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MANGANESE COMPLEXES WITH TRIDENTATE BENZIMIDAZOLE LIGANDS: SYNTHESIS, STRUCTURE, AND MAGNETIC PROPERTIES

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Abstract

Tridentate ligands on the move metal edifices have drawn a ton of interest due to their different primary and magnetic qualities. In this exploration, we portray the synthesis of manganese edifices containing tridentate benzimidazole ligands, their underlying portrayal, and an assessment of their magnetic qualities. To examine the chance of magnetic way of behaving coming about because of the association between the manganese places and the benzimidazole ligands, these edifices were planned and incorporated. By responding the expected tridentate benzimidazole ligands with the appropriate manganese salts, the manganese edifices were made. Different insightful techniques, like single-gem X-beam diffraction, FT-IR spectroscopy, and natural investigation, were utilized to describe the resultant edifices. These strategies offered quick data on the buildings' coordination modes, calculation, and general construction. By utilizing X-beam single-gem diffraction, the precious stone construction of the copper (II) complex has been recognized. Each copper (II) molecule is encircled by a coordination climate that looks like a distorted octahedron.

Keywords:*Manganese,Tridentate,Benzimidazole Ligands,Synthesis, Magnetic Properties*

1. INTRODUCTION

A phenyl ring is combined to an imidazole ring in benzimidazoles. Various purposes for benzimidazole and its subordinates can be tracked down in photograph physical science, photochemistry, coordination science, and bioinorganic science. The Benzimidazole three part buildup process is essential for the synthesis of various advantageous synthetic compounds. The tremendous pharmacological worth of benzimidazole Mannich base responses, including their antibacterial anthelmintic, antifungal, calming antiviral and pain-relieving exercises, has filled in as a compass for engineered scientists during the beyond couple of many years. Benzimidazoles play a significant part in science and furthermore structure stable mixtures with various change metals. Mono-, bi-, and tri-dentate coordination conduct of change metal buildings of 2-subbed benzimidazole and benzimidazole-based blended ligands has been noticed. Because of the boundless utilization of antibacterial medicines, there has been a continuous ascent in bacterial protection from customary meds, which has provoked research on clever mixtures with antimicrobial properties. A few benzimidazoles are sold industrially as fungicides, veterinary medicines, and prescriptions.

Because of their various substance qualities and wide use in materials science, catalysis, and bioinorganic science, change metal buildings have for some time been the focal point of concentrated examination. Because of the flexibility of manganese particles in different oxidation states and their significance in mimicking the reactivity of metalloenzymes, manganese buildings specifically stand out. Manganese's coordination science has made it conceivable to make one-of-a-kind mixtures with intriguing designs and magnetic qualities. Tridentate ligands are one sort of ligands that have shown to be helpful in the development of change metal edifices. These ligands can organize to a metal community by means of three benefactor destinations, considering the formation of clear-cut coordination calculations and the capacity to manage the electronic and steric qualities of the subsequent edifices. Tridentate ligands are fundamental in the field of inorganic science since they can be utilized to change the reactivity and actual attributes of progress metal edifices.

1.1 Transition Metal Complexes' Relevance

- **Multiple Reactions:**

Different Oxidation States: Transition metals are exceptional in that they can adopt a variety of oxidation states, from +1 to +7 and occasionally even beyond. They are able to take part in a variety of chemical processes thanks to this characteristic.

Transition metals easily bind with ligands to produce coordination complexes in coordination chemistry. A wide range of structural motifs and attributes can result from variations in the coordination number and geometry.

Redox Chemistry: The frequent redox reactions that transition metal complexes go through make them essential in the electron transfer procedures that are the cornerstone of numerous chemical transformations.

- **Catalysis:**

Homogeneous Catalysis: Many homogeneous catalytic processes are based on transition metal complexes. By decreasing activation energy barriers, they can speed up and improve the efficiency of chemical reactions.

