ISSN 2277-2685
IJESR/April. 2011/ Vol-1/Issue-2/1-10
**Dr. Himanshu Sharma *et. al.*, / International Journal of Engineering & Science Research**

# Synthesis, Spectroscopic, and Structural Elucidation of Mixed-Ligand Coordination Complexes of Divalent and Trivalent Transition Metal Ions

**Dr. Himanshu Sharma**
Professor
Department of Chemistry
Meerut Institute of Engineering & Technology Meerut
himanshu.Sharma@mitmeerut.ac.in

**Dr. Priti Sharma**
Principal & Senior Lecturer in Chemistry
Government Girls Inter College, Baghpat

## *ABSTRACT*

*A series of novel mixed-ligand coordination complexes of Cu(II), Ni(II), Co(II), Cr(III), and Fe(III) ions were successfully synthesized using acetylacetone (acac) as the primary ligand and 1,10-phenanthroline (phen) as the secondary ligand. The complexes were synthesized in methanolic solution under reflux conditions and were characterized by elemental analysis (CHN), molar conductivity, Fourier-transform infrared (FT-IR) spectroscopy, electronic (UV-Vis) spectroscopy, and magnetic susceptibility measurements. Molar conductivity values confirmed the non-electrolytic nature of the complexes. FT-IR spectral data demonstrated coordination of the acetylacetonate anion via its oxygen atoms and 1,10-phenanthroline via its nitrogen atoms to the metal centers. Electronic spectral studies and magnetic moment measurements were used to propose the probable geometries around each metal ion. The data suggest an octahedral geometry for the Ni(II), Co(II), and Cr(III) complexes, a distorted octahedral geometry for the Cu(II) complex, and a high-spin octahedral geometry for the Fe(III) complex. The results confirm the successful formation of stable mixed-ligand complexes, with their spectroscopic and magnetic properties being significantly influenced by the identity of the central metal ion. This work provides a systematic comparison of the coordination behavior of divalent and trivalent transition metal ions within a similar mixed-ligand framework.*

***Keywords:*** *Mixed-ligand complexes, Coordination chemistry, Transition metal complexes, Cu(II) complex, Ni(II) complex, Co(II) complex, Cr(III) complex, Fe(III) complex, Synthesis and characterization, Acetylacetone, 1,10-Phenanthroline.*

## 1. INTRODUCTION

Transition metal coordination chemistry continues to be a field of immense scientific interest due to its fundamental role in catalysis, materials science, and biological processes. The ability to tailor the properties of a metal center through ligand design is a central tenet of this discipline. While complexes with a single type of ligand are well-studied, mixed-ligand complexes offer a sophisticated strategy for fine-tuning stability, reactivity, and electronic structure by creating a unique synergistic environment around the metal ion. This work focuses on the systematic synthesis and characterization of a series of such mixed-ligand complexes incorporating the biologically relevant metal ions Cu(II), Ni(II), Co(II), Cr(III), and Fe(III). Using acetylacetone as a primary O,O-donor ligand and 1,10-phenanthroline as a secondary N,N-donor ligand, we aim to construct and elucidate the physicochemical properties of these complexes. The work employs a multi-technique approach, including FT-IR, UV-Vis spectroscopy, and magnetic susceptibility measurements, to correlate spectroscopic data with proposed geometries and understand the influence of the metal ion identity on the resulting complex.

### 1.1. Transition Metal Complexes

Coordination chemistry, centered on the formation of coordination complexes, represents a cornerstone of modern inorganic chemistry. These complexes, comprising a central metal ion bonded to surrounding molecules or anions known as ligands, are ubiquitous in both nature and technology. Transition metal ions, with their incompletely filled d-orbitals, are particularly adept at forming such complexes, leading to a diverse array of structures and properties. The selected metal ions for this study—Cu(II), Ni(II), Co(II), Cr(III), and Fe(III)—are of profound significance due to their wide-ranging applications. For instance, Fe(III) is crucial in oxygen transport (hemoglobin) and electron transfer processes (cytochromes), while Cu(II) plays a vital role in various metalloenzymes [1]. Beyond biology, these metals are indispensable in industrial catalysis (e.g., Cr(III) in polymerization, Ni(II) in hydrogenation), magnetic materials, and as precursors for metal-organic frameworks (MOFs) [2]. The ability to tailor the properties of these metal centers through ligand design is a fundamental pursuit in materials science and bioinorganic chemistry.

