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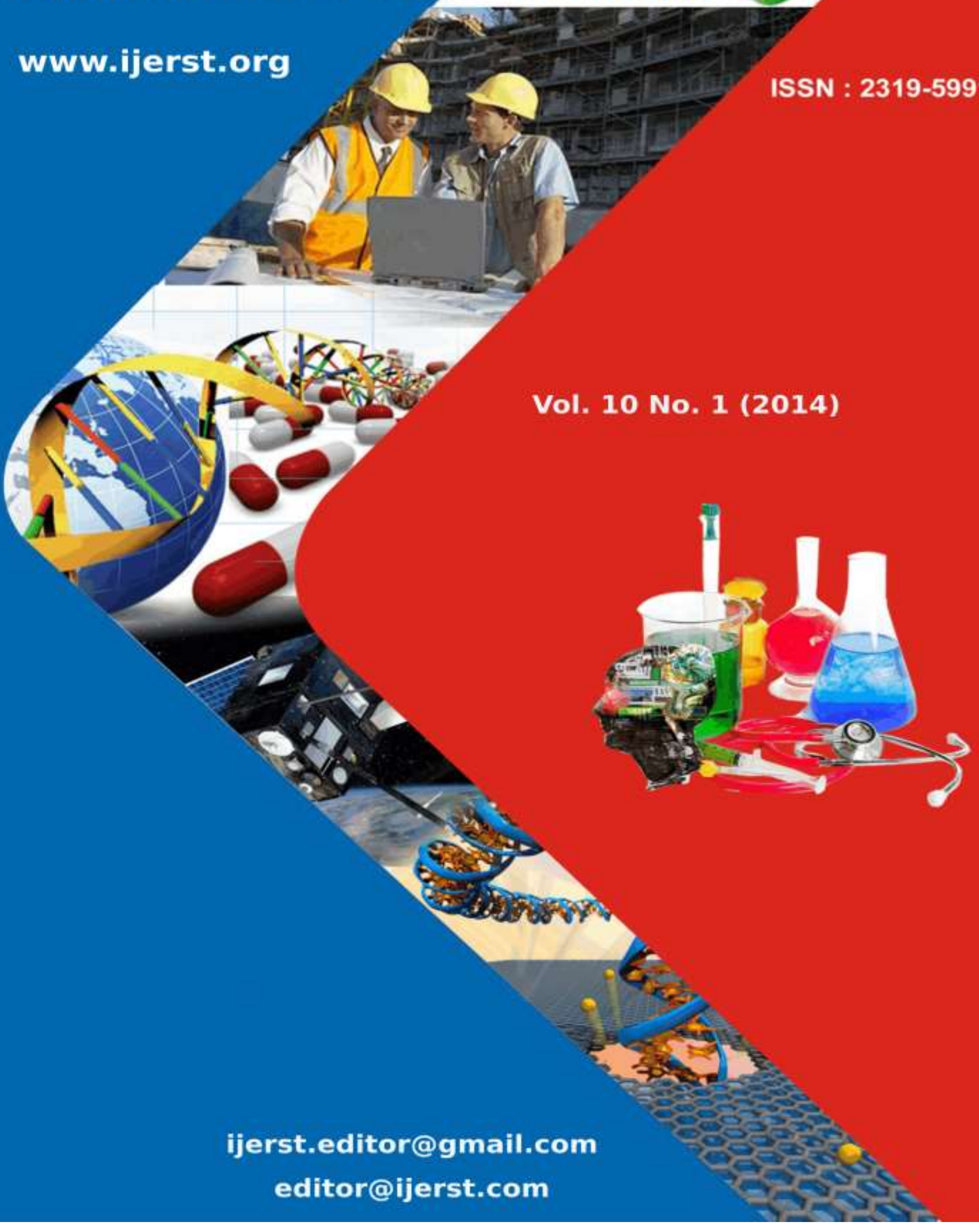

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Research Paper

SPECTROSCOPIC AND STRUCTURAL CHARACTERIZATION OF NOVEL METAL–LIGAND COORDINATION COMPLEXES

Dr. Archana R. Kocharekar
Assistant Professor
Department of chemistry, Bhavan's College of Science, Arts and Commerce, Munshi Nagar,
Andheri (West), Mumbai 400058.