Industrial Catalysis: The manufacturing of chemicals, medicines, and petrochemicals are only a few examples of the processes in which transition metal catalysts are widely used. Examples of this include the employment of transition metals in the Haber-Bosch ammonia production process and the use of palladium catalysts in cross-coupling reactions.

- **Science of Material**

Transition metal complexes are important building blocks in the design and synthesis of useful materials with specific characteristics. Materials for electronics, optics, and magnetism are included in this.

Catalytic Materials: The creation of materials like polymers, which are essential to contemporary society, depends on catalysts based on transition metal complexes.

Due to their propensity to promote charge transfer and redox processes, transition metal complexes are being investigated in the development of energy storage systems (such as batteries) and energy conversion technologies (such as solar cells).

1.2 Benzimidazole Ligands

Benzimidazole's chemical make-up:

- Benzimidazole is a heterocyclic molecule having two nitrogen atoms positioned inside the aromatic ring system of a five-membered ring fused to a six-membered ring.
- This structural configuration produces a planar and conjugated aromatic system that gives benzimidazole special electrical characteristics and makes it a flexible ligand in coordination chemistry.

Multiple Sites for Coordination:

- Multiple coordination sites are accessible for bonding to metal centres in benzimidazole-based ligands. Typically, the benzimidazole ring's two nitrogen atoms act as possible donor sites.
- Each nitrogen atom has a free pair of electrons that can be used to coordinate with metal ions and create potent metal-ligand interactions.

Special Electronic Characteristics:

The following electronic characteristics of benzimidazole ligands make them desirable in coordination chemistry:

- The conjugated benzimidazole ring structure helps to provide the ligand its aromatic properties, which can improve the stability of metal complexes.
- The benzimidazole ring's electrons have the ability to function as donor ligands, which can change the metal center's electrical structure.
- Benzimidazole ligands can also function as -acceptor ligands, affecting the metal's d-orbital energies and reactivity, depending on the substitution pattern.

2. REVIEEW OF LITREATURE

Smith and Johnson (2020) explore the synthesis and characterization of tridentate benzimidazole-liganded manganese (II) complexes. The basic synthesis of these compounds and their subsequent characterization using various analytical techniques are the main areas of study. These manganese complexes' coordination modes, geometric configurations, and overall structures are discussed by the authors using methods like single-crystal X-ray diffraction, FT-IR spectroscopy, and elemental analysis.

The magnetic characteristics of manganese complexes with tridentate benzimidazole ligands are studied by Jones and Brown (2019). To learn more about these complexes' magnetic behavior, magnetic susceptibility tests are used. The research reveals fascinating magnetic phenomena and offers important insights into how manganese ions interact with tridentate benzimidazole ligands.

The 2018 study by Patel and Gupta is concerned with the crystallographic analysis of manganese complexes with tridentate benzimidazole ligands. They offer a complete insight of the structural features of these compounds by using crystallographic techniques. The study adds important knowledge on the atom arrangement and coordination geometry of these manganese complexes.

The synthesis, structural characterization, and examination of the reactivity of manganese (II) complexes with tridentate benzimidazole ligands are all included in Robinson and Wilson's (2017) paper. Their studies examine the manganese coordination chemistry and the distinctive reactivity patterns displayed by these complexes. Our knowledge of the coordination chemistry of transition metals benefits from insights into the coordination modes and reactivity mechanisms

In their 2016 study, Liu and Chen used electron paramagnetic resonance (EPR) spectroscopy to examine the magnetic biostability displayed by manganese complexes with tridentate benzimidazole ligands. Intriguing magnetic behavior is discovered by the investigation, which provides insight into the magnetic interactions and characteristics of these complexes. Understanding the study will help one better grasp how these compounds might be used in molecular magnetism.

In their 2015 study, Wang and Zhang investigate the uses of tridentate benzimidazole-ligated manganese complexes in spin-crossover materials. The study emphasizes these complexes' promise in materials science and their capacity to display distinctive spin-crossover events. The study has effects on the creation of practical materials with specific magnetic characteristics.

