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Combined Raman and UV–Vis Spectroscopic Study on Metal–Ligand Complexes: Probing Electronic and Vibrational Coupling in Coordination Chemistry

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Abstract

This study presents a combined UV–Visible and Raman spectroscopic investigation of selected first-row transition metal complexes—$Co(acac)_2$, $Ni(en)_3$, and $Cu(sal)_2$—coordinated to bidentate nitrogen and oxygen donor ligands. UV–Vis spectra revealed well-resolved d–d transitions and metal-to-ligand charge transfer (MLCT) bands, from which ligand field splitting energies (Δ_0) were calculated. Raman spectra showed characteristic metal–ligand (M–N and M–O) stretching vibrations in the 470–525 cm^{-1} range, correlating positively with ligand field strength. $Cu(sal)_2$ displayed the strongest ligand field and highest MLCT intensity, while $Ni(en)_3$ showed the lowest Δ_0 and Raman frequency. A significant linear relationship was observed between Δ_0 values and corresponding Raman shifts, affirming the interplay between electronic excitation and vibrational properties. Density Functional Theory (DFT) calculations, including TD-DFT and harmonic vibrational frequency analysis, validated the experimental assignments. This dual-spectroscopy framework enhances our understanding of metal–ligand bonding and offers predictive capability for designing coordination complexes with tailored optical and vibrational properties. The results have practical implications in catalysis, optoelectronics, and chemical sensing.

Keywords: UV–Vis spectroscopy, Raman spectroscopy, ligand field theory, metal–ligand bonding, coordination complexes, DFT, Co(II), Ni(II), Cu(II), charge transfer

1. Introduction

1.1 Background

Transition metal–ligand complexes represent a cornerstone of modern inorganic, organometallic, and bioinorganic chemistry. These coordination compounds exhibit a wide array of geometries, oxidation states, and bonding configurations, leading to diverse chemical and physical properties. Their ability to modulate electronic structure through ligand substitution or metal variation has made them indispensable in catalysis, from industrial-scale hydrogenation using Wilkinson's catalyst to metalloenzyme mimetics for biochemical processes (Crabtree, 2020; Huheey et al., 2013). Metal–

ligand complexes are also foundational to artificial photosynthesis, photodynamic therapy, molecular magnetism, and the development of coordination polymers and metal–organic frameworks (MOFs) (Farrugia, 2021; Huang et al., 2020). The electronic properties of these complexes, particularly the energy levels and nature of their frontier orbitals, determine their reactivity, catalytic efficiency, and photochemical behaviour. These are largely governed by the nature of the ligand field created by coordinating atoms (N, O, S, P, etc.), which split the degenerate d-orbitals of transition metals into different energy levels based on crystal field or ligand field theory (Cotton et al., 1999).

Moreover, the metal–ligand bonding environment—whether it involves strong π-backbonding, synergistic σ-donation, or weak field interactions—dictates spectroscopic responses, including absorption in the visible and near-UV regions. These transitions are sensitive indicators of metal oxidation states, geometry, and ligand donor strength (Lever, 1984). As such, understanding how metal–ligand interactions influence both electronic and vibrational properties is crucial for the rational design of new catalysts, photofunctional materials, and biomimetic systems. A systematic spectroscopic study that correlates electronic and vibrational signatures with bonding characteristics can significantly advance both theoretical models and practical applications in coordination chemistry (Kaim & Schwederski, 2014).

1.2 Spectroscopy Overview

Spectroscopic methods provide critical insight into the electronic and vibrational structure of metal–ligand complexes. Among these, ultraviolet–visible (UV–Vis) absorption spectroscopy and Raman spectroscopy are particularly powerful and complementary tools. UV–Vis spectroscopy primarily probes electronic transitions involving d-orbitals and ligand–metal interactions. For transition metal complexes, three major types of absorptions are typically observed: (1) d–d transitions within the metal centre; (2) ligand-to-metal charge transfer (LMCT), where electron density moves from ligand to metal; and (3) metal-to-ligand charge transfer (MLCT), common in low-spin d^6 complexes and polypyridyl ligands (Lever, 1984; Cotton et al., 1999). The energies and intensities of these bands provide qualitative and quantitative information on ligand field splitting, metal oxidation state, and coordination geometry (Jones et al., 2020).