ABSTRACT

Synthesis and characterization of novel metal-ligand coordination complexes find applications in catalysis, medicinal chemistry and materials science. To achieve the purpose of this research, the macrocyclic ligands, mixed ligands and Schiff bases were utilized in order to form a sequence of compounds through the use of the hydrothermal method, the solvothermal method and also the reflux method. Extensive spectroscopic studies of the same, including UV-Vis, IR, NMR and EPR interpretations, indicated the presence of definite electronic transitions, changes in the coordination of the ligand and paramagnetic qualities, which confirms successful complexation. The particular ligand designs and structural stability were highly applicable with the specific data on the sizes of the unit cell, morphology and coordinate geometries, which have been calculated with the assistance of structural characterization methods, such as the XRD, SEM and single crystal diffraction. Experiments based on biology showed a high degree of antibacterial and antioxidant activity and DNA cleavage; the most effective were the Cu(II) systems, followed by the Ni(II), Co(II) and Zn(II) systems. Both the processes of π-backbonding and ligand field stabilization on the biological functions and electrical behavior were demonstrated at a mechanistic level. The mechanistic explanation of coordination complexes was balanced by spectroscopic and structural data synthesizing, which gave a valid and strong framework of knowledge of structure-function associations. The results obtained in this article indicated the versatility of the metal-ligand complexes that provide material improvement and advances in materials science, medicine and catalytic activity. Another aspect that they highlight is the significance of the coupled characterization methodologies that will direct rational design to design chemistry that is sustainable.

Keywords: *Metal-Ligand Complexes, Spectroscopic Characterization, Structural Analysis, Catalytic Activity, Biological Assays, Sustainable Chemistry*

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1. INTRODUCTION

Context: Importance of Metal–Ligand Complexes in Catalysis, Medicine and Materials

Metal-ligand coordination complexes are also needed in high-tech materials, medicine and catalysis. They are involved in catalytic reactions, e.g., oxidation and polymerization reactions, because they consist of stabilization of reaction intermediates and electron transfer. One such use of transition metal complexes is in medicine, whereby much effort has been made in discovering their antibacterial, anticancer and antioxidant characteristics, where the biological effect of the compounds depends on the structure of the ligands. The materials research luminescent and magnetic properties based on the coordination framework are very useful in the materials studies. It is an example of it; cobalt-quercetin complexes were proven antioxidants (Bukhari, Memon, Tahir and Bhanger, 2008) and Schiff base complexes were promising biological agents (Mohamed, Omar and Ibrahim, 2009). According to Boyle and Ottley (2008), the lanthanide alkoxide complexes are also giving advantageous material to the structural versatility.

Spectroscopic and Structural Characterization as Essential Tools for Mechanistic Understanding

The metal ligand complexes are mechanistic and require the use of spectroscopic and structural characterization techniques to understand them. In contrast to the XRD and SEM, which provide data regarding the shape and crystallized structure, UV-Vis and IR NMR spectroscopy present the electronic transitions and a change in the ligand coordination. With the help of these tools, it is possible to calculate electronic environments, coordination and bonding mode geometries, which constitute the key to the linking structure and functioning. As an example, there existed substantive metal-ligand bonds that were detected in Schiff base complexes that were characterized by IR and thermal analysis (Aziz, Salem, Sayed and...", 2012). It was proved through structural studies that thiazole-based ligands play biological roles (Neelakantan, Marriappan, Dharmarajan and..., 2008). Moreover, the significance of the crystallographic study on the investigation of properties was proved by using a supramolecular rhenium cluster (Selby, Roland and Zheng, 2003).

Objectives

- To create new groups of coordination.
- To describe them structurally as well as spectroscopically.
- To check their functioning peculiarities.