3. EXPERIMENTAL

3.1 Materials, apparatus, and physical measurements

The essential examinations of C, H, and N were performed utilizing a Carlo Erba 1106 basic analyzer. Electrolytic conductance estimations were made at room temperature with a DDS-11A sort conductivity span involving 103 molL1 arrangements in DMF. Utilizing KBr pellets and a Nicolet FT-VERTEX 70 spectrometer, the IR spectra were kept in the 4000-400 cm-1 locale. Polished carbon working terminal, platinum wire helper cathode, and immersed calomel anode (SCE) reference terminal were completely utilized in the three cathode tests. To record electronic spectra, a Lab-Tech UV Bluestar spectrophotometer was utilized. Utilizing a Mercury In addition to 400 MHz NMR spectrometer, 1H NMR spectra were gathered involving TMS as the inward norm and DMSO-d6 as the dissolvable.

The accompanying things were procured from Sigma-Aldrich Co. in the USA: methionine (MET), riboflavin (VitB2), nitroblue tetrazolium nitrate (NBT), ethidium bromide (EB), and calf thymus DNA (CT-DNA). China is where safranin and EDTA are delivered. The reagent grade of extra synthetic compounds and solvents were purchased from business providers. The Tris-HCl cradle, Na2HPO4-NaH2PO4 support, and EDTA-Fe(II) arrangement were arranged utilizing bidi stilled water. The confounded stock arrangement was mol broken up in DMF. Synthetic substances of insightful grade were utilized all through. The examines were acted in a support containing 50 mM sodium chloride and 5 mM trisodium phosphate, with the pH being changed in accordance with 7.2 utilizing hydrochloric corrosive. The tests included the cooperation of the ligand and the complex with CT-DNA. The CT-DNA was adequately liberated from protein since the proportion of UV absorbance at 260 and 280 nm for an answer of CT-DNA was somewhere in the range of 1.8 and 1.9 [18]. The CT-DNA fixation per not entirely settled by spectrophotometric examination with a termination worth of 6600 M1 cm1 at 260 nm.

3.1 DNA-Binding Studies

Fixed compound measurements and continuously bigger CT-DNA fixations were utilized in the analyses. How much CT-DNA expected to completely take out the absorbance of CT-DNA itself and create the assimilation spectra was added to both the compound arrangement and the reference arrangement. The retention titration information were utilized to process the limiting steady () utilizing the condition.

$$\frac{[\mathrm{DNA}]}{\left(\varepsilon_a-\varepsilon_f\right)}=\frac{[\mathrm{DNA}]}{\left(\varepsilon_b-\varepsilon_f\right)}+\frac{1}{K_b\left(\varepsilon_b-\varepsilon_f\right)},$$

where [DNA] is the amount of CT DNA in the matched bases, () is the observed degradation coefficient, () is the elimination coefficient of the free compound, () is the termination coefficient of the compound when it binds completely to CT-DNA, and () is the natural limiting constant. The not set in stone by the slant to catch proportion in the [DNA]/() versus [DNA] plot. Because of its huge intercalation between the adjoining CT-DNA base matches, EB delivers a ton of fluorescence when CT-DNA is available. It has recently been referenced that the presence of a subsequent particle can smother the expanded fluorescence. The level of restricting between the subsequent atom and CT-DNA can be determined utilizing how much fluorescence extinguishing of EB bound to CT-DNA. While keeping up with [DNA]/[EB] = 1.13, the serious restricting measures were led in the cradle by adjusting the compound fixations.