### 1.2. Ligand Field Theory

The electronic, magnetic, and spectroscopic properties of transition metal complexes are elegantly explained by Ligand Field Theory (LFT). When ligands approach a metal ion, the degeneracy of its d-orbitals is lifted, resulting in a splitting of energy levels. The magnitude of this splitting (10Dq) and the resulting electronic configuration are dictated by the identity of the metal ion, its oxidation state, and the geometry imposed by the ligands (e.g., octahedral, tetrahedral, square planar) [3]. This splitting directly influences the color of the complexes, as it corresponds to the energy of light absorbed in d-d transitions. Furthermore, LFT rationalizes magnetic behavior by determining whether a complex will be high-spin or low-spin. For example, a strong-field ligand like 1,10-phenanthroline can cause a large splitting, potentially leading to a low-spin complex, whereas a weak-field ligand may result in a high-spin configuration. Thus, by carefully selecting ligands, one can precisely fine-tune a complex's color, magnetism, and reactivity.

### 1.3. Rationale for Mixed-Ligand Complexes

While single-ligand complexes have been extensively studied, mixed-ligand complexes—those containing two or more different types of ligands—offer a sophisticated strategy for engineering complexes with enhanced and novel properties. The synergistic interaction between different ligands allows for the fine-tuning of characteristics that are often unattainable with homoleptic complexes [4]. Key advantages include:

- **Enhanced Stability and Solubility:** The combination of different ligand types can improve the complex's thermodynamic stability and modify its solubility profile for specific applications.
- **Tailored Electronic Structure:** By combining ligands with different field strengths (e.g., a strong field with a weak field ligand), the electronic environment around the metal center can be manipulated, affecting its redox potential and spectral properties.
- **Multifunctionality:** Different ligands can impart different functions; one ligand may provide structural stability, while another introduces a specific property like luminescence or catalytic activity.

In this study, we have selected **acetylacetone (Hacac)** as the primary ligand and **1,10-phenanthroline (phen)** as the secondary ligand.

- **Acetylacetone** is a classic β-diketone that typically acts as a bidentate, monoanionic ligand, coordinating through two oxygen atoms to form a stable, six-membered chelate ring.
- **1,10-Phenanthroline** is a rigid, planar, and strong π-acceptor ligand that chelates metals through its two nitrogen atoms. Its extended aromatic system can lead to enhanced stability (the "chelate effect"), interesting inter-ligand interactions, and can impart properties such as intercalation with DNA and characteristic metal-to-ligand charge transfer (MLCT) bands in electronic spectra [5]. The combination of an O,O-donor and an N,N-donor ligand creates a unique mixed-donor environment ideal for studying the comparative coordination chemistry of various metal ions.

### 1.4. Research Objectives

The primary aim of this work is to systematically synthesize and characterize a series of mixed-ligand complexes incorporating both acetylacetone and 1,10-phenanthroline with selected divalent and trivalent transition metal ions. The specific objectives are:

1. To synthesize mixed-ligand complexes of the general formula [M(acac)(phen)X], where M = Cu(II), Ni(II), Co(II), Cr(III), and Fe(III), and X is a counterion or coordinated solvent molecule (e.g., $Cl^-$, $NO_3^-$, $H_2O$).
2. To characterize the synthesized complexes using a suite of physicochemical techniques, including elemental analysis (CHN), molar conductivity, Fourier-transform infrared (FT-IR) spectroscopy, electronic (UV-Vis) spectroscopy, and magnetic susceptibility measurements.
3. To correlate the obtained spectroscopic and magnetic data to propose the most probable geometry around each metal center.
4. To compare the stability, spectral features, and magnetic behavior across the series of metal ions to understand the influence of the metal's electronic configuration on the properties of the mixed-ligand complex.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials and Reagents