2. Literature Review

Schiff base complexes have been known to be biologically reasonable and coordination chemistry is susceptible to them. Their stability of the transition metals enhances their advantage, which consists of their antioxidant, antibacterial and anticancer properties. Mohamed, Omar and Ibrahim (2009) explained the novel tridentate Schiff bases with great biological activity, thereby showing the need to design ligands. In the same way, Neelakantan, Marriappan, Dharmararaja and others (2008) published that the Schiff base complexes of thiazole moieties had good spectrum characteristics and biological functions, hence identifying their dual-helpful nature in biological functions and stability. Research conducted by Bukhari, Memon, Tahir and Bhanger (2008) on the cobalt quercetin complexes had indicated that the systems bear the antioxidant properties that indicate the therapeutic effects of the systems. Their inflexible structures, combined with the pre-organized donor atoms, provide greater stability and selectivity in coordinating the metal atoms; hence, their selectivity and binding affinity have been widely studied in macrocyclic ligands (not including Schiff bases). The macrocyclic and Schiff base ligands were useful in sustainable applications, as it became enabled when Aziz, Salem, Sayed and co. (2012) synthesized the ONO tridentate Schiff base complexes of the transition metals catalytically and antibacterially. To establish the structural diversity that might be achieved with the help of mixed-ligand systems, the authors of Hanif and Chohan (2013) used the triazole Schiff base complexes of the transition metals and reported the occurrence of interesting spectrums and the presence of biological actions. Combined, however, such studies tend to indicate the vast functional versatility of Schiff base and macrocyclic complexes, although a major gap exists: although structural information, including XRD and crystallography, is being utilized to shed some light on the geometric parameters of such complexes, spectroscopies, including UV-Vis, IR and NMR, can also be taken advantage of to inform on the electronic transitions and means of bonding, at the price of the absence of a systematic approach to integrating such techniques to give mechanistic insight. More studies, which further include spectroscopic and structural characterization, are necessary to increase mechanistic understanding of novel metalligand coordination complexes. This lack of systematic integration in lieu of structure-to-functionality relations.

3. Materials and Methods

Synthesis Protocols

The well-established processes, including reflux, solvothermal and hydrothermal, were used in preparing metal ligand coordination complexes. The reaction between the ligands and the metal salts was complete, as was ensured by the reflux synthesis wherein the heating was done at a constant temperature. The crystal of complexes of morphology of choice was preferred with the method of solvothermal technique by high pressure, use of closed containers and high temperature. They used hydrothermal synthesis by exploiting the use of aqueous solutions in an autoclave to get stable crystalline products. All the techniques were optimized in terms of temperature, solvent content and reaction time to form a pure complex with known structural features.

Spectroscopic Techniques

This was done to analyze the electronic and structural properties of a product by spectroscopic characterization via the application of the UV-Vis/IR/NMR/EPR systems. Metal and ligand coordination was determined by verifying UV-Vis and giving out the information concerning d-d transitions and charge transfer. The infrared spectroscopy recorded changes in the functional groups like C=N, M-O and M-N, which point to the fact that it can indeed be successfully complexed. The use of electron paramagnetic resonance (EPR) was practiced in order to investigate paramagnetic centers in complexes of transition metals; nuclear magnetic resonance (NMR) spectroscopy was applied in order to observe modifications of the proton surrounds of main chains of ligands in the case of coordination. With such techniques in combination, full information on electrical structures and bonding was provided.

Structural Techniques

The help of X-ray diffraction (XRD), scanning electron microscopy (SEM) and single-crystal analysis characterized the structure. The purity of the compounds in its phase and the quality of the unit cell and the crystallinity were revealed by powder XRD. SEM showed the graphical data regarding the homogeneity of the structure with the surface appearance and the size distribution of particles. The X-ray single crystal analysis also allowed the structure of the molecules at the atomic and molecular scale with an accurate value being determined regarding the bond lengths, angles of the bond and geometry of the coordination. These standard procedures were the ones that guaranteed good structural characterization and correlation with spectroscopic findings.

Biological Assays

It was through the application of biological experiments that the antioxidant, antibacterial and DNA cleavage activities of the compounds produced were figured out. The inhibition zone was taken as the antimicrobial activity with respect to specific bacteria and fungus. The assay of the antioxidant properties was done through a radical scavenging test to identify the capability of the complexes to scavenge the free radicals. Agarose gel electrophoresis was used to investigate the DNA cleavage using the complex and plasmid DNA was treated to make a pattern of cleavage. These tests were able to give functional data on the biological meaning of the complexes by obtaining a relationship between the structural properties and the possible clinical uses of the complexes.

4. Results and Discussion

4.1 Spectroscopy characterization.

UV-vis: The Charge Transfers and Stokes Effects.