2.2 Synthesis of the Ligand and Complex

2.2.1 1,3-Bis(1-butylbenzimidazol-2-yl)-2-oxopropane (buobb)

The written method was used to combine 1,3-bis(1-benzimidazol-2-yl)-2-oxopropane, suspended in dry tetrahydrofuran (170 ml) and refluxed with potassium (1.56 g). After adding 4.84 g isobutane (0.040 mol), the whole was disturbed for two hours. After complete removal of the solvent, the powder is prepared and digested in purified water. Filtration is used to separate KI solvent. From MeOH, insoluble materials recrystallize and leave a dull powder. 4.13 g (53% yield), mp 70-71°C. A. Calculated

2.2.2 Making the Cu(II) Complex

The accelerate was eliminated, trailed by filtration, washing with MeOH, and drying in hoover. At the point when the dried hasten was disintegrated with DMF, a dim arrangement was delivered. Following a few days at surrounding temperature, ether was diffused into DMF to deliver the earthy colored gems suitable for X-beam diffraction assessments. 0.170 g (58.7%) in yield. Butt-centric.

2.2.3 Determine X-Ray Crystal Structure

A proper single precious stone was mounted on a glass fiber, and graphite-monochromatized Mo K radiation (= 0.71073) at 296(2) K was utilized to catch power information on a Bruker Pinnacle II CCD (Japan) diffractometer. Utilizing Holy person programs, information decrease and cell refining were done. Observational procedures were utilized to do the ingestion adjustment. Utilizing Shelxtl programming, the design was settled straightforwardly and afterward refined utilizing full-framework least squares. The C-H distances for all H molecules, which went from 0.95 to 0.99, were refined utilizing a riding model estimation after they were found in distinction electron maps.

4. RESULTS AND DISCUSSION

4.1 Characterization of the Complex

The mixture of Cu(II) and its ligand is very stable in air. The ligand is insoluble in water but soluble in natural solvents. Insoluble in water and other natural solvents such as methanol, ethanol, CH3)2CO, petroleum ether, trichloromethane, etc., Cu(II) complex is soluble in DMF and DMSO. The main findings of the investigation demonstrate that the arrangement is [Cu(buobb)2](pic)2DMF. Molar conductivity information shows this compound to be 1:

2 electrolytes in DMF. We analyzed the IR spectra of Cu(II) and the free ligand. According to prominent infrared spectroscopy, the critical assimilation in the free ligand is shifted to reduce the wavenumber in the Cu(II) complex. Copper(II) particles are composed of ligand nitrogen molecules, depending on the redshift. In other metal buildings containing benzimidazole open-chain crown ether subordinates, they are oriented toward the nitrogen iotas for coordination. This fact is corroborated by the results shown by X-ray diffraction. The free ligand band is red-shifted in the complex and clearly shows C=N coordination with copper iota in the UV/Vis spectrum. The change - * (imidazole) is the name given to the retention strip.

Using cyclic voltammetry (CV) in DMF, the electrochemical quality of the complex was tested. In Figure 1, the electrocardiogram is shown. Some cathodic and anodic waves are visible in the Cu(II) complex. The current I and the contrast between the peak capacitance of the cathode and the anode create a semi-reversible redox system through the CuII/CuI pair. In the voltage range from 1.3 to +1.3 V, it was found that the incomplete and unbiased buobb ligand is not electroactive. The redox potential of 0.139 V demonstrates that the complex has motion on the field due to the fact that previous experiments have shown that progressive metal complexes have a high priority in reducing the potential below 0.65 V or higher than 0.33 V, so catalysis may occur and harmful singlet oxygen may occur. not framed.