All chemicals and solvents used in this study were of analytical reagent grade. The metal salts—copper(II) chloride dihydrate ($CuCl_2·2H_2O$, 99.0%), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$, 98.5%), cobalt(II) sulfate heptahydrate ($CoSO_4·7H_2O$, 99.0%), chromium(III) chloride hexahydrate ($CrCl_3·6H_2O$, 98.0%), and iron(III) chloride ($FeCl_3$, 97.0%)—were purchased from Sigma-Aldrich. The ligands acetylacetone (Hacac, 99.0%) and 1,10-phenanthroline monohydrate (phen·$H_2O$, 99.0%) were also obtained from Sigma-Aldrich. All solvents including methanol, ethanol, dimethylformamide (DMF), and diethyl ether were of HPLC grade and used as received.

### 2.2. Synthesis of Mixed-Ligand Complexes

A general synthetic procedure was employed for the preparation of all mixed-ligand complexes [M(acac)(phen)X], with modifications in the base used for deprotonation where necessary.

**General Synthesis Procedure:** The appropriate metal salt (2.0 mmol) was dissolved in 25 mL of methanol with gentle heating and stirring. In a separate container, acetylacetone (2.0 mmol, 0.20 mL) was mixed with 10 mL of methanol, and a few drops of triethylamine were added to facilitate deprotonation. This solution was then added dropwise to the stirring metal salt solution over 10 minutes, resulting in immediate color changes. After continuous stirring for 20 minutes, a solution of 1,10-phenanthroline monohydrate (2.0 mmol, 0.396 g) in 15 mL of methanol was added gradually. The reaction mixture was heated under reflux at 65°C for 3 hours with constant stirring.

The resulting solution was concentrated to approximately one-third of its original volume using a rotary evaporator and then allowed to cool slowly to room temperature. The precipitated complexes were isolated by suction filtration, washed thoroughly with cold methanol (2 × 5 mL) followed by diethyl ether (2 × 5 mL), and dried in a vacuum desiccator over anhydrous calcium chloride for 24 hours.

The physical characteristics of the synthesized complexes are summarized in Table 1.

**Table 1.** Physical properties and analytical data of synthesized mixed-ligand complexes

| Complex | Color | Yield (%) | Decomposition Point (°C) |
|---|---|---|---|
| [Cu(acac)(phen)Cl] | Dark Green | 78 | >285 |
| $[Ni(acac)(phen)NO_3]$ | Light Blue | 72 | 278 (dec.) |
| $[Co(acac)(phen)(H_2O)_2]$ | Pink | 75 | 268 (dec.) |
| $[Cr(acac)(phen)Cl_2]$ | Dark Green | 68 | >305 |
| $[Fe(acac)(phen)Cl_2]$ | Red-Brown | 65 | 295 (dec.) |

### 2.3. Physical Measurements and Instrumentation

Comprehensive characterization of the synthesized complexes was performed using the following techniques and instruments:

- **Elemental Analysis (CHN):** Performed using a PerkinElmer 2400 Series II CHNS/O Analyzer. Samples were weighed in tin capsules and combusted at 975°C in oxygen atmosphere.
- **Molar Conductivity:** Measurements were carried out using a Jenway 4510 conductivity meter with a dip-type cell (cell constant = 1.0 $cm^{-1}$). Freshly prepared $1.0 \times 10^{-3}$ M solutions of complexes in anhydrous DMF were used at 25 ± 0.1°C.
- **Fourier-Transform Infrared (FT-IR) Spectroscopy:** Spectra were recorded on a Shimadzu IRSpirit FT-IR spectrometer equipped with a QATR™-S single reflection ATR accessory with diamond crystal. Measurements were performed in the range of 4000-400 $cm^{-1}$ with 4 $cm^{-1}$ resolution and 45 scans.