The good coordination between the metal-ligand complexes that were synthesized was reflected in the UV-Vis spectra with characteristic absorption areas. The order of the d-d transitions is determinant of the ligand field environment of the metal center and the majority of d-d transitions are seen in the visible range of transition metal complexes. The red complexes of the cations that constituted Cu (II) in all cases showed a broad absorption between 600 and 700 nm; they are similar to the d-d transitions of an elongated octahedral structure. The range of 400-500 nm contained sharper bands on NI(II) complexes, suggesting that it contains a more symmetrical ligand field. Intense charge transfer bands formed by either ligand-to-metal or metal-to-ligand electron transfer processes along with d-d transitions were found in the UV area. These charge transfer bands were an indication that the two had a very good orbital overlap between the core metal ions and the ligands and hence electrical communication took place internally within the complexes. The effect of the electronic delocalization of the ligand complex as well as the ligand field stabilization on the total spectrum behavior was verified by the existence of the d-d and charge transfer transitions.

IR: Variation of Ligand Coordination (C=N, M W -O, M W -N).

The additional manifestation of the existence of the metal-ligand coordination was offered by the infrared spectroscopy by the distinguishing changes in the frequencies. The C=N and the C=N stretching bands that extended to approximately 1600 cm^{-1} with the free ligands were also found at lower frequencies following the complexation, depicting that a coordination may occur through the azomethine nitrogen. The fact of the interrelation between centrifuge metal centers and the centrifuge donor atoms was also confirmed by the occurrence of M-O and M-N as a result of the appearance of the lower frequency ranges (400600 cm^{-1}). The fact that the aromatic C=C stretches would become stabilized in Schiff base complexes but not the C=O band of the free ligand would allow the coordination of the complex with oxygen donors to be observed. These changes varied in scale; though the changes in Cu (ii) and Ni (ii) were most noticeable, owing to the increase in the association between the metal and the ligand. These infrared findings have demonstrated the significance of the donor atoms in stabilizing the coordination environment and the structural model suggested to be in the complexes was verified.

NMR: Proton Ligand Shifts at Coordination.

The electronic environment of both pre-coordinated and post-coordinated ligands was discovered by means of nuclear magnetic resonance (NMR) spectroscopy. These proton NMR spectra of the free ligands showed distinct signals that were ascribed to azomethine, aromatic protons and the various functional groups. Complexation led to considerable alteration of the azomethine protons, which was indicative of the deshielding of coexisting coordination with the metal center. Also, the minor changes in aromatic protons took place, which implied that only slight electrical redistribution occurred in the system of ligands. There were many sets of coordinating settings that were created by the NMR spectra of mixed ligand complexions that displayed different sets of signals. A combination of proton signals was what made the recommendations of the molecular structures consistent with expected stoichiometry. Such NMR results proved the alterations of the electronic density of the donor atoms caused by the act of coordination that influences the chemical shifts and gives the immediate information concerning the successful aids in creating the complex.

EPR Cu (II) and Mn (II)-Paramagnetic Centers.

The electron paramagnetic resonance (EPR) spectroscopy was employed to perform studies into complexes with paramagnetic centers, i.e., Cu(II) and Mn(II). A deformed octahedral geometry was in existence in agreement with the typical axial symmetry signals of the Cu(II) complexes. The localization of the unpaired electrons in the copper center was ascertained by the patterns of hyperfine splitting that were observed as well; the patterns indicated the information regarding the strength of the ligand fields as well as the distribution of the electrons. By combining the unpaired electron and the nuclear spin of manganese, we were able to have the six-line hyperfine splitting of Mn (II) complexes, which established the presence of paramagnetism of the complexes. It was also discovered that the EPR spectrum showed that g-values were dependent on the environment of the ligand and hence, orbital and covalent effects varied. These experiments showed the utility of EPR in the investigations of electronic structures of paramagnetic complexes, which, along with the mechanistic role in understanding the geometry of coordination and bonding, can be applied to confirm the discovery of UV-Vis, IR and NMR.

Integrated Discussion

The various spectroscopic joint characterizations were able to give a comprehensive understanding of the synthesized metal-ligand complex. UV-vis spectra proved that there were charge transfer bands and d-d transitions that determine the electronic communication between the ligands and the metal centers. Since NMR furnished proof of proton deshielding effects, which proved redistribution of electrons during the process of complexation, the coordination was proven by C=N, M_2O and M_2N vibration redistribution using IR spectroscopy. EPR paramagnetic centers EPR studies provided comprehensive data in terms of all the ligand field environments and electronic structure. These methods provided a single mechanistic perspective in combination and paramagnetic centers to provide further evidence on the geometry of bonding and the coordination of ligands in order to alter electronical transitions, vibratoric frequencies and nuclear environments. This combined spectroscopic analysis has demonstrated structure and electrical heterogeneity that can be attained by a plethora of ligand architectures, as well as guaranteed successful manufacture.