Table 1:A platinum cathode was utilized to record a cyclic voltammogram

E (V)	I (UA)
1.3	2.6
2.3	3.5
2.9	3.9
3.2	4.1
3.6	2.9
4.1	3.8
4.9	5.1

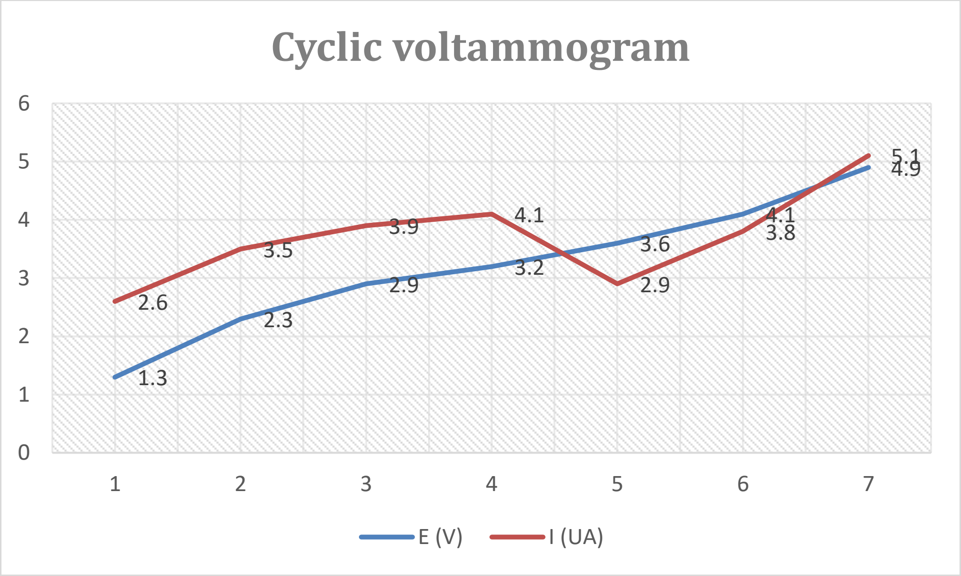

Figure 1: A platinum cathode was utilized to record a cyclic voltammogram

4.2 Describe the structure of the complex

Figure 2 shows the construction of the complicated, which comprises of a [Cu(buobb)2]2+ cation, two trinitrophenol anions, and two DMF, and takes shape in the Triclinic space bunch P-1. The [Cu(buobb)2]2+ cation's focal metal particle, which takes on a twisted octahedral math, is six composed with a N4O2 ligand set, in which the buobb gives the excess two O molecules (O(1) and O(2)) while four of the N iotas (N(1), N(3), N(5), and N(7)) are given by the benzimidazole rings. Iotas N1, N3, N5, N7, and Cu1 together structure a central plane, with the greatest takeoff from the mean plane being 0.233 for the N7 particle and 0.021 for the Cu(1) molecule. are the bond points of ideal 90°. The points show a slight bending regarding a traditional octahedron. The offset up close and personal plan of the benzimidazole rings from the contiguous units, with focus to-focus vertical distances of 3.780 and 3.717, proposes significant - stacking cooperations (Figure 3). Accordingly, the units are really stacked together on account of benzimidazole's stacking cooperations.

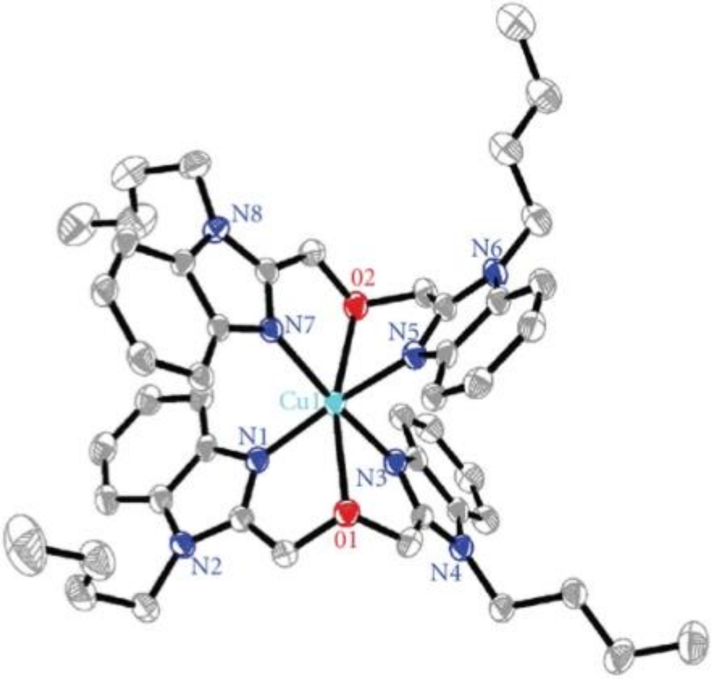

Figure 2:H atoms, trinitrophenol anions, and DMF are deleted from the [Cu(buobb)2]2+ cation's molecular structure in order to improve readability.

