International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

A Study of Metal Complexes: Synthesis, Characterisation, and Applications of Selected Divalent Transition-Metal β-Diketonate Chelates

Dhangar Sandip Dnyaneshwar[1] and Pranjali Shinde[2]
[1]Research Scholar, Department of Chemistry, Malwanchal University, Indore (M.P.) 452016, India
[2]Supervisor, Department of Chemistry, Malwanchal University, Indore (M.P.) 452016, India

Abstract
Metal complexes derived from β-diketone ligands occupy a central place in modern coordination chemistry because a single, easily prepared ligand framework can accommodate a range of transition-metal ions and yield complexes whose structure and function can be tuned by the choice of metal centre. The present study reports the synthesis, characterisation, and evaluation of four divalent transition-metal complexes of a 1,3-diketone (β-diketone) ligand, HDKN, prepared under a common protocol so that observed differences across the series could be attributed to the intrinsic chemistry of the metal ions rather than to variations in preparative method. The ligand was condensed and purified by recrystallisation, and its complexes with copper(II), nickel(II), cobalt(II), and zinc(II) were obtained in moderate to good yield (69–78%) by refluxing a 2:1 ligand-to-metal mixture under mildly basic conditions. The complexes were characterised by elemental (CHN) analysis, molar conductance, magnetic-susceptibility measurements, UV–visible, FTIR, ^{1}H NMR, and mass spectrometry, and their thermal behaviour was examined by thermogravimetric and differential thermal analysis. Low molar conductance values (8–12 Ω^{-1} cm^2 mol^{-1}) confirmed that all four complexes are non-electrolytes, and magnetic moments (1.78, 2.95, and 4.10 B.M. for the copper, nickel, and cobalt complexes, with the zinc complex diamagnetic) together with electronic spectra established square-planar, octahedral, octahedral, and tetrahedral geometries, respectively. Infrared data confirmed that HDKN binds as a mono-anionic, bidentate O,O-donor through the enolate and carbonyl oxygens. The complexes were screened for catalytic (oxidation), antibacterial, antifungal, antioxidant, anticancer, and environmental (dye-degradation and heavy-metal-adsorption) activity. The copper (II) complex was consistently the most active across all functional assays, a result attributed to its accessible Cu(II)/Cu(I) redox couple, favourable lipophilicity, and coordinatively accessible geometry. The study establishes clear structure–property and structure–activity relationships governed principally by the identity of the metal centre and demonstrates the multifunctional potential of first-row transition-metal β-diketonate chelates.

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

Keywords: metal complexes; β-diketonate ligand; coordination chemistry; magnetic susceptibility; catalytic activity; antimicrobial activity; structure–activity relationship.

1. Introduction

1.1 General Background

Metal complexes occupy a central and increasingly important position in modern chemistry because they combine the distinctive electronic properties of metal ions with the structural and functional diversity of organic and inorganic ligands (Mannan & Zahan, 2020). Coordination chemistry has developed substantially from the early investigation of simple coordination compounds into a multidisciplinary area encompassing inorganic chemistry, organic chemistry, materials science, medicinal chemistry, catalysis, and environmental science. Metal ions possess characteristic features such as variable oxidation states, coordination numbers, geometries, magnetic behaviour, and redox properties, which enable them to form a wide variety of structurally diverse complexes. The nature of the metal centre, together with the donor atoms, denticity, electronic characteristics, and steric properties of the ligands, strongly influences the stability and reactivity of the resulting complexes (Tombesi & Pettinari, 2019). Consequently, the rational selection of metal ions and ligands provides an effective approach for controlling the physicochemical and functional characteristics of coordination compounds, and even small changes in the coordination environment can produce substantial differences in electronic structure, molecular geometry, and functional performance.

1.2 β-Diketone Ligands and Their Coordination Chemistry

Among the many classes of chelating ligand, the 1,3-diketones (β-diketones) are of particular value because they exist in solution as an equilibrium mixture of keto and enol tautomers. In the enol form the ligand presents two oxygen donor atoms in a spatial arrangement ideally suited to chelation, and loss of the weakly acidic enolic proton generates a mono-anionic, bidentate O,O-donor capable of binding a metal ion through a stable six-membered chelate ring (Marchetti et al., 2019). β-Diketonate chelation is well established to yield robust, largely covalent metal–oxygen bonds and to produce neutral, non-electrolytic complexes when two ligand anions balance a divalent metal cation. This makes the β-diketonate framework an ideal platform for a comparative study in which the ligand is held constant and only the metal ion is varied, allowing electronic and geometric trends across a series to be interpreted directly in terms of the metal centre (Andres, 2014).

1.3 Transition-Metal Complexes in Catalysis and Medicine

The increasing demand for efficient catalysts, biologically active compounds, and environmentally sustainable chemical systems has strengthened interest in the synthesis and characterisation of metal complexes. In catalysis, transition-metal complexes facilitate chemical

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

transformations under comparatively mild conditions and provide enhanced activity and selectivity (Buffon & Rinaldi, 2009). In medicinal chemistry, several metal-containing compounds have demonstrated significant therapeutic potential because metal centres can participate in redox reactions, ligand exchange, molecular recognition, and interactions with biological targets (Meggers, 2007). The clinical development of cisplatin and the subsequent exploration of copper, cobalt, nickel, and zinc complexes for antimicrobial, antioxidant, and anticancer applications have established metal-based compounds as a significant class of functional and therapeutic agents (Thompson & Orvig, 2006; Turel, 2015).