Raman spectroscopy, on the other hand, probes molecular vibrations, particularly those that change polarizability. In metal complexes, it is highly effective for detecting symmetric metal–ligand bond stretching modes, often observed in the 200–600 cm^{-1} region depending on the metal and its ligating atoms (Ferraro et al., 2003). Raman offers advantages over infrared (IR) spectroscopy in aqueous or polar media and for vibrational modes involving symmetrical stretching, which are often IR-inactive. It is especially valuable in determining coordination modes (e.g., mono- vs. bidentate), distinguishing ligand isomerism, and identifying metal–ligand bond strengths (Mishra et al., 2018).

Together, UV–Vis and Raman spectroscopy allow for a dual approach: UV–Vis probes energy-level structures and charge transfer processes, while Raman focuses on bond characteristics and vibrational signatures. When applied in tandem, especially under identical solvent and concentration conditions, these techniques provide a comprehensive view of electronic–vibrational coupling in metal complexes. However, such integrative studies remain relatively rare in literature, and few offer both quantitative correlations and computational validation (Singh & Gupta, 2022). Therefore, this combined spectroscopic framework is essential for understanding and predicting the behaviour of coordination compounds in diverse chemical contexts.

1.3 Objective

Despite the vast body of literature on transition metal complexes, most studies tend to specialise in either electronic or vibrational spectroscopy, with few attempting a simultaneous and integrative analysis using both UV–Vis and Raman techniques. This represents a critical knowledge gap, especially considering the potential insights such integration could provide. The main objective of this research is to systematically investigate the electronic and vibrational properties of a representative series of first-row transition metal complexes—specifically Co(II), Ni(II), and Cu(II)—coordinated to a variety of bidentate N- and O-donor ligands. These include ethylenediamine (en), acetylacetonate (acac), and salicylaldehyde derivatives, all of which offer differing ligand field strengths and coordination geometries (Baschieri et al., 2019; Mukherjee et al., 2021).

This study employs UV–Vis spectroscopy to examine electronic transitions such as d–d absorptions and charge-transfer bands. We aim to correlate the observed transition energies (e.g. 10Dq values) with the nature of the metal and ligand, and to extract molar absorptivity values (ε) as indicators of transition probability and geometry (Lever, 1984). In parallel, Raman spectroscopy will be used to identify metal–ligand vibrational modes and to determine how these shift with ligand identity and metal centre. Vibrational assignments will be further validated through DFT calculations, which will simulate both UV–Vis spectra via TD-DFT and vibrational frequencies using harmonic analysis (Frisch et al., 2016).

This dual approach allows us to explore the interplay between electronic structure and vibrational dynamics in a chemically diverse but systematically designed set of coordination compounds. We hypothesise that the combination of experimental spectra and computational validation will not only reveal how metal–ligand bonding affects spectroscopic behaviour but will also establish generalisable trends applicable to broader coordination chemistry. Ultimately, the findings will have direct relevance to catalyst design, transition metal-based sensors, and photoactive materials, where fine-tuning electronic and vibrational properties is crucial (Wang & Yam, 2020).

2. Literature Review

2.1 Previous Studies

Over the past several decades, UV–Vis spectroscopy has served as an essential tool in characterising the electronic transitions of transition metal complexes. Early interpretations of ligand field effects stem from crystal field theory, which quantitatively explains d–d transitions in octahedral and tetrahedral geometries (Lever, 1984). In octahedral systems, for instance, the splitting of d-orbitals gives rise to well-defined absorption bands, such as the ^4T1g → ^4T2g transitions in Co(II) or ^1A1g → ^1T1g transitions in d^8 Ni(II) complexes. Numerous studies have extended this framework, assigning charge transfer (CT) bands—particularly ligand-to-metal (LMCT) and metal-to-ligand (MLCT)—based on molar absorptivity values, symmetry selection rules, and empirical ligand field splitting energies (Jones et al., 2020; Baschieri et al., 2019). These UV–Vis studies are especially abundant for Schiff base complexes, where the π-conjugation of the ligand affects both d–d and CT transitions. In their work on Ni(II) and Cu(II) salicylaldehyde-Schiff base complexes, Ghosh et al. (2018) observed that increasing electron-donating capacity of substituents on the ligand framework led to systematic bathochromic shifts in absorption maxima.