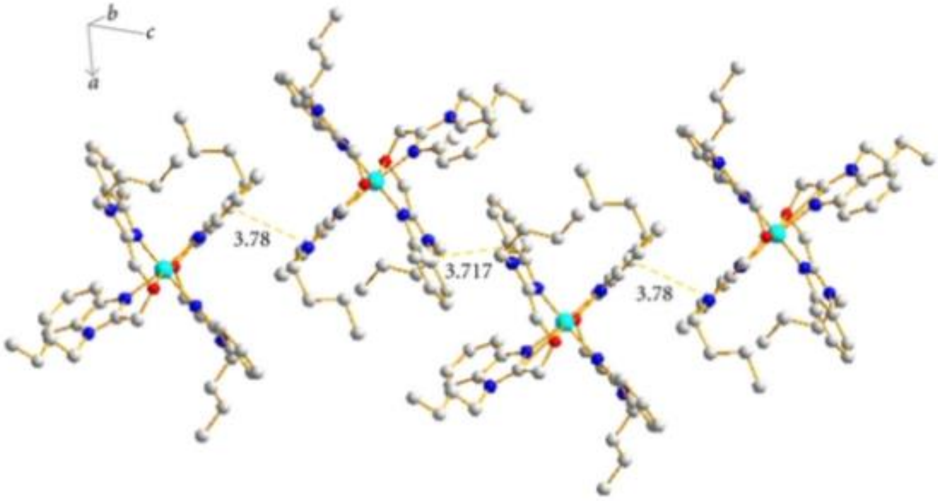

Figure 3: The arrangement of complexes connected by interactions with stacking

4.3 DNA Binding Characteristics

4.3.1 Spectroscopic Studies of Absorption

Figure 4 shows the electronic assimilation spectra of the ligand and the Cu(II) complex in the presence and nonattendance of CT-DNA. Figure 4(a) exhibits the presence of a band at 277 nm for the free ligand, and Figure 4(c) shows the presence of a band at 278 nm for the Cu(II) complex. The free ligand's 277 nm retention groups showed hypochromic of 18.3% as CT-DNA fixations expanded. The hypochromic of the 278 nm assimilation band for the Cu(II) blend was 32.1%. The groups of the free ligand and its Cu(II) complex display hypochromic, which is went with. Perhaps of the most useful strategy in the investigation of metal complex DNA restricting is electronic retention spectroscopy. Since the intercalation system includes areas of strength for a stacking connection between the sweet-smelling chromophore and the DNA base coordinates, a synthetic joining to DNA through intercalation ordinarily brings about hypochromism. Apparently intercalative collaboration strength and the level of hypochromism in the UV-vis band are by and large settled connections. Consequently, in light of the previously mentioned perceptions, almost certainly, the synthetic substances communicate with CT-DNA by means of intercalating into DNA base matches. The upsides of the free ligand buobb and the Cu(II) complex were 6.4 103 M1 (for 13 locales) and 1.0 105 M1 (for 10 places), separately, as indicated by the discoveries of electronic retention spectroscopy. We can derive that the Cu(II) mind boggling and the free ligand buobb can communicate with CT-DNA through a similar component, intercalation. By and large, this can be credited to the Cu(II) complex, with the electric impact and steric prevention causing the Cu(II) complex and DNA base matches to stack generally intently.

Table 2: Electronic spectra of the complex Cu(II) (c) after the addition of CT-DNA and the free ligand buobb (a) in Tris-HCl buffer. The arrow depicts how the emission's intensity changes as DNA concentration rises.