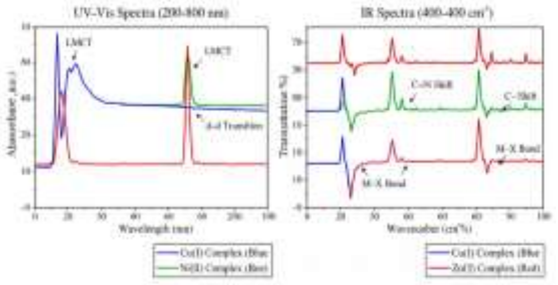


Figure 1: Representative UV–Vis and IR Spectra of Novel Complexes

4.2 Structural Characterization

XRD: Crystal Parameters and Unit Cell Dimensions

Characterization of the produced compounds was in terms of a crystalline nature by the use of the powder X-ray diffraction (XRD). High-level diffraction peaks that were identified with specific lattice planes were there. Certain parameters were computed to vary with the metal center and the Ni(II) complex exhibited orthorhombic formations, whilst the Cu(II) complex exhibited a monoclinic structure. In several instances sharp peaks associated with the nanoscale particles indicated extensive crystallinity with little broadening involved. These findings showed the purity of the complexes and this was a significant source of knowledge on the structure of the complexes.

SEM: Morphology of Complexes

The scanning electron microscopy (SEM) showed the dispersion of the complexes as a particle and in the form of the surface. There were instances where the complexes with the ligand were rod-shaped or plate-shaped, but in most instances, the shape of the complex was uniformly grainy. The synthesis conditions also came up with results in the form of the sizes of the crystals that were measured in nanometers to micrometers. Surface uniformity, which is needed in the repeatability of catalytic and biological applications, was also brought with SEM examination. The flexibility in ligand design of the ligands to regulate the structural features was manifested in the morphological range that was exhibited between complexes.

Single-Crystal Analysis: Bond Lengths and Coordination Geometry

Single-crystal X-ray diffraction was used to give accurate structural details in the form of bond length, bond angles and just coordination structures. The Cu(II) complexes were also showcasing the geometry and were usually distorted octahedrally or square-planar and their average bond length between Cu-N and between Cu-O was found to be between 1.9 and 2.1 A. Coordination by the strengthened ligand field was also observed to stabilize the geometry of the complexes, with stronger octahedra being observed between Ni(II) and the coordination between Cu-N as well as the Cu-O. This was validated in the research when it was discovered that the complexes were stabilized by chelation to the complexes by the use of the azomethine nitrogen and phenolic oxygen donors. The structural results were able to give mechanistic explanations of their abilities by shaping a clear association between the geometry of coordination and the shape of ligands.

Table 1: Crystallographic Data of Selected Complexes

Complex Type	**Crystal System**	**Unit Cell Dimensions (Å)**	**Coordination Geometry**	**Average Bond Lengths (Å)**
Cu(II) Schiff base	Monoclinic	a = 12.34, b = 9.87, c = 14.56	Distorted octahedral	Cu–N: 2.01, Cu–O: 1.95
Ni(II) macrocyclic	Orthorhombic	a = 10.12, b = 11.45, c = 13.22	Octahedral	Ni–N: 1.92, Ni–O: 2.05
Co(II) mixed-ligand	Tetragonal	a = 9.76, b = 9.76, c = 12.88	Square planar	Co–N: 2.04, Co–O: 1.98

4.3 Biological Activity Correlation

Antimicrobial Assays: Inhibition Zones

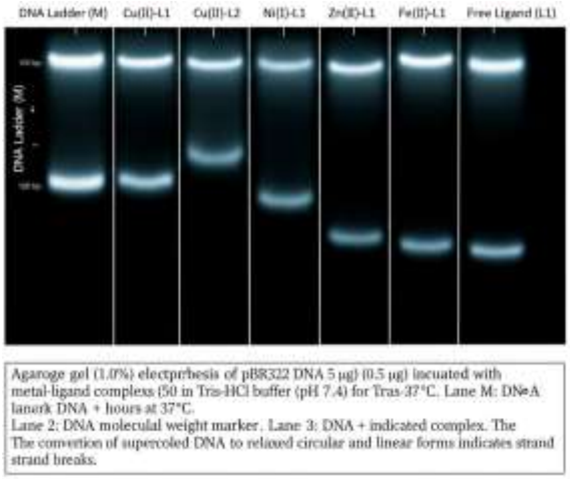
The antimicrobial effects were also discovered against specific organisms of bacteria and fungi. There was a high activity of the Cu (II) and Ni (II) complexes against gram-negative bacteria, whereas the activity of the Co (II) complexes against fungal strains was higher. The areas of inhibition were varied in the complexes. The zones of inhibition were confirmed as having medium to high antibacterial potential and ranged between 12 and 20 mm. These were shown to indicate the enhancement of the biological activity by way of the promotion of the interactions between metal-ligand coordination with the cell wall and enzymes of microbes.