Parallel to UV–Vis developments, Raman spectroscopy has also emerged as a crucial technique for probing metal–ligand interactions, particularly metal–oxygen (M–O) and metal–nitrogen (M–N) vibrational modes. These vibrations, typically observed between 200 and 600 cm^{-1}, provide a direct measure of bond strength, coordination geometry, and ligand denticity (Ferraro et al., 2003). For example, Sahoo et al. (2021) demonstrated that Raman-active M–N stretches in Co(II) ethylenediamine complexes could differentiate between cis and trans isomers. In copper acetylacetonate ($Cu(acac)_2$), characteristic Raman bands appear near 460 cm^{-1} (M–O stretch), confirming bidentate chelation. Salen-type complexes have also been extensively studied; Raman peaks in the 500–600 cm^{-1} range correspond to symmetric M–O and M=N stretches, validating ligand binding and planarity (Kovács et al., 2019). These examples illustrate that both UV–Vis and Raman spectra carry rich structural information, but typically they are applied in isolation, even though their combination can yield greater interpretive power.

Numerous individual investigations of UV–Vis and Raman spectroscopy on transition metal complexes underscore the growing interest in exploring their electronic and vibrational characteristics. For example, Ni(II) and Co(II) complexes with bidentate ligands such as acetylacetonate (acac) and salicylaldehyde derivatives have been extensively studied via UV–Vis to understand ligand field parameters and determine 10Dq values (Al-Yasari et al., 2020). These studies often report electronic transitions in the visible range with λ_{max} values ranging between 500 and 700 nm, depending on metal ion and coordination environment. MLCT bands, particularly in Co(III) and Cu(I) complexes with π-acceptor ligands such as 2,2'-bipyridine or phenanthroline, have also been widely documented (Wang & Yam, 2020). Raman spectroscopy, in contrast, provides finer structural information. For instance, in a comparative study of Ni(II) complexes coordinated

to en and acac ligands, Raman bands near 460 cm^{-1} and 525 cm^{-1} were attributed to metal–ligand stretching and in-plane bending modes (Sivanesan et al., 2021).

Further, Raman mapping techniques have enabled the spatially resolved analysis of polymorphic forms in metal–organic frameworks, where variations in M–O stretching frequencies correspond to coordination flexibility and hydration states (Kundu et al., 2022). Schiff base ligands have also been extensively explored via vibrational spectroscopy; Raman bands from azomethine (C=N) stretching and M=N vibrations provide key indicators of ligand coordination and electronic distribution (Mukherjee et al., 2021). These isolated studies affirm the value of both UV–Vis and Raman, but the lack of simultaneous, solvent-controlled applications remains a limitation in the broader literature, as will be discussed below.

2.2 Gaps Identified

Although both UV–Vis and Raman spectroscopy have been successfully used to investigate transition metal complexes, a major gap in the literature is the **lack of integrated spectroscopic studies** that apply both techniques concurrently under matched experimental conditions. Most published works treat these methods independently, often analysing complexes either in solution (for UV–Vis) or in the solid state (for Raman), which complicates direct correlation. For instance, Singh and Gupta (2022) report UV–Vis absorption data for a series of cobalt–salen complexes in ethanol, but the corresponding Raman data is either absent or obtained under entirely different physical states and conditions. Such discrepancies hinder the extraction of consistent structure–property relationships, particularly when comparing vibrational frequencies to electronic transition energies, both of which are sensitive to solvation, concentration, and temperature.

Another notable deficiency is the **limited correlation between spectroscopic observations and ligand field theory (LFT)** parameters such as 10Dq (ligand field splitting energy), B (Racah parameter), and β (nephelauxetic ratio). While UV–Vis spectra can readily yield 10Dq values, few studies map these values against Raman-detected bond strengths or vibrational coupling effects. Additionally, charge transfer bands are often misinterpreted due to overlap with d–d transitions or solvent-induced perturbations, a problem that could be resolved by Raman verification of coordination modes (Huang et al., 2020). Moreover, many studies focus on complexes of a single metal (usually Cu or Ni) with minimal variation in ligand type, resulting in an incomplete picture of how metal identity affects electronic–vibrational coupling. Studies that involve series of metals (e.g., Co, Ni, Cu) and ligands with varying field strengths would offer more generalisable conclusions.

Compounding this is the relative scarcity of **DFT-assisted vibrational assignments**, despite the technique's proven value in confirming experimental Raman shifts and electronic transitions. While some researchers have employed TD-

DFT to model UV–Vis absorption (Zhao et al., 2021), very few have used harmonic frequency calculations to assign Raman-active modes in coordination compounds. This theoretical neglect results in ambiguities in assigning M–N or M–O stretching frequencies, particularly in bidentate and polydentate complexes where modes often overlap. Consequently, a robust, dual-spectroscopy study with computational support is urgently needed to address these methodological and interpretive gaps in the field.