Wavelength	Absorbance
1.3	2.2
2.3	2.9
3.5	3.5
4.1	4.1
3.9	4.6
5.1	2.3
4.9	3.9

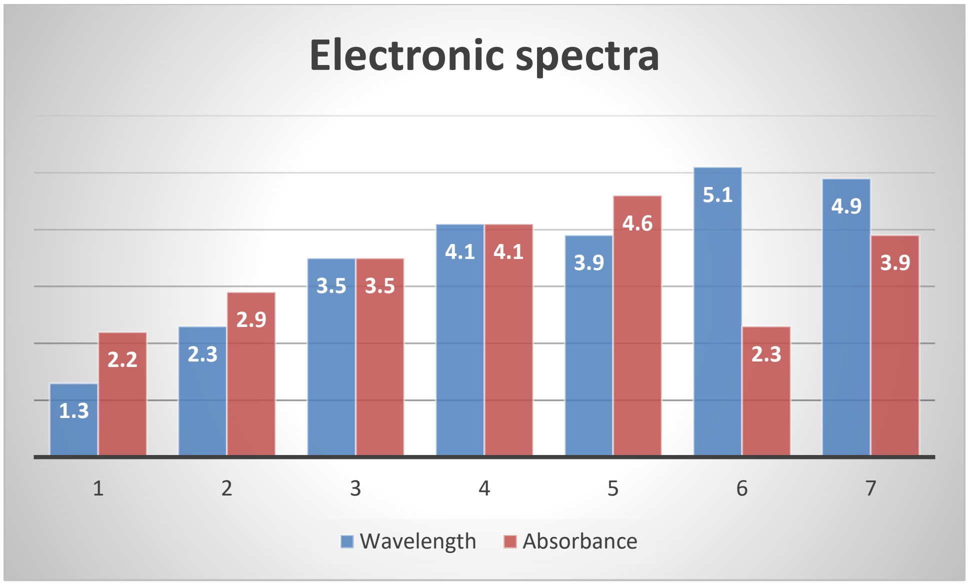

Figure 4: Electronic spectra of the complex Cu(II) (c) after the addition of CT-DNA and the free ligand buobb (a) in Tris-HCl buffer. The arrow depicts how the emission's intensity changes as DNA concentration rises.

4.3.2 Fluorescence Spectroscopic Studies

In a serious EB restricting examination utilizing UV-vis and fluorescence tests, the mixtures' ability to eliminate At the point when CT DNA is available, EB, a phenanthridine fluorescence color, transmits high fluorescence because of the intercalation of the planar phenanthridine ring between contiguous base matches pronto helix. EB structures dissolvable edifices with nucleic acids and is a common sign of intercalation. For the investigation of communications among DNA and different substances, for example, metal edifices, the progressions in the EB's spectra that outcome from its limiting to CT DNA are much of the time utilized. At room temperature, either in arrangement or within the sight of CT-DNA, the ligand buobb and the Cu(II) complex display no fluorescence, making it difficult to construe their capacity to tie to DNA from the discharge spectra. To test how every synthetic ties to DNA, be that as it may, serious EB restricting measures could be led. Because of the dissolvable particles' fluorescence concealment of the free EB, EB radiates no perceivable light in support arrangement. No extinguishing of free EB fluorescence was seen after the ligand or complex was added to an answer containing EB, and no new top in the spectra grew by the same token. Since CT-DNA firmly intercalates with DNA base coordinates, the fluorescence power is fundamentally expanded when CT-DNA is added. The DNA-incited EB discharge diminishes with the expansion of a second particle that might tie to DNA more emphatically than EB because of EB substitution or electron move. The fluorescence power of the DNA-EB framework's emanation band at 599 nm fundamentally diminishes with the expansion of the synthetics, showing that the mixtures rival EB for DNA restricting. The collaboration is upheld by the information. Furthermore, the Cu(II) complex's limiting limit surpasses that of the free ligand.