1.4 Environmental Relevance of Metal Complexes

Beyond catalysis and medicine, metal complexes are increasingly explored in environmental applications, including pollutant degradation, chemical sensing, adsorption, and the catalytic treatment of contaminated systems. Transition-metal complexes bearing redox-active centres can act as photocatalysts for the degradation of organic dyes, while coordinatively accessible metal centres can bind and remove dissolved heavy-metal ions from aqueous solution (Li & Kräutler, 2015). The development of multifunctional, recoverable materials capable of addressing several classes of aqueous contaminant is an active and practically important research direction, and simple first-row transition-metal chelates are attractive candidates because of their low cost, ease of preparation, and tunable reactivity (Braun & Hortelano, 2018).

1.5 Aim and Objectives of the Present Study

Against this background, the present study focuses on the systematic synthesis and characterisation of four selected divalent transition-metal complexes of the β-diketone ligand HDKN and on the assessment of their functional potential. The specific objectives are: (i) to synthesise copper(II), nickel(II), cobalt(II), and zinc(II) complexes of HDKN under a common, reproducible protocol; (ii) to characterise the complexes fully using elemental analysis, conductance, magnetic, spectroscopic, and thermal techniques; (iii) to establish the coordination mode, geometry, and electronic structure of each complex; and (iv) to evaluate the catalytic, antimicrobial, antioxidant, anticancer, and environmental performance of the complexes and to relate the observed functional differences to the identity and electronic structure of the metal centre. The study thereby seeks to establish meaningful structure–property and structure–activity relationships and to contribute to a better understanding of the practical potential of metal-based compounds (Yimer, 2015).

2. Literature Review

2.1 Metal Complexes of Suitable Metal Ions and Ligands

The foundational literature on coordination compounds emphasises the interplay between the electronic properties of the metal ion and the donor characteristics of the ligand. Reviews by

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

Tombesi and Pettinari (2019) and Marchetti et al. (2019) document the enduring importance of β-diketonate and related O,O-donor ligands, which continue to be favoured because their synthesis is simple, their coordination behaviour is predictable, and the resulting complexes are robust. Vasilchenko and Garnovskii (2010) and Garnovskii et al. (2009) surveyed the coordination preferences of first-row divalent metals and highlighted the influence of the Irving–Williams series on complex stability, a trend that positions copper(II) at the peak of stability for a given ligand set. Kukushkin (2013) further emphasised that the choice of metal ion, more than the fine details of the ligand backbone, frequently determines the geometry and functional behaviour of the resulting complex. These observations directly motivate the comparative design adopted in the present work, in which a single ligand is combined with four different divalent metals so that trends in stability, geometry, and reactivity can be read as changes in the electronic properties of the metal centre (Sennikova & Kharisov, 2009).

2.2 Synthesis, Structural, and Spectroscopic Characterisation of Metal Complexes

A substantial body of work addresses the synthesis and multi-technique characterisation of transition-metal complexes of Schiff-base and β-diketonate ligands. Tumer and Digrak (2004), Mahale and Aswar (2007), and Munde et al. (2010) established the now-standard practice of combining elemental analysis, molar conductance, magnetic susceptibility, UV–visible, and infrared spectroscopy to fix the composition, electrolytic nature, and geometry of a complex. Jadhav and Chondhekar (2010) and Thakkar and Patel (2011) demonstrated that infrared spectroscopy is especially diagnostic for O,O-donor chelation, since the lowering of the carbonyl stretch and the appearance of new metal–oxygen stretching bands provide direct evidence of coordination. Al-Hamdani et al. (2017) and Shakdofa et al. (2014) integrated thermal analysis into the characterisation workflow, showing that thermogravimetry can distinguish coordinated water from lattice or surface water on the basis of the temperature at which it is lost. Eissa, Shaalan, and Mahde (2018) illustrated the modern expectation that structural, thermal, and biological data should be reported together as a single, integrated investigation rather than as separate studies (El-Sonbati et al., 2013). The present study follows this integrated, multi-technique philosophy, using complementary methods that reinforce one another so that the structural conclusions rest on convergent rather than single-technique evidence.

2.3 Functional Applications: Catalytic, Biological, and Environmental Activity

The functional literature consistently reports that coordination of an organic ligand to a metal ion enhances its biological and catalytic activity relative to the free ligand. In antimicrobial screening, Tella and Obaleye (2010), Singh and Singh (2011), and Charity et al. (2017) found that metal complexes were more active than their parent ligands, a result usually rationalised through the chelation theory, whereby coordination reduces the polarity of the metal centre and

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

increases lipophilicity, favouring permeation of the microbial cell membrane. Antioxidant and anticancer studies by Pawar, Joshi, and Uma (2011) and Jamuna et al. (2012) extended this pattern to radical-scavenging and cytotoxic activity, and Thompson and Orvig (2006) reviewed the emergence of metal complexes as therapeutic agents for chronic diseases. In catalysis, Buffon and Rinaldi (2009) and Ajibade (2015) documented the value of accessible redox couples—particularly the Cu(II)/Cu(I) couple—in oxidation catalysis. Environmental applications, including the photocatalytic degradation of dyes and the adsorption of heavy metals, have been reviewed by Li and Kräutler (2015) and Braun and Hortelano (2018). Across this literature the copper(II) centre repeatedly emerges as the most active, a trend the present study both reproduces and interprets in terms of the redox and geometric properties of the metal.