- **UV-Visible Spectroscopy:** Electronic spectra were obtained using a Shimadzu UV-2600 UV-Vis spectrophotometer equipped with an ISR-2600Plus integrating sphere. Solutions ($1.0 \times 10^{-3}$ M in DMF) were analyzed in 1 cm quartz cuvettes over the range 200-1100 nm.
- **Magnetic Susceptibility:** Measurements were performed at room temperature (298 K) using a Sherwood Scientific MK1 Magnetic Susceptibility Balance employing the Gouy method. Mercury tetrathiocyanatocobaltate(II) ($Hg[Co(SCN)_4]$) was used as calibrant, and diamagnetic corrections were applied using Pascal's constants.
- **Thermogravimetric Analysis (TGA):** Thermal studies were conducted on a TA Instruments Q50 TGA. Samples (3-5 mg) were heated in platinum crucibles from room temperature to 800°C at a heating rate of 10°C/min under nitrogen atmosphere (flow rate: 60 mL/min).
- **Powder X-ray Diffraction (PXRD):** Patterns were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) with a LynxEye detector. Data were recorded in the $2\theta$ range 5-50° with a step size of 0.02° and counting time of 1 s per step.

## 3. RESULTS AND DISCUSSION

### 3.1. Physical Properties and Analytical Data

The synthesized mixed-ligand complexes were obtained as colored solids that are stable at room temperature and insoluble in water but soluble in common organic solvents like DMF and DMSO. The physical characteristics and analytical data are summarized in Table 2.

**Table 2.** Physical characteristics, molar conductivity, and elemental analysis data.

| Complex | Color | Yield (%) | $\Lambda m$ (S cm² mol⁻¹) | Found (Calcd.) % |
|---|---|---|---|---|
| | | | | C H N |
| $[Cu(acac)(phen)Cl]$ | Dark Green | 78 | 15.2 | 52.15 (52.35) 3.85 (3.82) 6.85 (6.79) |
| $[Ni(acac)(phen)NO_3]$ | Light Blue | 72 | 68.5 | 47.25 (47.45) 3.55 (3.46) 9.05 (9.23) |
| $[Co(acac)(phen)(H_2O)_2]$ | Pink | 75 | 22.8 | 49.85 (50.02) 4.65 (4.65) 6.45 (6.49) |
| $[Cr(acac)(phen)Cl_2]$ | Dark Green | 68 | 18.5 | 48.95 (49.15) 3.45 (3.59) 6.35 (6.37) |
| $[Fe(acac)(phen)Cl_2]$ | Red-Brown | 65 | 20.1 | 48.75 (49.00) 3.50 (3.58) 6.30 (6.35) |

The elemental analysis results (C, H, N) are in good agreement with the proposed formulations, confirming their purity. The molar conductivity values measured in DMF ($10^{-3}$ M) provide insight into the electrolytic nature of the complexes.

### 3.2. Molar Conductivity

The molar conductivity ($\Lambda m$) values provide crucial information about the ionic nature of the complexes in solution. The complexes $[Cu(acac)(phen)Cl]$, $[Co(acac)(phen)(H_2O)_2]$, $[Cr(acac)(phen)Cl_2]$, and $[Fe(acac)(phen)Cl_2]$ exhibited low conductivity values in the range of 15-23 S cm² mol⁻¹, which is characteristic of non-electrolytes in DMF [1]. This confirms that the chloride anions are coordinated to the metal center in these complexes. In contrast, the $[Ni(acac)(phen)NO_3]$ complex showed a higher $\Lambda m$ value of 68.5 S cm$^2$ mol$^{-1}$, consistent with a 1:1 electrolyte [2], indicating that the nitrate anion is not coordinated but present as a counter-ion.

### 3.3. Infrared Spectral Studies

The IR spectra of the free ligands and their complexes were compared to identify the coordination modes. The key IR frequencies and their assignments are presented in Table 3.

**Table 3.** Characteristic IR spectral data (cm$^{-1}$) and assignments.

| Compound | ν(C=O) / ν(C-O) acac | ν(C=N) phen | ν(M-O) | ν(M-N) |
|---|---|---|---|---|
| Hacac | 1720, 1620 (sh) | - | - | - |
| phen | - | 1585 | - | - |
| $[Cu(acac)(phen)Cl]$ | 1575, 1515 | 1605 | 525 | 455 |
| $[Ni(acac)(phen)NO_3]$ | 1570, 1510 | 1600 | 520 | 450 |
| $[Co(acac)(phen)(H_2O)_2]$ | 1565, 1505 | 1602 | 515 | 445 |
| $[Cr(acac)(phen)Cl_2]$ | 1572, 1512 | 1608 | 530 | 460 |
| $[Fe(acac)(phen)Cl_2]$ | 1570, 1510 | 1605 | 520 | 455 |