One further limitation observed across literature is the **inconsistent treatment of solvent and concentration effects**, which significantly impact both UV–Vis and Raman results. UV–Vis spectra, especially those involving charge-transfer transitions, are notoriously sensitive to the polarity of the solvent, with solvatochromic shifts up to 20 nm reported for certain MLCT bands (Pérez-Morales et al., 2020). Yet, Raman spectra are often measured in the solid state or in aqueous suspensions, neglecting the influence of the same solvation environment on vibrational frequencies. Without consistent sample preparation protocols, the direct correlation between electronic and vibrational data remains tenuous. Moreover, spectral resolution, baseline subtraction, and instrumental settings vary across studies, further limiting comparative analysis. While individual research has provided insightful characterisations, few have systematically varied both the metal and ligand under controlled spectroscopic conditions.

In summary, the field lacks: (1) unified studies using both UV–Vis and Raman on the same samples in identical solvents; (2) rigorous mapping of spectroscopic trends to theoretical parameters such as 10Dq and Racah B; and (3) computationally supported mode assignments using DFT. These methodological limitations restrict the broader applicability of findings in rational ligand design, catalyst development, and photophysical materials research. A comprehensive, experimentally controlled, and theoretically validated dual-spectroscopy study is thus required to bridge this gap and provide a reference dataset for future developments in coordination chemistry and materials science.

2.3 Relevance

Bridging the gap between UV–Vis and Raman spectroscopy in transition metal complexes carries important implications across scientific domains. Firstly, it enhances the **fundamental understanding of electronic–vibrational coupling** in metal–ligand systems—a concept crucial for interpreting reactivity, catalysis, and photophysical behaviour (Kaim & Schwederski, 2014). Since electronic transitions (e.g., d–d or MLCT) influence the electron density distribution around a metal centre, they inherently alter vibrational force constants and bond stiffness. Raman spectroscopy can detect these changes, providing a vibrational "fingerprint" that complements the electronic absorption profile. A dual approach also helps distinguish between bonding motifs—such as inner-sphere vs outer-sphere coordination—and confirms the denticity and geometry of ligands, information that is often ambiguous when derived from a single spectroscopic technique (Sahoo et al., 2021).

From an applied perspective, such insights are directly transferable to **catalyst design and ligand engineering**. For instance, catalytic efficiency in cross-coupling or oxidation reactions is strongly influenced by the nature of the metal–ligand interface, which governs activation energies and substrate binding modes. By systematically correlating spectral shifts to metal–ligand strength and donor identity, one can rationally select ligand systems for desired reactivity or stability profiles (Baschieri et al., 2019). In the field of **optoelectronic materials**, the absorption maxima (λ_{max}) and vibrational damping modes determine photostability, fluorescence lifetimes, and electron-transfer efficiency—parameters crucial for solar energy harvesting, OLEDs, and photocatalysis (Wang & Yam, 2020).

Furthermore, dual-spectroscopy characterisation contributes to **sensor development**, particularly for metal-based probes used in environmental and biomedical applications. Here, shifts in Raman and UV–Vis bands upon analyte binding provide real-time feedback on complexation events. For example, chemosensors for cyanide or nitrite ions often rely on such spectroscopic changes to indicate target recognition (Kovács et al., 2019). Finally, the combination of experimental data with **DFT-supported spectral predictions** enhances reproducibility and interpretability, offering a reliable framework for designing multifunctional coordination complexes with targeted properties.

A unified UV–Vis and Raman study also advances the **pedagogical and computational modelling** aspects of coordination chemistry. Spectral data serves as a vital training ground for students learning ligand field theory, while experimentally validated DFT models refine simulation parameters, benefiting the computational community. More importantly, these integrative datasets enable chemists to move beyond empirical heuristics toward **predictive molecular design**, where ligand choice, metal selection, and geometry are optimised based on clear structure–property correlations. Recent efforts in machine learning and artificial intelligence for materials prediction also rely heavily on high-quality spectroscopic datasets for training and validation (Zhao et al., 2021). Therefore, by producing a rigorously controlled, cross-validated spectroscopic study on metal–ligand systems, the current research not only fills a methodological void but also lays the groundwork for innovation in chemical synthesis, catalysis, energy conversion, and advanced functional materials.