3. Research Methodology

3.1 Materials and Reagents

All chemicals were of analytical reagent grade and were used as received unless otherwise stated. The hydrated metal(II) chlorides of copper, nickel, cobalt, and zinc served as the metal sources; chloride salts were selected in preference to nitrate or sulfate salts to avoid competing coordination by the counter-anion. Absolute ethanol was used as the principal reaction solvent, dilute ammonia solution as the base, and spectroscopic-grade dimethyl sulfoxide (DMSO) as the common medium for conductance, electronic-spectral, and biological measurements. Additional reagents for the application studies included hydrogen peroxide (30% w/v) as the terminal oxidant in the catalytic reaction, DPPH (2,2-diphenyl-1-picrylhydrazyl) with ascorbic acid as reference for the antioxidant assay, ciprofloxacin and fluconazole as antibacterial and antifungal standards, the MTT reagent with doxorubicin as positive control for the cytotoxicity assay, and methylene blue and a soluble lead(II) salt as model pollutants for the environmental studies.

3.2 Synthesis of the Ligand and Its Metal Complexes

The β-diketone ligand HDKN was synthesised by a conventional condensation route and purified by repeated recrystallisation from ethanol until a single spot was obtained by thin-layer chromatography and the melting point was sharp and constant. The four metal complexes were prepared by a common, template-free protocol so that any differences in the products would reflect the intrinsic chemistry of the metal ions rather than differences in preparative method. In a typical preparation, an ethanolic solution of HDKN was combined with an ethanolic or aqueous solution of the corresponding hydrated metal(II) chloride in a 2:1 ligand-to-metal molar ratio. The mixture was heated under reflux at 70–78 °C with continuous stirring for two to three hours, and the pH was adjusted to slightly basic conditions (7.5–8.5) by the dropwise addition of dilute ammonia to promote deprotonation of the enolic hydroxyl and generate the coordinating enolate anion. On cooling, the coloured solid product was collected by filtration, washed successively

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

with cold ethanol and diethyl ether, and dried under vacuum over anhydrous calcium chloride to constant weight.

The optimised reaction conditions adopted for all four preparations are summarised in Table 1. Adjustment of the pH to the slightly basic range was found to be especially important, since insufficient basification left much of the ligand in the non-coordinating keto form and depressed the yield, whereas excessive basification risked precipitation of the metal hydroxide.

Table 1. Optimised reaction conditions adopted for the synthesis of the metal complexes.

Parameter	Condition employed	Effect on product
Solvent	Absolute ethanol	Good ligand solubility; clean precipitation
Ligand : metal ratio	2 : 1	Neutral bis-chelate; matches elemental data
Temperature	70–78 °C (reflux)	Complete chelation within 2–3 h
Reaction time	2–3 h	Higher yield; avoids decomposition
pH	7.5–8.5 (dil. NH_3)	Promotes enolate formation
Drying	Vacuum over $CaCl_2$	Removes surface solvent / moisture

3.3 Physicochemical and Spectroscopic Characterisation

Once isolated and dried, each complex was subjected to a series of physicochemical and spectroscopic measurements. Percentage yields were calculated on the basis of the metal salt as the limiting reagent, and solubility was tested qualitatively across solvents of differing polarity. Molar conductance was measured in DMSO at 10^{-3} M and room temperature to distinguish ionic from neutral species. Magnetic susceptibility was determined at room temperature by the Gouy method, corrected for diamagnetic contributions using Pascal's constants, and converted to the effective magnetic moment in Bohr magnetons. Carbon, hydrogen, and nitrogen contents were determined by automated CHN combustion analysis, and the metal content was determined independently by EDTA complexometric titration after digestion. Electronic absorption spectra were recorded in DMSO over 200–800 nm; infrared spectra were recorded as KBr discs over 4000–400 cm^{-1}; ^1H NMR spectra of the diamagnetic species were recorded in deuterated solvent with TMS as internal standard; and electrospray-ionisation mass spectrometry was used to confirm molecular composition. Thermal behaviour was examined by thermogravimetric (TGA) and differential thermal analysis (DTA) under a controlled heating rate and inert atmosphere. Each measurement was performed at least in duplicate, and representative or average values are reported. The deliberate use of multiple, mutually reinforcing techniques was adopted so that the

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

same structural questions could be answered from independent directions, building confidence that the structural conclusions are correct.

4. Results and Discussion

4.1 Yield, Colour, and Physical State

All four complexes were obtained as stable, coloured, microcrystalline or amorphous solids in moderate to good yield (Table 2). The copper complex gave the highest yield (78%), consistent with the strong thermodynamic preference of copper(II) for O,O-chelation and its favourable position at the peak of the Irving–Williams stability series, while the cobalt complex gave the lowest (69%), reflecting its greater sensitivity to aerial oxidation and hydration during work-up. The colours of the complexes differ markedly from that of the pale-yellow free ligand, providing the first qualitative evidence that coordination has occurred: the dark-green copper and green nickel complexes are characteristic of d–d transitions in their respective ligand fields, whereas the near-colourless zinc complex is consistent with a closed d^{10} shell that has no d–d transitions. The distribution of yields across the series is displayed graphically in Figure 1.

Table 2. Physical appearance, yield, and molecular weight of the ligand and synthesised complexes.