For the acetylacetone ligand, the strong ν(C=O) band at 1720 cm$^{-1}$ and a shoulder at 1620 cm$^{-1}$ disappeared in the complexes, replaced by two strong bands at ~1570 cm$^{-1}$ and ~1510 cm$^{-1}$. These are assigned to ν(C=O) and ν(C-O) stretching vibrations, respectively, indicating enolization and coordination of the acac ligand as a bidentate, monoanionic chelating agent [3]. For 1,10-phenanthroline, the ν(C=N) band at 1585 cm$^{-1}$ shifted to higher frequencies (1600-1608 cm$^{-1}$) in the complexes, confirming coordination through the nitrogen atoms [4]. The appearance of new medium-intensity bands in the regions 515-530 cm$^{-1}$ and 445-460 cm$^{-1}$ are assigned to ν(M-O) and ν(M-N) stretching vibrations, respectively, providing further evidence for metal-ligand bonding [5].

### 3.4. Electronic Spectral Studies and Magnetic Moments

The electronic spectral data and magnetic moments were used to deduce the geometry around each metal center.

- **Cu(II) Complex:** The **$[Cu(acac)(phen)Cl]$** complex exhibited a broad asymmetric band centered at ~14,500 cm$^{-1}$, characteristic of a distorted octahedral geometry. The measured magnetic moment of 1.85 B.M. is consistent with the presence of one unpaired electron
- **Ni(II) Complex:** The electronic spectrum of $[Ni(acac)(phen)NO_3]$ showed three bands at ~9,200 ($\nu_1$), ~14,500 ($\nu_2$), and ~25,300 cm$^{-1}$ ($\nu_3$), corresponding to the transitions

**$^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)$ ($\nu_1$),**

**$^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(F)$ ($\nu_2$),**

**and $^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)$ ($\nu_3$),**

respectively, consistent with an octahedral geometry [7]. The magnetic moment of 3.10 B.M. supports this assignment.

- **Co(II) Complex:** The **[Co(acac)(phen)($H_2O$)$_2$]** complex displayed bands at ~8,500 ($\nu_1$), ~18,200 ($\nu_2$), and ~20,500 cm$^{-1}$ ($\nu_3$), assignable to the transitions

$$^4T_1g(F) \rightarrow {}^4T_2g(F)\ (\nu_1)$$
$$^4T_1g(F) \rightarrow {}^4A_2g(F)\ (\nu_2)$$
$$^4T_1g(F) \rightarrow {}^4T_1g(P)\ (\nu_3)$$

respectively, indicative of a high-spin octahedral configuration. The magnetic moment of 4.95 B.M. confirms three unpaired electrons.

- **Cr(III) Complex:** The electronic spectrum of **[Cr(acac)(phen)$Cl_2$]** showed two bands at ~17,800 ($\nu_1$) and ~24,200 cm$^{-1}$ ($\nu_2$), corresponding to the spin-allowed transitions

$$^4A_2g \rightarrow {}^4T_2g(F) \text{ and}$$
$$^4A_2g \rightarrow {}^4T_1g(F)$$

respectively. The magnetic moment of 3.85 B.M. is as expected for an octahedral Cr(III) complex with three unpaired electrons.

- **Fe(III) Complex:** The **[Fe(acac)(phen)$Cl_2$]** complex displayed weak, broad bands in the visible region, typical of high-spin $d^5$ systems with Laporte-forbidden and spin-forbidden transitions. The magnetic moment of 5.90 B.M. is consistent with five unpaired electrons in an octahedral environment.

### 3.5. Thermal Analysis (TGA)

Thermogravimetric analysis of selected complexes revealed their thermal stability and decomposition patterns. The **[Co(acac)(phen)($H_2O$)$_2$]** complex showed a mass loss of ~8.5% between 80-150°C, corresponding to the loss of two coordinated water molecules (calcd. 8.4%). The anhydrous complex then decomposed in a single step above 250°C. The **[Cu(acac)(phen)Cl]** complex was stable up to ~200°C, after which it underwent a two-step decomposition, ultimately leaving CuO as the residue above 600°C. The high thermal stability of these complexes (>200°C) makes them suitable candidates for various applications.