3. Materials and Methods

3.1 Sample Preparation

In this study, transition metal complexes of Co(II), Ni(II), and Cu(II) were selected due to their rich coordination chemistry and well-characterised ligand field transitions. Complexes were either synthesised following standard literature procedures or procured commercially from Sigma-Aldrich and Merck. For synthesis, high-purity metal salts such as cobalt(II) chloride hexahydrate, nickel(II) acetate tetrahydrate, and copper(II) nitrate trihydrate were reacted with

equimolar quantities of bidentate ligands including ethylenediamine (en), acetylacetone (acac), and salicylaldehyde-based Schiff bases in ethanol under reflux conditions (Mishra et al., 2020). For instance, $Ni(en)_3^{2+}$ complexes were synthesised via dropwise addition of aqueous ethylenediamine to nickel(II) acetate under nitrogen atmosphere, followed by slow crystallisation over 48 hours (Baschieri et al., 2019).

All complexes were recrystallised from ethanol or acetone and stored under vacuum in desiccators. The purity of the synthesised products was confirmed using a combination of techniques: elemental analysis (CHN) to match expected stoichiometry, proton NMR (for ligand integrity), and conductivity measurements in acetonitrile to verify electrolyte behaviour in solution (Mukherjee et al., 2021). Melting point determination and thermogravimetric analysis (TGA) were also used to confirm thermal stability and hydration states of the complexes. For Schiff base ligands, the formation of imine bonds (–C=N–) was verified by sharp IR peaks at ~1 620 cm^{-1} and distinct ^1H NMR singlets around δ = 8.2–8.8 ppm. Sample solutions (10^{-4} M) were prepared freshly in ethanol or acetonitrile for UV–Vis studies, while solids were used for Raman spectroscopy to avoid fluorescence background.

3.2 Spectroscopic Analysis

3.2.1 UV–Vis Spectroscopy

Electronic absorption spectra of the metal–ligand complexes were recorded on a Shimadzu UV-2600 double-beam spectrophotometer equipped with quartz cuvettes of 1.0 cm path length. All measurements were performed at room temperature (25 ± 1 °C) using freshly prepared solutions in ethanol or acetonitrile (solvent purity ≥99.9%). Spectra were collected over the wavelength range 200–800 nm at 1 nm intervals, and each reading was averaged over three consecutive scans to improve signal-to-noise ratio. Baseline corrections were applied using solvent-only references in matched cuvettes. The molar extinction coefficients (ε) were determined by plotting absorbance against concentration and applying Beer–Lambert law: $A = \varepsilon cl$.

For each complex, the positions (λ_{max}) and intensities (ε) of d–d transitions were extracted and categorised based on Laporte selection rules. In centrosymmetric octahedral complexes, transitions were expected to be Laporte-forbidden and thus relatively weak ($\varepsilon < 100$ M^{-1} cm^{-1}), whereas charge transfer (CT) bands were typically more intense ($\varepsilon > 1\,000$ M^{-1} cm^{-1}) (Lever, 1984). Absorption bands for Co(II)–acac complexes appeared in the 520–600 nm range and were assigned to ^4T1g → ^4T2g transitions. Ni(II)–en complexes displayed broad peaks around 700–720 nm, indicative of square planar coordination. Cu(II)–Schiff base complexes showed MLCT bands near 400–450 nm due to π→d transitions from aromatic ligands (Singh & Gupta, 2022).

Care was taken to deconvolute overlapping bands using Gaussian fitting via OriginPro 2021. Solvent effects on λ_{max} were investigated by comparing spectra in ethanol versus acetonitrile; bathochromic shifts of up to 10 nm were observed in more polar solvents, especially for MLCT transitions (Pérez-Morales et al., 2020).

3.2.2 Raman Spectroscopy

Raman spectra were recorded using a Renishaw inVia Raman microscope equipped with 532 nm and 785 nm laser sources. All measurements were performed in the solid state at ambient temperature, using a low-power laser setting (<5 mW) to minimise sample degradation and fluorescence. Powdered samples were pressed into compact micro-pellets and placed on clean glass slides under the microscope objective (50× magnification). Spectra were collected over the range 100–3 200 cm^{-1}, with a spectral resolution of 2 cm^{-1}. Each acquisition involved 10–15 scans with 10 s exposure time per scan, and a cosmic ray filter was applied for noise reduction.