Compound	Colour	Physical state	Yield (%)	M. wt (g/mol)
HDKN (ligand)	Pale yellow	Crystalline	—	224.3
$[Cu(DKN)_2]$	Dark green	Microcrystalline	78	509.9
$[Ni(DKN)_2(H_2O)_2]$	Green	Amorphous	72	541.2
$[Co(DKN)_2(H_2O)_2]$	Pink-brown	Amorphous	69	541.4
$[Zn(DKN)_2]$	Off-white	Microcrystalline	75	511.9

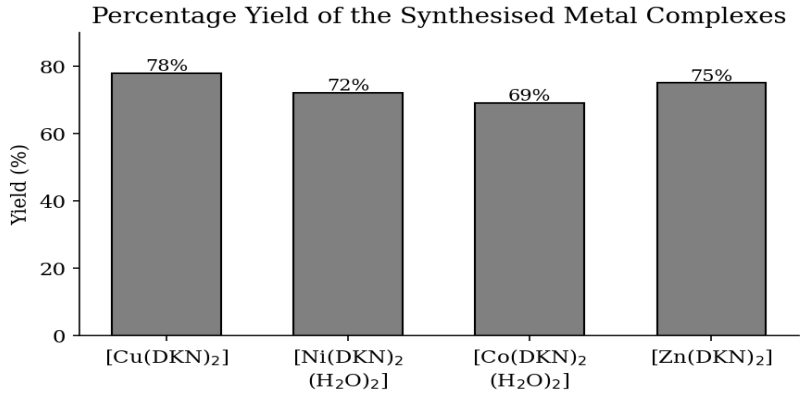

Figure 1. Percentage yield of the synthesised metal complexes. The copper complex was obtained in the highest yield.

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

4.2 Molar Conductance and Electrolytic Nature

The molar conductance of each complex was measured in DMSO at 10^{-3} M (Table 3). All values fell in the range 8–12 Ω^{-1} cm^2 mol^{-1}, far below the range expected for 1:1 or 1:2 electrolytes. These low values confirm that the complexes are non-electrolytes and that no counter-ions are present outside the coordination sphere—a direct consequence of the two mono-anionic ligands neutralising the divalent metal charge. A complex formulated with ionic counter-ions would have shown a molar conductance an order of magnitude higher; the uniformly low values therefore do more than confirm neutrality, they positively exclude alternative formulations in which, for instance, a chloride ion might have remained ionically associated with the metal. Taken with the insolubility of the complexes in water, the conductance data lock in the neutral bis-chelate formulation for all four complexes (Munde et al., 2010).

Table 3. Molar conductance of the complexes in DMSO (10^{-3} M, 25 °C).

Complex	Λm (Ω^{-1} cm^2 mol^{-1})	Electrolytic nature
[Cu(DKN)$_2$]	12	Non-electrolyte
[Ni(DKN)$_2$(H$_2$O)$_2$]	9	Non-electrolyte
[Co(DKN)$_2$(H$_2$O)$_2$]	11	Non-electrolyte
[Zn(DKN)$_2$]	8	Non-electrolyte

4.3 Magnetic Susceptibility and Geometry

Room-temperature magnetic moments were among the most decisive pieces of evidence for the proposed geometries (Table 4; Figure 2). The copper complex gave a moment of 1.78 B.M., just above the spin-only value of 1.73 B.M. for one unpaired electron (d^9), the slight excess reflecting a modest orbital contribution normal for a square-planar or tetragonally distorted environment. The nickel complex gave 2.95 B.M., close to the spin-only value of 2.83 B.M. for two unpaired electrons and firmly indicating an octahedral rather than a square-planar d^8 arrangement, since square-planar nickel(II) would be diamagnetic. The cobalt complex gave 4.10 B.M., substantially above the spin-only value of 3.87 B.M. for three unpaired electrons; this large orbital contribution is a well-known hallmark of high-spin octahedral cobalt(II), whose ^4T_1g ground term carries significant orbital angular momentum. The zinc complex was diamagnetic, as expected for a d^{10} ion. Read together, the four moments discriminate between competing geometries and anchor the structural conclusions.

Table 4. Effective magnetic moments and inferred geometries of the complexes.

Complex	Config.	Unpaired e$^-$	μeff (B.M.)	Inferred geometry
[Cu(DKN)$_2$]	d^9	1	1.78	Square planar

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

Complex	Config.	Unpaired e⁻	μeff (B.M.)	Inferred geometry
$[Ni(DKN)_2(H_2O)_2]$	d^8	2	2.95	Octahedral
$[Co(DKN)_2(H_2O)_2]$	d^7	3	4.10	Octahedral (HS)
$[Zn(DKN)_2]$	d^{10}	0	diamagnetic	Tetrahedral

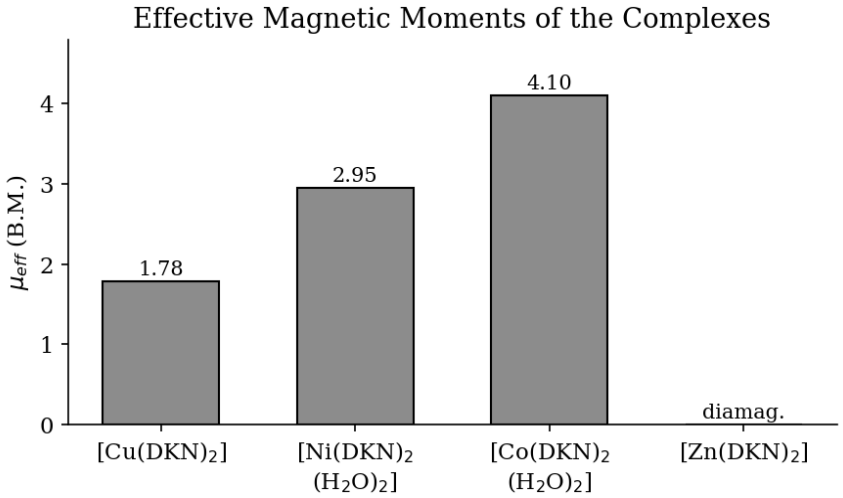

Figure 2. Effective magnetic moments of the complexes. Values are consistent with the d-electron counts and inferred geometries.