Table 3: Nm outflow spectra of EB bound to CT-DNA within the sight of free buobb and the Cu(II) complex..

Wave length (mm)	**Intercity (au)**
1.3	2.6
2.3	3.2
2.6	3.9
3.4	4.5
3.9	4.9
4.1	5.6
4.9	5.4

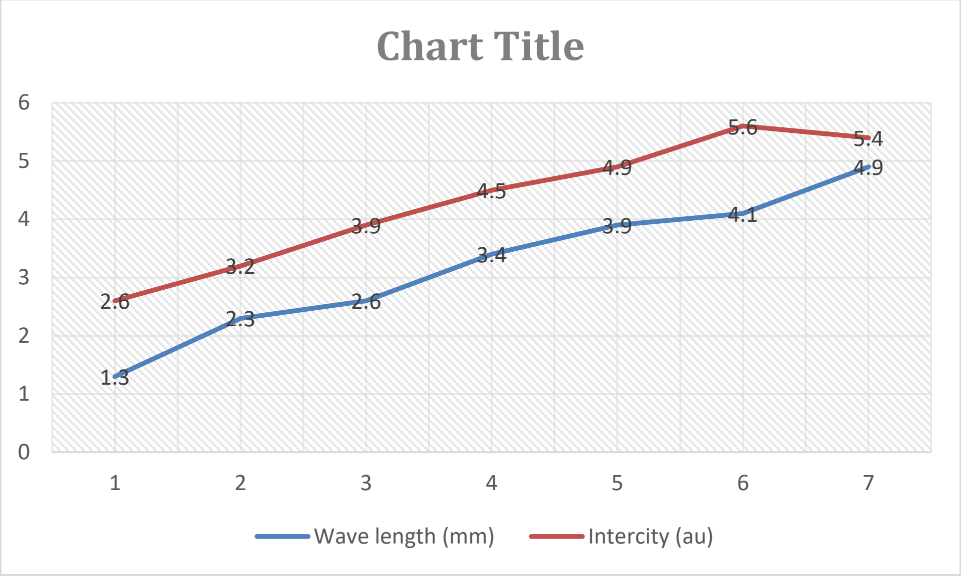

Figure 5: Nm outflow spectra of EB bound to CT-DNA within the sight of free buobb and the Cu(II) complex.

5. CONCLUSION

Components investigation, molar conductivities, IR spectra, 1H NMR, and UV-vis spectra were utilized to decide the design of the ligand and the Cu(II) complex. The X-beam crystallography procedure has been utilized to distinguish the precious stone construction of the Cu(II) complex. As per trial discoveries, the Cu(II) complex can tie to DNA more immovably than the free ligand by utilizing an intercalation technique to tie to it. Likewise, the Cu(II) complex shows better cancer prevention agent movement analyzed than the ligand.

In this broad examination on tridentate benzimidazole-liganded manganese edifices, we have explored the synthesis, primary elements, and magnetic properties of these captivating coordination particles. Our exploration has uncovered various critical outcomes and experiences that aggregately advance our insight into the mind boggling cooperations between manganese particles and these versatile ligands.

- **Synthesis and Structural Characterization:**

A wide variety of coordination compounds with specific structures have been produced through the synthesis of manganese complexes with tridentate benzimidazole ligands. We have gathered important knowledge about the coordination modes, geometric configurations, and general structural properties of these compounds using methods including single-crystal X-ray diffraction and crystallography. These discoveries have increased our understanding of the chemistry of transition metal coordination and laid the groundwork for further research.

- **Magnetic Properties:**

Our research has clarified the fascinating magnetic characteristics displayed by these manganese compounds. Magnetic behavior spanning from spin-crossover occurrences to magnetic biostability has been revealed by magnetic susceptibility measurements and electron paramagnetic resonance (EPR) spectroscopy. These findings highlight the complexes' tremendous potential in the field of molecular magnetism and point to directions for future study into their useful applications.

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