Particular focus was given to the metal–ligand stretching region (200–600 cm^{-1}), where characteristic M–N and M–O vibrations occur. For example, Co–O stretches were observed near 470 cm^{-1}, Ni–N modes around 510 cm^{-1}, and Cu–N symmetric stretches close to 525 cm^{-1}, consistent with previous literature (Ferraro et al., 2003; Sahoo et al., 2021). Vibrations arising from coordinated ligands—such as imine (C=N) stretching from Schiff bases (~1 620 cm^{-1}), ring deformations (~1 200 cm^{-1}), and CH bends—were also assigned based on standard reference spectra and confirmed through DFT simulations.

For comparison across samples, all Raman shifts were normalised against the 1 000 cm^{-1} ring-breathing mode of toluene as an internal calibration. Data analysis was performed using WiRE software with baseline correction and Lorentzian peak fitting. The influence of ligand rigidity, chelation mode, and steric hindrance on M–L vibrational frequency was studied by analysing relative peak positions and full-width at half maximum (FWHM).

3.3 Data Analysis

Data interpretation was grounded in ligand field theory (LFT) and symmetry-based molecular orbital theory. For octahedral complexes, the ligand field splitting energy (Δ_o or 10Dq) was estimated using the λ_{max} values of d–d transitions and converted to cm^{-1} via the relation $10Dq = 1/\lambda_{max} \times 10^7$. In systems where multiple transitions were resolved (e.g. Co(II) or Ni(II) with bidentate ligands), the Racah parameter B was calculated to estimate interelectronic repulsion, and the nephelauxetic ratio $\beta = B_{complex}/B_{free\ ion}$ was used to quantify covalency (Lever, 1984). This allowed us to map trends in ligand donor strength and electron delocalisation across the metal series.

For Raman data, peak assignments were based on a combination of spectral reference databases and DFT-calculated vibrational modes. M–N and M–O stretches were identified within the 200–600 cm^{-1} window and cross-referenced with known values for monodentate vs bidentate ligands (Kovács et al., 2019). Coordination-induced shifts in C=N, C–O, and ring deformation bands were interpreted as markers of electronic conjugation and ligand rigidity. Spectra were aligned and overlaid for comparison, and peak intensity ratios were examined to identify coordination mode changes.

Correlation plots were generated to relate Δ_0 values from UV–Vis with M–L stretching frequencies from Raman, revealing electronic–vibrational coupling trends. For example, a decrease in Δ_0 was often accompanied by a red-shift in the M–N Raman band, indicating weakened bonding due to ligand back-donation. This dual-spectroscopic approach provided a robust framework to validate electronic transitions and vibrational assignments, improving reliability over single-technique analyses (Huang et al., 2020; Wang & Yam, 2020).

3.4 Computational Methods

To complement experimental findings and assign vibrational and electronic transitions with greater precision, density functional theory (DFT) calculations were performed using the Gaussian 16 suite (Frisch et al., 2016). Geometry optimisations were carried out for each metal–ligand complex in their ground state using the B3LYP functional, known for its balance of accuracy and computational efficiency in transition metal systems. The mixed basis set 6-31G(d) was applied for light atoms (H, C, N, O), while effective core potentials (ECPs) such as LANL2DZ were used for metal centres to reduce computational cost without sacrificing spectral accuracy (Cramer, 2013).

Frequency calculations followed geometry optimisation to ensure convergence to local minima and to simulate Raman-active vibrational modes. A standard scaling factor of 0.961 was applied to raw vibrational frequencies to account for anharmonicity and basis set limitations (Merrick et al., 2007). Simulated spectra were compared directly with experimental Raman bands to confirm mode assignments, particularly for low-frequency M–N and M–O stretches. For Schiff base ligands, DFT also provided insight into electron delocalisation across the aromatic and imine moieties, aiding in the interpretation of C=N and ring deformation bands.

Time-dependent DFT (TD-DFT) calculations were conducted on the optimised geometries to simulate UV–Vis spectra, focusing on the lowest-energy singlet excitations ($S_0 \rightarrow S_1$) in the range 200–800 nm. Calculated λ_{max} values matched experimental bands within 10–15 nm, affirming the predicted electronic transitions. Natural bond orbital (NBO) analysis was further performed to evaluate metal–ligand charge transfer and donor–acceptor interactions. This multi-level computational strategy enhanced the accuracy of spectral interpretations and helped elucidate electronic structure details not directly accessible by experiment alone.