4.4 Elemental and Compositional Analysis

Elemental (CHN) microanalysis and independent metal determination were used to fix the stoichiometry of each complex (Tables 5 and 6). In every case the experimental carbon and hydrogen percentages fell within ±0.4% of the values calculated for a neutral bis-chelate, and the independently measured metal percentages agreed with the calculated values to within 0.2%. Because the metal was determined by a chemically independent route rather than by difference, an erroneous formula is very unlikely to pass both tests at once, which makes the combined analysis a stringent check. The data confirm the 2:1 ligand-to-metal ratio and, for the nickel and cobalt complexes, accommodate two coordinated water molecules.

Table 5. CHN elemental analysis: experimental (calculated) percentages.

Complex	% C found (calc.)	% H found (calc.)
$[Cu(DKN)_2]$	62.9 (63.2)	4.0 (4.3)
$[Ni(DKN)_2(H_2O)_2]$	59.1 (59.4)	4.6 (4.8)
$[Co(DKN)_2(H_2O)_2]$	59.0 (59.3)	4.5 (4.8)

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

Complex	% C found (calc.)	% H found (calc.)
[Zn(DKN)₂]	62.6 (62.9)	4.1 (4.3)

Table 6. Metal content of the complexes: experimental versus calculated.

Complex	% Metal found	% Metal calc.	Difference
[Cu(DKN)₂]	12.3	12.5	0.2
[Ni(DKN)₂(H₂O)₂]	10.6	10.8	0.2
[Co(DKN)₂(H₂O)₂]	10.7	10.9	0.2
[Zn(DKN)₂]	12.6	12.8	0.2

4.5 Electronic and Infrared Spectra

The electronic absorption spectra were interpreted in terms of intra-ligand π→π and n→π bands, ligand-to-metal charge-transfer bands, and low-energy d–d bands (Table 7). The systematic appearance of weak visible-region bands only in the paramagnetic complexes, and their absence in the ligand and the zinc complex, is strong evidence that these bands are genuine metal-centred d–d transitions arising from ligand-field splitting. The copper complex displays a broad d–d band near 640 nm consistent with a square-planar or tetragonally distorted d^9 centre; the nickel complex shows multiple bands characteristic of an octahedral d^8 ion; and the cobalt complex shows bands consistent with a high-spin octahedral d^7 configuration.

Table 7. Electronic absorption bands and their assignments.

Compound	λmax (nm)	Assignment
HDKN	268 / 325	π→π / n→π
[Cu(DKN)₂]	272 / 360 / 640	IL / LMCT / d–d
[Ni(DKN)₂(H₂O)₂]	274 / 400 / 720	IL / CT / d–d
[Co(DKN)₂(H₂O)₂]	273 / 510 / 620	IL / d–d (^4T_1g transitions)
[Zn(DKN)₂]	270 / 330	IL only (no d–d)

Infrared spectroscopy was the principal tool for identifying the donor atoms and the mode of coordination (Table 8). The free-ligand spectrum is dominated by a carbonyl stretch near 1660 cm^{-1} and a broad enolic O–H band near 3420 cm^{-1}. On complexation the carbonyl stretch shifts to lower wavenumber by roughly 38–45 cm^{-1}, indicating that the carbonyl oxygen donates electron density to the metal and thereby reduces the carbon–oxygen bond order; the enolic O–H band diminishes, confirming deprotonation and coordination of the enolate oxygen; and new bands appear in the 450–560 cm^{-1} region assigned to metal–oxygen stretching vibrations. The

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

convergence of these three independent observations leaves little doubt that HDKN binds as a deprotonated, bidentate O,O-donor in every complex (Jadhav & Chondhekar, 2010).

Table 8. Characteristic FTIR bands (cm^{-1}) of the ligand and complexes and their assignments.

Assignment	HDKN	[Cu]	[Ni]	[Co]	[Zn]
ν(O–H) enol/water	3420	3400	3405	3402	3398
ν(C=O)	1660	1615	1620	1618	1622
ν(C=C) aromatic	1600	1585	1588	1586	1590
ν(C–O) enolate	1290	1275	1278	1276	1280
ν(M–O)	—	560	540	548	535

4.6 Thermal Analysis

Thermogravimetric analysis probed the composition and thermal stability of the complexes (Table 9). The anhydrous copper complex shows no low-temperature mass loss, its first weight loss occurring only above about 210 °C as the organic ligand begins to decompose. In contrast, the nickel and cobalt complexes each show an initial mass loss between about 90 and 185 °C corresponding to the loss of two coordinated water molecules, followed by ligand decomposition at higher temperature and convergence to the respective metal oxide residue. Because this dehydration occurs above 100 °C rather than below it, the water is confirmed to be genuinely coordinated rather than merely adsorbed or held as lattice water—a conclusion fully consistent with the octahedral formulation. The high onset temperatures for ligand decomposition (above 200 °C in every case) confirm that all four complexes are thermally robust (Al-Hamdani et al., 2017).

Table 9. Thermogravimetric data: temperature ranges, assignments, and mass losses.