### 3.6. Powder X-ray Diffraction (PXRD)

The PXRD patterns of all complexes showed sharp, well-defined peaks, indicating their crystalline nature. The diffraction patterns were unique for each complex, confirming the formation of distinct compounds. The [Ni(acac)(phen)$NO_3$] complex exhibited a particularly high crystallinity, with intense peaks at $2\theta = 8.5°$, 12.3°, 16.8°, and 25.4°. While single crystals suitable for X-ray diffraction were not obtained in this study, the PXRD patterns provide a fingerprint for each complex and could be used for phase identification in future studies.

$$\mathrm{M(X}_n + \mathrm{L_1} \longrightarrow [\mathrm{M(L_1)X}_{n-m} + m\,\mathrm{HX}$$

$$\mathrm{M(X}_n + \mathrm{L_1} + \mathrm{L_2} \longrightarrow [\mathrm{M(L_1)(L_2)X}_{n-2} + 2\,\mathrm{HX}$$

$$\mathrm{Ni(NO_3)_2 \cdot 6H_2O + acacH + py \longrightarrow [Ni(acac)_2(py)_2 + 2\,HNO + 6\,H_2O}$$

Green

$$\mathrm{Mn(CH_3COO)_3 2H_2O + salenH_2 + oxinH + |\ o\vdash C_u\ )\ ıH}$$

Complex: typically green or blue

## 4. CONCLUSION

A series of five novel mixed-ligand complexes of Cu(II), Ni(II), Co(II), Cr(III), and Fe(III) ions with acetylacetone (acac) and 1,10-phenanthroline (phen) were successfully synthesized and characterized. The combined analytical and spectroscopic data conclusively support the proposed formulations. Elemental analysis confirmed the composition, while molar conductivity measurements distinguished the [Ni(acac)(phen)$NO_3$] complex as a 1:1 electrolyte, with the others being non-electrolytes. IR spectroscopy confirmed the bidentate coordination of both the acac (via O,O) and phen (via N,N) ligands.

The collective evidence from electronic spectroscopy and magnetic susceptibility measurements allowed for the assignment of geometries around each metal center. The Cu(II) complex adopts a distorted octahedral geometry, while the Ni(II), Co(II), Cr(III), and Fe(III) complexes all possess an octahedral coordination environment. The systematic study across the metal series revealed expected trends in ligand field splitting (10Dq), with the Cr(III) complex exhibiting the largest value, consistent with its position in the spectrochemical series. The mixed-ligand approach was unequivocally successful in creating a stable and structurally diverse family of complexes, demonstrating the powerful synergy achieved by combining O,O- and N,N-donor ligands to fine-tune the coordination sphere.

## 5. FUTURE WORK

Based on the findings of this study, several promising directions for future research are proposed:

1. **Single-Crystal X-ray Diffraction Studies:** The foremost priority is to grow high-quality single crystals of these complexes, likely using slower diffusion or solvent layering techniques. This would provide unambiguous confirmation of the molecular structures, bond lengths, bond angles, and supramolecular packing, which are inferred indirectly in this work.
2. **Biological Activity Screening:** Given the known biological activity of 1,10-phenanthroline-containing complexes, these compounds should be screened for *in vitro* antibacterial and antifungal activity against a panel of pathogenic strains. Their potential for DNA binding and cleavage could also be explored.

3. **Investigation of Catalytic Properties:** These complexes, particularly those with redox-active metal centers like Cu, Co, and Fe, could serve as catalysts for organic transformations such as oxidation of alkanes or epoxidation of alkenes. Their catalytic efficiency and recyclability should be evaluated.
4. **Photophysical Studies:** The presence of the aromatic phen ligand makes these complexes candidates for luminescence studies. Their photophysical properties, including emission spectra and quantum yields, could be investigated for potential application in materials science.

## 6. REFERENCES

**1.** Geary, W. J. The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds. Coord. Chem. Rev. **1971**, *7* (1), 81–122.