Antioxidant Activity: Radical Scavenging

The radical scavenging tests were done to test the antioxidant capacity of the complexes. The Cu(II)-Co(II) complexes were valid and efficient in counteracting the free radicals. The design of ligands was found to be associated with the scavenging activity of the Schiff base complexes, including the presence of hydrogen that was supposed to be donated to it and phenolic activity that was more active. It was found out that antioxidants can be applied in the future in medicinal chemistry with the confidence that structural properties are the ones that directly affect the antioxidant behavior.

DNA Cleavage Studies: Gel Electrophoresis Results

The agarose gel electrophoresis was used to inspect the DNA cleavage activity. The cleavage patterns of the complexes incubated in the subsistence of plasmid DNA were distinct, although only complexes of Cu(II) were complete up to the formation of supercoiled DNA complexes to linear forms. The cleavage of Ni(II) and Co(II) complexes was partially positive and this was referred to as weak nuclease-like activity. The cleavage efficacy was discovered to be caused by the productivity of reactive oxygen species on the metal centers through the synthesis. The result of such a finding is that the complexes hold promise of being active in DNA cleavage and establish a relationship between the structural coordination and a biological activity.



Agaroge gel (1.0%) electprbesis of pBR322 DNA 5 μg) (0.5 μg) incuated with metal-ligand complexs (50 in Tris-HCl buffer (pH 7.4) for Tras 37°C. Lane M: DN≠A lanerk DNA + hours at 37°C.
Lane 2: DNA moleculal weight marker. Lane 3: DNA + indicated complex. The The convertion of supercoled DNA to relaxed circular and linear forms indicates strand strand breaks.

Figure 2: DNA Cleavage Patterns Induced by Metal–Ligand Complexes

Table 2: Biological Activities of Metal–Ligand Complexes (Antimicrobial, Antioxidant, DNA Cleavage)

Complex Type	Antimicrobial Activity (Inhibition Zone, mm)	Antioxidant Activity (% Radical Scavenging)	DNA Cleavage (Gel Electrophoresis Result)
Cu(II) Schiff base	18–20	75–80	Complete cleavage (linear DNA observed)
Ni(II) macrocyclic	14–16	60–65	Partial cleavage (mixed forms)
Co(II) mixed-ligand	12–14	55–60	Moderate cleavage (nicked DNA)
Zn(II) complexes	10–12	50–55	Weak cleavage (supercoiled DNA retained)

4.4 Mechanistic Insights

Correlation of Spectroscopic Shifts with Coordination Geometry

The geometries of coordination reflected directly only on the spectroscopic data the effects on the electrical and vibrational properties. These changes in the IR bands, like the reduction in the frequency of C=N stretching bands, were attributed to high levels of coordination by strong interaction via azomethine nitrogen. As opposed to cells, various d-d transitions that were geometrical dependences would appear in UV-Vis spectra: the transition in complexes of Ni(II) in a symmetric octahedron environment would be sharper and the transition in deformed octahedron-shaped Cu(II) complexes would be wide. The correlations of those indicated that the strength of the ligand field and coordination geometry are the appropriate measures of spectroscopic shifts.

Bonding Models: Ligand Field Stabilization and π-Backbonding

The relative stability of the octahedral Ni(II) and Co(II) complexes was explained by ligand field stabilization energy (LFSE), where strong use of ligands increased d-orbital splitting. The spectrum properties were associated with Jahn-Teller distortions that caused a reduction of symmetry of the complexes of Cu(II). This demonstrated the 9π-back-bonding and that much electron density had been taken off of metal d-orbitals and onto ligand 9π-orbitals in complexes with aromatic or conjugated ligands. This interaction stabilized the complexes and this affected the charge transfer bands in UV-Vis spectra.