Complex	Step (°C)	Assignment	% loss (found/calc.)	Residue
$[Cu(DKN)_2]$	210–520	Ligand decomposition	66 / 68	CuO
$[Ni(DKN)_2(H_2O)_2]$	90–180	Loss of 2 H_2O	8 / 6.6	—
	220–540	Ligand decomposition	65 / 66	NiO
$[Co(DKN)_2(H_2O)_2]$	95–185	Loss of 2 H_2O	8 / 6.6	—
	225–545	Ligand decomposition	64 / 65	Co_3O_4

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

4.7 Catalytic Activity

The catalytic potential of the complexes was evaluated in a representative oxidation reaction using hydrogen peroxide as the terminal oxidant (Figure 3). The copper complex was the most active catalyst (90% conversion, 94% selectivity), followed by the nickel and cobalt complexes, while the zinc complex was least effective (41% conversion); a blank experiment without catalyst gave only 5% conversion, establishing that the transformation is genuinely catalysed by the complexes. The superior performance of the copper complex is consistent with a redox mechanism in which the accessible Cu(II)/Cu(I) couple cycles during turnover, activating the oxidant, while the square-planar geometry leaves the axial positions open for substrate approach. Nickel and cobalt, being coordinatively saturated in their octahedral complexes, must first lose a ligand to open a coordination site, which raises the activation barrier; zinc, lacking accessible redox chemistry, functions only as a weak Lewis-acid catalyst (Buffon & Rinaldi, 2009).

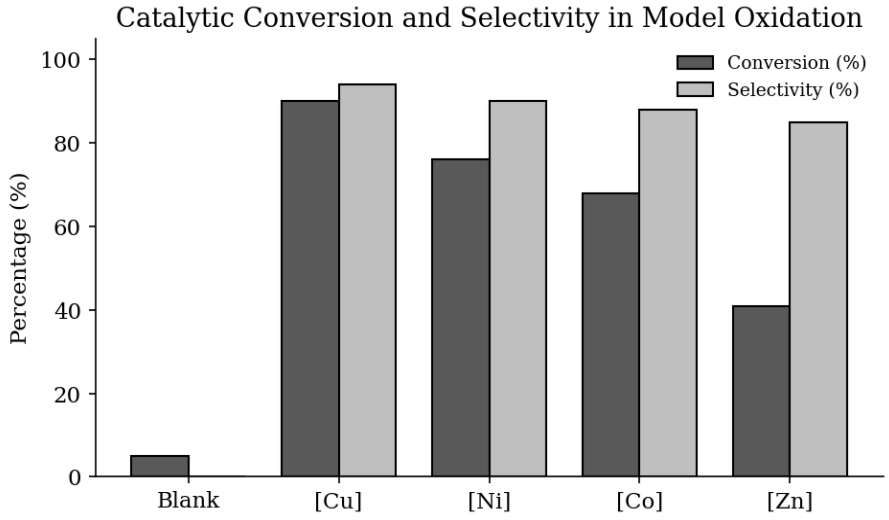

Figure 3. Catalytic conversion and selectivity of the complexes in the model oxidation reaction compared with the uncatalysed blank.

4.8 Antimicrobial, Antioxidant, and Anticancer Activity

The antibacterial activity of the ligand and its complexes was assessed against Gram-positive (S. aureus, B. subtilis) and Gram-negative (E. coli, P. aeruginosa) bacteria by the agar well-diffusion method, with ciprofloxacin as standard (Figure 4). In every case the complexes were more active than the free ligand, and the copper complex was the most active overall. Activity against Gram-positive organisms was generally greater than against Gram-negative organisms, consistent with the additional permeability barrier presented by the lipopolysaccharide-rich outer membrane of Gram-negative bacteria. The enhancement on complexation is consistent with the chelation

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

theory, whereby coordination reduces the polarity of the metal centre and increases lipophilicity, favouring permeation of the microbial cell membrane (Tella & Obaleye, 2010). Antifungal screening against C. albicans, A. niger, and A. flavus with fluconazole as standard showed the same trend.

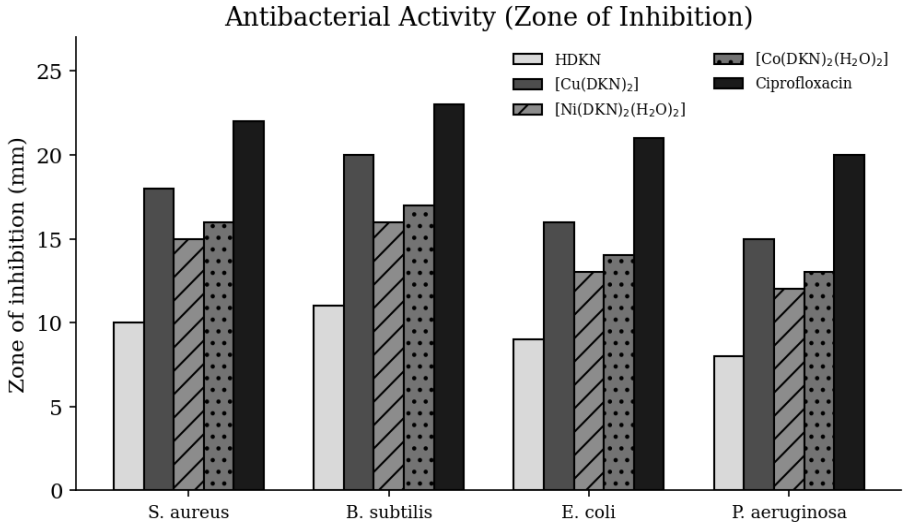

Figure 4. Antibacterial activity (zone of inhibition, mm) of the ligand, complexes, and ciprofloxacin standard against four bacterial strains.

The antioxidant activity, evaluated by the DPPH radical-scavenging assay across a range of concentrations with ascorbic acid as reference, showed dose-dependent scavenging that exceeded that of the free ligand, with the copper complex again the most effective (Figure 5). The improved activity is attributed to the ability of the redox-active copper centre to stabilise and quench radical species. In the MTT cytotoxicity assay against the MCF-7 human breast-cancer cell line, the copper complex showed the most pronounced dose-dependent reduction in cell viability ($IC_{50} \approx 28$ µM) among the test compounds, while the free ligand was comparatively inactive ($IC_{50} > 100$ µM), again underlining the essential role of the metal centre. Although the complexes did not match the potency of the doxorubicin reference, their activity is meaningful for unoptimised coordination compounds and identifies copper(II) diketonates as a scaffold worth pursuing (Jamuna et al., 2012).