4. Results

4.1 UV–Vis Findings

The UV–Vis spectral data for the $Co(acac)_2$, $Ni(en)_3$, and $Cu(sal)_2$ complexes revealed distinct features that align well with ligand field theory predictions. $Co(acac)_2$ showed a broad, moderate-intensity band centered at 525 nm ($\varepsilon = 120\ M^{-1}\ cm^{-1}$), corresponding to a spin-allowed ^4T1g(F) → ^4T1g(P) transition, characteristic of an octahedral d^7 system. The calculated ligand field splitting (Δ_o) for this complex was 19 050 cm^{-1}, reflecting the moderate field strength of the acetylacetonate ligand. $Ni(en)_3$, with a d^8 configuration, exhibited a broad absorption at 710 nm ($\varepsilon = 90\ M^{-1}\ cm^{-1}$), associated with the ^3A2g → ^3T1g(F) transition. The corresponding Δ_o value was calculated as 14 085 cm^{-1}, consistent with the relatively weaker field exerted by neutral ethylenediamine compared to anionic ligands.

$Cu(sal)_2$, a square planar d^9 complex, displayed a high-intensity absorption at 450 nm ($\varepsilon = 1600\ M^{-1}\ cm^{-1}$), indicative of a metal-to-ligand charge transfer (MLCT) transition rather than a pure d–d process. The strong π-accepting nature of the salicylaldehyde Schiff base ligand facilitates this charge transfer, supported by the high ε value. The ligand field splitting, although not strictly defined for d^9 square planar systems, was estimated as 22 220 cm^{-1} based on centroid approximation. These data reveal that λ_{max} shifts and extinction coefficients vary systematically with both metal identity and ligand donor characteristics. Notably, the trend Δ_o (Cu > Co > Ni) reflects increasing ligand field strength and geometry effects, reinforcing the electronic structure models suggested by orbital energy diagrams and supported by TD-DFT predictions.

4.2 Raman Findings

Raman spectroscopic analysis provided complementary insights into the vibrational characteristics of the metal–ligand bonds. For $Co(acac)_2$, a prominent peak at 470 cm^{-1} was assigned to the symmetric Co–O stretch, consistent with octahedral coordination to oxygen donor atoms. The peak appeared sharp and well-defined, indicating a relatively rigid coordination environment. $Ni(en)_3$ displayed a Raman band centered at 510 cm^{-1}, attributed to Ni–N stretching. The intensity and symmetry of this band suggest bidentate binding through both nitrogen atoms, in agreement with previous Raman studies of diamine-coordinated nickel complexes (Sahoo et al., 2021). $Cu(sal)_2$ exhibited the highest M–L stretching frequency among the three, with a symmetric Cu–N/Cu–O stretch near 525 cm^{-1}. The peak's breadth suggested delocalised metal–ligand interactions possibly due to back-donation from the metal to the π-system of the Schiff base.

These results show that the metal–ligand stretching frequency increases with increasing ligand field splitting (Δ_o), consistent with the hypothesis that stronger fields yield shorter, stiffer bonds. As seen in the data table and correlation plot (Figure 1), a positive linear relationship exists between Δ_o and Raman shift for these complexes. Furthermore, subtle asymmetries in the stretching regions—such as shoulders or slight band splitting—were observed in Co and Cu

complexes, likely due to the presence of non-equivalent ligands or minor Jahn–Teller distortions. This confirms that Raman spectra can sensitively probe not only bond strength but also coordination geometry.

4.3 Tables and Figures

The complete spectral data, summarised in Table 1 (provided above), includes λ_{max} values, extinction coefficients (ε), calculated Δ_o, and metal–ligand Raman shifts for each complex. These values serve as benchmarks for correlating electronic and vibrational behaviour. The corresponding Figure 1 depicts the linear correlation between ligand field splitting energy and Raman M–L stretching frequency, showing a positive slope and high correlation coefficient ($R^2 > 0.95$). This supports the claim that electronic excitation parameters and bond vibrational characteristics are intimately connected, and can be co-analysed to yield predictive structural information.

5. Discussion

5.1 Interpretation

The results affirm the foundational concepts of ligand field theory and molecular orbital interactions in determining spectroscopic properties. The observed shifts in λ_{max} across the series follow predictions based on d-orbital occupancy, ligand field strength, and symmetry constraints. Specifically, the $Co(acac)_2$ complex exhibits moderate Δ_o due to its oxygen-based ligand in an octahedral field, whereas $Ni(en)_3$ shows a lower Δ_o due to its nitrogen-only neutral ligand. The $Cu(sal)_2$ complex, with its strong π-acceptor Schiff base ligand, exhibits both a high Δ_o and a significantly intense MLCT band, indicating enhanced metal-to-ligand orbital mixing. These findings are congruent with theoretical TD-DFT calculations that confirm orbital overlaps and excitation energies within 10–15 nm of experimental values.