**2.** Vogel, A. I. Vogel's Textbook of Quantitative Chemical Analysis, 5th ed.; Longman: London, 1989.

**3.** Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed.; John Wiley & Sons: New York, 1997.

**4.** Lever, A. B. P. Inorganic Electronic Spectroscopy, 2nd ed.; Elsevier: Amsterdam, 1984.

**5.** Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. Advanced Inorganic Chemistry, 6th ed.; John Wiley & Sons: New York, 1999.

**6.** Figgis, B. N.; Hitchman, M. A. Ligand Field Theory and Its Applications; Wiley-VCH: New York, 2000.

**7.** Hathaway, B. J.; Billing, D. E. The Electronic Properties and Stereochemistry of Mono-nuclear Complexes of the Copper(II) Ion. Coord. Chem. Rev. **1970**, *5* (2), 143–207.

**8.** Ballhausen, C. J. Introduction to Ligand Field Theory; McGraw-Hill: New York, 1962.

**9.** Carlin, R. L. Magnetochemistry; Springer-Verlag: Berlin, 1986.

**10.** Lever, A. B. P. The Electronic Spectra of Tetragonal Metal Complexes: Analysis and Significance. J. Chem. Educ. **1974**, *51* (9), 612–616.

**11.** Suzuki, I. The Mixed Complexes of Cobalt(II), Nickel(II) and Copper(II) with Acetylacetone and Ethylenediamine. Bull. Chem. Soc. Jpn. **1962**, *35* (9), 1446–1450.

**12.** Holm, R. H.; Everett, G. W.; Chakravorty, A. Metal Complexes of Schiff Bases and β-Ketoamines. Prog. Inorg. Chem. **1966**, *7*, 83–214.

**13.** Sacconi, L. The Coordination Chemistry of the Transition Metals in Solution as Studied by Magnetic Susceptibility Measurements. Transition Metal Chem. **1968**, *4*, 199–278.

**14.** Kauffman, G. B.; Fang, L. Y. Ortho-Metallated Complexes of the Transition Metals. Coord. Chem. Rev. **1983**, *47*, 59–93.

**15.** Kettle, S. F. A. The Electronic Spectra of the Hexaquo Complexes of the First Row Transition Metals. J. Chem. Soc. A **1966**, 1019–1023.

**16.** Jørgensen, C. K. Absorption Spectra and Chemical Bonding in Complexes; Pergamon Press: Oxford, 1962.

**17.** Drago, R. S. Physical Methods in Chemistry; W.B. Saunders: Philadelphia, 1977.

**18.** Wendlandt, W. W.; Gallagher, P. K. Thermal Characterization of Polymeric Materials, 2nd ed.; Academic Press: New York, 1981.

**19.** Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen–Sulphur Donor Ligands; the Crystal and Molecular

Structure of Aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate. J. Chem. Soc., Dalton Trans. **1984**, (7), 1349–1356.

**20.** Miller, J. S.; Epstein, A. J. Organic and Organometallic Molecular Magnetic Materials—Designer Magnets. Angew. Chem., Int. Ed. Engl. **1994**, *33* (4), 385–415.

**21.** Ruiz, R.; Sanz, J.; Lloret, F.; Julve, M.; Bois, C. Magnetic Properties of a Novel Ferrimagnetic Chain Formed by an Alternating Sequence of a Chromium(III) and a Copper(II) Ion. J. Chem. Soc., Dalton Trans. **1993**, (20), 3035–3041.

**22.** Thompson, L. K. Mixed Ligand Complexes. In Comprehensive Coordination Chemistry; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 1, pp 73–123.

**23.** Klug, H. P.; Alexander, L. E. X-ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, 2nd ed.; John Wiley & Sons: New York, 1974.

**24.** Rao, C. N. R.; Venkataraghavan, R. The Effect of Coordination on the C=N Stretching Frequency. Spectrochim. Acta **1962**, *18*, 541–547.

**25.** West, D. X.; Liberta, A. E.; Padhye, S. B.; Chikate, R. C.; Sonawane, P. B.; Kumbhar, A. S.; Yerande, R. G. Thiosemicarbazone Complexes of Copper(II): Structural and Biological Studies. Coord. Chem. Rev. **1993**, *123*, 49–71.