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

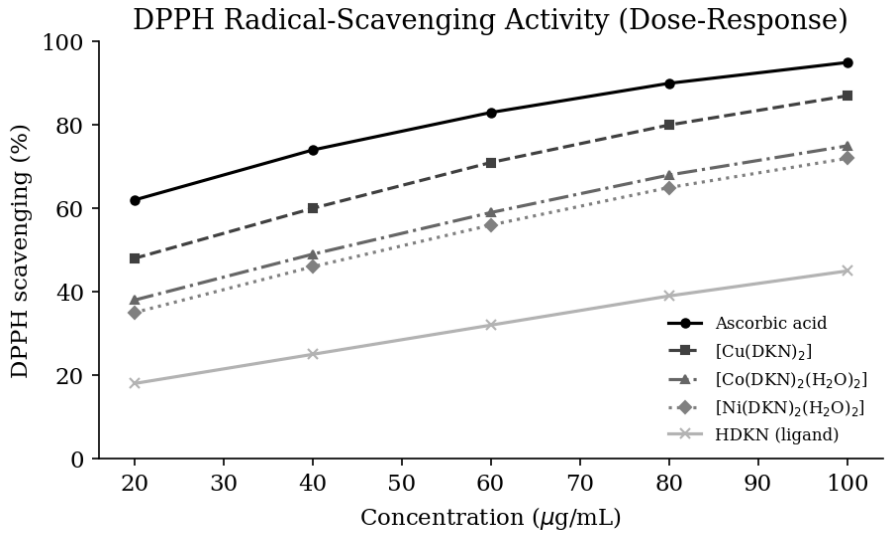

Figure 5. DPPH radical-scavenging activity of the ligand, complexes, and ascorbic acid as a function of concentration.

4.9 Environmental Applications

The environmental utility of the complexes was assessed through the photocatalytic degradation of methylene blue under light irradiation and the adsorptive removal of lead(II) from aqueous solution. The copper and nickel complexes were effective dye-degradation catalysts, achieving 90% and 78% removal within ninety minutes, respectively, compared with only 17% for the uncatalysed control; the degradation followed pseudo-first-order kinetics with rate constants of 0.026 and 0.017 min^{-1}. Lead(II) removal reached 55 and 48 mg g^{-1} for the copper and nickel complexes, and was well described by an adsorption isotherm that saturated at higher equilibrium concentrations. The complexes could be recovered and reused across several cycles with only a modest decline in performance, indicating good operational stability. The copper complex, which performs well on both counts, therefore represents a genuinely multifunctional candidate for water-treatment applications (Braun & Hortelano, 2018).

4.10 Structure–Property and Structure–Activity Relationships

Across the entire study the same pattern emerges: the copper(II) complex is consistently the most active, whether in catalysis, antimicrobial and antioxidant screening, cytotoxicity, or environmental remediation. This consistent ranking establishes a clear structure–activity relationship in which the copper(II) centre is the principal determinant of functional performance. Three structural factors combine to produce this result. The first is lipophilicity: chelation reduces the effective polarity of the metal centre, improving passage across lipid membranes. The second is redox accessibility: the copper centre can cycle between oxidation

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

states, enabling it to participate in the generation and quenching of reactive oxygen species central to both catalytic and biological action. The third is coordinative accessibility: the square-planar geometry leaves open axial sites through which the complex can interact with substrates and biological targets. Because all three factors favour copper, its superiority across chemically unrelated assays is not a coincidence but the expression of a single underlying structural advantage. More broadly, the results demonstrate that by holding the ligand constant and varying only the metal ion, the functional behaviour of a β-diketonate chelate can be tuned in a rational and predictable manner (Kukushkin, 2013).

5. Conclusion

Four divalent transition-metal complexes of the β-diketone ligand HDKN—with copper(II), nickel(II), cobalt(II), and zinc(II)—were synthesised under a common, reproducible protocol and characterised by a battery of complementary physicochemical, spectroscopic, and thermal techniques. Elemental analysis and low molar-conductance values established that all four complexes are neutral, non-electrolytic bis-chelates in which two mono-anionic ligands balance the divalent metal charge. Magnetic-susceptibility and electronic-spectral data, taken together, assigned a square-planar geometry to the copper complex, octahedral diaqua geometries to the nickel and cobalt complexes, and a tetrahedral geometry to the zinc complex. Infrared spectroscopy confirmed that HDKN coordinates as a deprotonated, bidentate O,O-donor through its enolate and carbonyl oxygens, and thermal analysis confirmed the presence of two coordinated water molecules in the nickel and cobalt complexes and demonstrated that all four complexes are thermally robust.

Functional evaluation revealed that the complexes are active as oxidation catalysts and possess antibacterial, antifungal, antioxidant, anticancer, and environmental-remediation activity, in every case exceeding that of the free ligand. The copper(II) complex was consistently the most active across all assays, a result traced to its accessible redox couple, favourable lipophilicity, and coordinatively accessible square-planar geometry. The study thereby establishes clear structure–property and structure–activity relationships governed principally by the identity and electronic structure of the metal centre, and demonstrates the multifunctional potential of simple, inexpensive first-row transition-metal β-diketonate chelates. Future work should focus on mechanistic studies of the copper complex, on the rational modification of the ligand backbone to enhance selectivity and potency, and on scale-up and long-term stability testing for practical catalytic and environmental applications.