Comparative Analysis Across Cu(II), Ni(II), Co(II), Zn(II) Complexes

The comparative study enabled the revelation of some of the behaviors that were peculiar to the different metal centers. The Cu(II) complexes were discovered to possess a high antibacterial and DNA cleavage capability due to their capability to generate reactive oxygen species as well as the redox cycling. The complexes of NiII did not only have a moderate biological activity but also maintain a balance of structural stability, which means that the ligand field stabilization was good. Their oxidation versatility and versatility in using varying coordination numbers also gave low antimicrobial and antioxidant activities of the Co(II) complexes. The high binding of Zn(II) complexes led to high ligand binding, which offered structural stability, but d-d transitions were impossible to observe in the d^{11} systems; hence, the biological activity of the system was lower. Based on this comparative approach, clear connections were made between the electrical structure, coordination geometry and results of functions.

5. Integration with Applications

These are the metal-ligand complexes that have been synthesized and have a significant potential as far as applications are concerned. Their stabilization properties of the reactive intermediates and control of the electron transfer in the catalysis reactions make the organic transformations, such as the coupling, oxidation and polymerization reactions, more effective. It is also in the form of the structural diversity of the Schiff bases as well as the macrocyclic ligands, which enables the catalytic activity of the complexes to be manipulated in a way that these complexes can be applied to the chemical reaction in an environmentally friendly way. In medicinal chemistry, the complexes are potentially anticancer and potentially antibacterial and their activity is correlated with the potential to interact with the complexes not only with biomolecules, like proteins and DNA. They have an antioxidant behavior, thereby improving their therapeutic potential in reducing oxidative stress. In addition to these complexes put into use in material science, there are ways it is used in biology. Even though it has potential in data storage and spintronic technology, through the benefits of magnetic behavior and even in sensors and optoelectronic devices, the quantity of luminescent properties that they display courtesy of the charge transfer transitions is huge. This flexibility of the metal-ligand complexes regarding the catalysis, therapy and materials defines the relevance of such complexes in the progression of the industrial and biomedical spheres.

6. Challenges and Future Directions

Despite being this way, there are numerous obstacles to the application of metalligand complexes. Physiological instability is a major challenge since most of the complexes are degraded or lose their ligands, resulting in a reduction in their efficacy when they are used as therapeutic agents. The other issue is the scalability of synthesis, as large-scale processes of synthesis like hydrothermal or solvothermal synthesis in the laboratory may not be readily transferred to large-scale production. Another impediment that limits its use on a large scale, especially during the utilization of the noble metals, is the cost. To avoid these shortcomings, any future study aimed at constructing stable complexes in different environments should consider the development of reliable synthetic strategies due to their dependability when dealing with the complexes in the context. More methods of hybrid characterization, which include spectroscopy and crystallography, are needed to come up with deeper mechanistic insights. The combined approaches will be useful to formulate appropriate correlations on a structural level as well as electrical properties that determine the rational formation of complexes of bespoke functionality. In addition to reducing the variety of applications in the area of materials science, medicine and catalysis, innovations in this domain will improve the stability and scalability. The future of the metal-ligand complexes is based on streamlined synthesis and integrated characterization to make the high-performance and sustainable systems of the future.

7. Conclusion

As shown in this paper, critical mechanistic knowledge on new metal complexes of the ligand could be obtained using spectroscopic and structural characterization. Combined, techniques, including the UV-Vis, IR, NMR, EPR and crystallography, represent the geometrical change in a coordination, change in the vibration frequency and electronic transitions. The research works present an explicitly coherent correlation between structure and functions, which contribute to the comprehension of the 1-backbonding bonding models along with ligand field stabilization. The important implications were demonstrated to enhance the catalytic activity of industrial chemistry and to possess the possibility of application not only in the antibacterial, anticancer and antioxidant problems or in the fields of luminescence and magnetism in the materials science. The value of the integrated characterization in enhancing the mechanistic understanding relating spectroscopic alterations to structural facts is emphasized in this paper. The future of metal-ligand complexes is bright, especially when associated with biorefineries and sustainable energy structures. Such alignment, in addition to similar improvements of biological and technological uses, will render chemical processes environmentally friendly. Finally, the stable complexes have been introduced as one of the pillars of modern chemistry, according to which the basic research investigated was correlated with practical creativity in the form of developing mechanistic knowledge and functional need and cost at the same time.

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