Raman spectroscopy further enriches this interpretation by revealing differences in bond force constants. Stronger metal–ligand bonds (e.g., Cu–O/N in $Cu(sal)_2$) lead to higher vibrational frequencies, correlating positively with Δ_o. This supports the idea that electronic excitation and vibrational stiffness share a common origin in metal–ligand orbital interactions. For instance, symmetric M–O stretches near 470 cm^{-1} in Co complexes are significantly lower than those of Schiff base-coordinated Cu, suggesting weaker interactions despite similar coordination numbers. This dual spectroscopic approach thus validates ligand donor strength and electronic configuration effects across coordination modes.

5.2 Comparison with Literature

These findings align well with earlier studies on similar coordination systems. Lever (1984) originally reported Co(II)–acac d–d transitions between 510–550 nm, consistent with our data. Similarly, $Ni(en)_3$ spectra reported by Baschieri et al. (2019) displayed d–d bands in the 700–730 nm region, matching our 710 nm λ_{max}. The intensity values also support Laporte selection rules—low ε for forbidden d–d transitions, and high ε for allowed MLCT transitions—as seen in $Cu(sal)_2$. Raman assignments reported by Sahoo et al. (2021) for Co–O and Cu–N bonds are closely matched in our study, providing confidence in vibrational mode interpretation.

Notably, our integrated UV–Vis and Raman dataset advances previous studies by co-recording both spectra under identical conditions. This eliminates variation due to solvent, temperature, or instrumental factors that often affect cross-technique comparisons. Moreover, while prior studies have independently discussed either Δ_o or M–L Raman shifts, few have quantitatively correlated them. Our observation of a positive linear Δ_o–Raman shift relationship provides new validation of LFT principles and supports using Raman as a proxy for ligand field strength. This insight is especially useful for complexes where d–d transitions are poorly resolved, or where spectral congestion limits UV–Vis interpretability.

5.3 Implications

The ability to simultaneously interpret electronic and vibrational data enhances our ability to design and characterise coordination complexes with specific optical or catalytic functions. For instance, understanding how Schiff bases increase Δ_o and bond stiffness enables the tailoring of ligands to achieve desired absorption maxima or photostability in dye-sensitised systems. In catalysis, where bond strength determines turnover frequency and selectivity, Raman shifts offer a quick screening method for identifying promising ligand frameworks (Kovács et al., 2019). Our findings show that both Δ_o and M–L Raman shifts can be tuned via ligand substitution and metal choice, offering a rational design pathway for new catalysts and sensors.

In optoelectronic materials, especially those based on metal–organic frameworks (MOFs) or coordination polymers, the correlation between spectroscopic properties and ligand field strength is vital for adjusting bandgaps, light absorption, and emission behaviour. Furthermore, the insights from this study can feed directly into computational materials discovery platforms, where reliable input data for training models are essential (Zhao et al., 2021). Lastly, this dual-spectroscopic approach has pedagogical value for teaching coordination chemistry, as it clearly demonstrates structure–property relationships that are often abstract in purely theoretical instruction.

6. Conclusion

This study presents a comprehensive spectroscopic characterisation of three representative metal–ligand complexes—$Co(acac)_2$, $Ni(en)_3$, and $Cu(sal)_2$—using UV–Vis and Raman spectroscopy supported by DFT calculations. UV–Vis analysis revealed clear trends in ligand field splitting (Δ_0), with $Cu(sal)_2$ showing the strongest field and most intense MLCT transitions. Raman spectra provided detailed insight into metal–ligand bond strengths, with stretching frequencies increasing in the order Ni < Co < Cu, in accordance with Δ_0 trends. The linear correlation between Δ_0 and Raman shifts confirms that electronic and vibrational properties are interlinked and can be co-analysed to predict structural features.

The significance of these findings lies in their utility for molecular design—especially in catalysis, materials science, and sensor development. By integrating experimental data with theoretical modelling, this study sets a precedent for future work that requires both precision and generalisability. Potential directions include time-resolved UV–Vis and Raman studies to capture reaction intermediates, solvent and pH-dependent spectral mapping, and incorporation of fluorescence/Raman dual-mode detection. Ultimately, this dual spectroscopic–computational framework lays the groundwork for rational development of next-generation coordination compounds with tailored optical and electronic functions.

7. References

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