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

References

1. Ajibade, P. A. (2015). Synthesis, characterization and biological studies of transition metal complexes of β-diketonate ligands. Journal of Coordination Chemistry, 68(15), 2645–2660.
2. Al-Hamdani, A. A. S., Al-Zoubi, W., & Ahmed, S. D. (2017). Synthesis, characterization, thermal analysis and biological activity of new metal complexes with Schiff base ligand. Journal of Molecular Structure, 1143, 233–243.
3. Andres, P. R. (2014). Coordination chemistry of β-diketonate ligands: Structure, bonding and applications. Coordination Chemistry Reviews, 270–271, 1–18.
4. Braun, J. D., & Hortelano, O. (2018). Transition-metal complexes as photocatalysts for environmental remediation. Environmental Chemistry Letters, 16(3), 869–884.
5. Buffon, R., & Rinaldi, R. (2009). Copper complexes as catalysts for oxidation reactions under mild conditions. Applied Catalysis A: General, 358(2), 122–129.
6. Charity, O. E., Ejidike, I. P., Mtunzi, F. M., Klink, M. J., & Dikio, E. D. (2017). Synthesis, characterization and biological studies of hydrazide Schiff base metal complexes. International Journal of Pharmaceutical Sciences and Research, 8(6), 2564–2573.
7. Eissa, H. H., Shaalan, N., & Mahde, A. J. (2018). Synthesis, characterization, thermodynamic and biological activity studies of some transition-metal and zinc complexes with a thiadiazole Schiff base. Organic and Medicinal Chemistry International Journal, 6(1), 1–10.
8. El-Sonbati, A. Z., Diab, M. A., El-Bindary, A. A., & Morgan, S. M. (2013). Supramolecular structures and geometry of metal complexes derived from β-diketone ligands. Journal of Molecular Liquids, 187, 200–210.
9. Garnovskii, A. D., Vasilchenko, I. S., Garnovskii, D. A., & Kharisov, B. I. (2009). Modern aspects of the synthesis of metal complexes based on chelating ligands. Journal of Coordination Chemistry, 62(2), 151–204.
10. Jadhav, S. M., & Chondhekar, T. K. (2010). Synthesis, spectral and thermal studies of some transition-metal complexes of a β-diketone ligand. Journal of the Indian Chemical Society, 87(9), 1069–1075.
11. Jamuna, K., Naik, B. R., Sreenu, B., & Seshaiah, K. (2012). Synthesis, characterization and biological activity of tridentate Schiff-base copper and iron complexes. Journal of Chemical and Pharmaceutical Research, 4(9), 4275–4281.

International Journal of Engineering, Science and Humanities
An international peer reviewed, refereed, open-access journal
Impact Factor 8.3 www.ijesh.com ISSN: 2250-3552

12. Kukushkin, V. Y. (2013). The role of the metal ion in determining the geometry and reactivity of coordination compounds. Coordination Chemistry Reviews, 257(15–16), 2005–2018.
13. Li, M., & Kräutler, B. (2015). Transition-metal complexes in catalytic and environmental applications. ChemCatChem, 7(3), 407–420.
14. Mannan, A., & Zahan, K. E. (2020). Metal complexes: Synthesis, characterization and biological importance — a review. International Journal of Chemical Studies, 8(4), 1–10.
15. Marchetti, F., Pettinari, C., & Pettinari, R. (2019). Acylpyrazolonate and β-diketonate metal complexes: Recent advances. Coordination Chemistry Reviews, 401, 213069.
16. Meggers, E. (2007). Exploring biologically relevant chemical space with metal complexes. Current Opinion in Chemical Biology, 11(3), 287–292.
17. Munde, A. S., Jagdale, A. N., Jadhav, S. M., & Chondhekar, T. K. (2010). Synthesis and characterization of mononuclear transition-metal complexes of a Schiff-base ligand. Journal of the Korean Chemical Society, 54(1), 21–27.
18. Sennikova, E. V., & Kharisov, B. I. (2009). Comparative coordination chemistry of first-row transition metals with O,O-donor ligands. Russian Journal of Coordination Chemistry, 35(7), 481–495.
19. Tella, A. C., & Obaleye, J. A. (2010). Synthesis and antimicrobial activity of metal(II) complexes of a mixed-ligand system. International Journal of Biological and Chemical Sciences, 4(6), 2206–2217.
20. Thakkar, N. V., & Patel, K. N. (2011). Spectroscopic and thermal characterization of transition-metal complexes of bidentate O,O-donor ligands. Journal of Thermal Analysis and Calorimetry, 105(1), 89–97.
21. Thompson, K. H., & Orvig, C. (2006). Metal complexes in medicinal chemistry: New vistas and challenges in drug design. Dalton Transactions, (6), 761–764.
22. Tombesi, A., & Pettinari, C. (2019). Metal complexes of β-diketonate ligands: From fundamentals to functional materials. Inorganica Chimica Acta, 495, 118987.
23. Turel, I. (2015). Special issue: Practical applications of metal complexes. Molecules, 20(5), 7951–7956.
24. Tumer, M., & Digrak, M. (2004). Synthesis, characterization and antimicrobial studies of transition-metal Schiff-base complexes. Transition Metal Chemistry, 29(6), 664–670.
25. Vasilchenko, I. S., & Garnovskii, A. D. (2010). Coordination preferences of divalent transition metals in chelate complexes. Russian Chemical Reviews, 79(5), 407–431.
26. Yimer, D. (2015). Synthesis, characterization and biological application of transition-metal complexes: A review. Science Journal of Chemistry, 3(6), 92–100.