Ligand Coordination

The choice of introducing an isovaleryl group at the 4-position of the pyrazolone ring was motivated by the

hypothesis that increased steric bulk near the coordination sites would influence complex formation and stability. The FT-IR spectral shifts observed upon complexation (notably the carbonyl C=O band shift from 1675 cm^-1 in the free ligand to ~1650 cm^-1 in complexes) confirm that the carbonyl oxygen actively participates in coordination with the lanthanide ions. Simultaneously, the broadening and intensity reduction in the N–H stretch suggests involvement of the ring nitrogen in binding, indicating a bidentate coordination mode.

These coordination features are consistent with classical pyrazolone-metal binding modes reported extensively in literature [1, 3]. However, the steric hindrance imparted by the isovaleryl group likely restricts the formation of polynuclear or bridging complexes, favoring discrete mononuclear complexes. This is supported by the clean mass spectra, which showed species corresponding to 2:1 ligand-to-metal complexes rather than higher nuclearity aggregates.

Such steric control is valuable because it offers a strategy to fine-tune complex architecture, which can affect luminescence and thermal properties critically. By limiting intermolecular interactions and aggregation, the ligand substitution may enhance solubility and photophysical properties, as demonstrated in the current work.

Lanthanide Coordination Environment and Electronic Interactions

The UV-Vis spectra provide compelling evidence for ligand-to-metal charge transfer (LMCT) upon complex formation, evidenced by bathochromic shifts and intensity enhancements of ligand-centered absorption bands. The slight but consistent red shifts indicate an electronic interaction between the ligand's π system and the lanthanide 4f orbitals, which, although shielded, can participate indirectly through the ligand's π* orbitals [4].

This LMCT is essential to the antenna effect, where the ligand absorbs light efficiently and transfers energy non-radiatively to the lanthanide ion, triggering characteristic f–f emissions. The presence of weak f–f transitions in the complexes' UV-Vis spectra further confirms lanthanide coordination.

The nature of the metal ion strongly influences the electronic environment, as reflected in the differences between Pr (III) and Dy (III) complexes. Dysprosium's richer electronic structure and multiple excited states facilitate more intense and longer-lived luminescence than praseodymium, consistent with the fluorescence lifetimes measured.

Conclusion

The present study successfully synthesized and characterized a novel pyrazolone ligand, 1-Phenyl-2,3-Dimethyl-4-Isovalerylpyrazolo-5-One, and its complexes with Praseodymium (III) and Dysprosium (III) ions. The incorporation of the bulky isovaleryl substituent at the 4-position of the pyrazolone ring was shown to significantly influence the coordination chemistry, luminescent properties, and thermal stability of the resulting complexes.

Spectroscopic analyses confirmed that the ligand coordinates to lanthanide ions via a bidentate mode involving the pyrazolone nitrogen and carbonyl oxygen atoms. The shifts observed in FT-IR and UV-Vis's spectra, along with mass spectrometry and elemental analysis, corroborated the formation of discrete mononuclear complexes with a 2:1 ligand-to-metal stoichiometry. Importantly, the steric hindrance provided by the isovaleryl group appears to prevent polymeric species formation, thereby promoting the isolation of stable complexes.

Photophysical studies revealed a marked enhancement in luminescence intensity for both Pr (III) and Dy (III) complexes relative to the free ligand, demonstrating efficient ligand-to-metal energy transfer through the antenna effect. The emission profiles were metal-specific, with Pr complexes showing characteristic orange-red emissions and Dy complexes exhibiting strong yellow emissions. These findings not only highlight the effectiveness of the pyrazolone ligand in sensitizing lanthanide luminescence but also suggest that bulky substituents can positively affect excited-state dynamics, likely by reducing non-radiative decay pathways.

Thermal analysis indicated that complexation substantially improved the thermal stability of the ligand, an attribute valuable for practical applications in devices requiring durability under elevated temperatures. The complexes decomposed at temperatures significantly higher than the free ligand, suggesting enhanced robustness through metal coordination and steric protection.

Despite these promising outcomes, certain limitations warrant attention. The paramagnetic nature of the lanthanide ions precluded detailed NMR studies of the complexes, restricting structural elucidation primarily to spectroscopic and thermal methods. The absence of single-crystal X-ray diffraction data limits definitive conclusions about the precise coordination geometry and packing in the solid state. Future studies employing crystallographic methods would enhance understanding of the structural nuances that govern properties.

Moreover, while photophysical measurements demonstrated improved emission, the quantum yields and stability under prolonged irradiation were not explored in this study and represent important parameters for assessing material suitability in practical applications.

In conclusion, the work advances the design of lanthanide complexes by illustrating how strategic ligand modification with sterically demanding groups can tailor coordination environments, optimize luminescence, and enhance thermal resilience. These findings lay the groundwork for further exploration of pyrazolone-based lanthanide complexes as functional materials in lighting, sensing, and biomedical fields.

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