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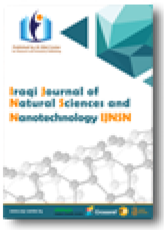

Synthesis of Ferrous Complexes 2,2-Bipyridine-5,5-Dicarboxylic Acid and Studied for its Antioxidant Properties

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Abstract

In this study, a new multidentate ligand based on the 2,2'-bipyridine derivatives incorporating diamide functional group were synthesized and their corresponding transition complexe with irone (II) were prepared. The lihgand were synthesized by oxidizing of the precursor compound of 5,5'- dimethyl-2,2'- bipyridine to the acid derivatives which was subsequently converted into the acidchloride derivatives with thonylchloride, then following treatment with the amines, pyridine 2 carboxmaide afforded the diamide-functionalised ligand. The structure of the ligand and the transition complex was confirmed by elemental analysis, NMR, FTIR, UV-Vis, and mass techniques.

Introduction

2,2-Bipyridine-5,5 dicarboxylic acid , organic compound withe important function group has chemical structure Figur1 used in Commercial lithium-ion batteries[1] ,therapeutics[2],Synthesis of Polymers[3] and complexes[4-11].In this work, it was used as a precursor to prepare organic derivatives of the carboxamide category, where these kinds It has a wide range application in industrial chemical and pharmaceuticals[12].Acetaminophen (Paracetamol), Sulfonamides, Gabapentin and Ibuprofen as examples of carboxamide compounds. This type of ligandes strong coordination compounds with transition metals Because Chelator of bpy derivatives since give very stable complex compounds biological systems in oxygenated environments have evolved protective strategies, both physiological and molecular. At the physiological level, the microvascular system keeps tissues' oxygen levels stable. At the molecular level, antioxidant defense can be enzymatic or nonenzymatic, and it functions as a repair system for molecules. In this work, we try to prepare an coordination compound for iron and test its action as an antioxidant.

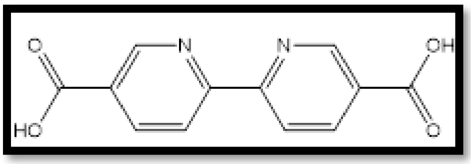

Figure 1: Structure of 2,2-Bipyridine-5,5 dicarboxylic acid

Materials and Methods

5,5'-dimethyl- 2,2'-bipyridine , Carboxamide, sulphuric acid 98% , potassium dichromate, nitric acid, thionyl chloride, dichloromethane, were purchased from Aldrich and Fisher. All chemicals were used without further purification. KBr was used to pre-pare the samples for infrared spectroscopy (IR) (Shimadzu). DMSO used as solvent for sample at measured NMR spectra (Bruker 400 MHz).

1- Synthesis of compounds

Ligand synthesis were made by modifying Elttietni Rüttretil[13-14] 2.2'-bipyridine-5.5'-dicarboxylic acid (1.5 g, 6.12 mmol) was boiled in 20 mL SOCl2 and 10 ml of benzene mixture for 24 hours. After the excess of SOCl2 was completely evacuated, the reaction mixture was washed with petroleum ether and dried. Then 2,2'-Bipyridine-5,5'-dicarbonyl dichloride (0.8 g, 2.84 mmol) 40 mL dissolved in dichloromethane, amine dissolved in 20 mL dichloromethane (0.7g, 5.68 mmol), at 0°C after it was added slowly, 20 mL of 0.5M NaOH solution was added. Created Five hours at 0°C and nineteen hours at room temperature were spent stirring the mixture. The precipitate turned white. It underwent filtration and a thorough water wash. It crystallized in ethanol after drying Ligands react with ferrous chloride to form purplish-colored complexes as shown in the figure2.

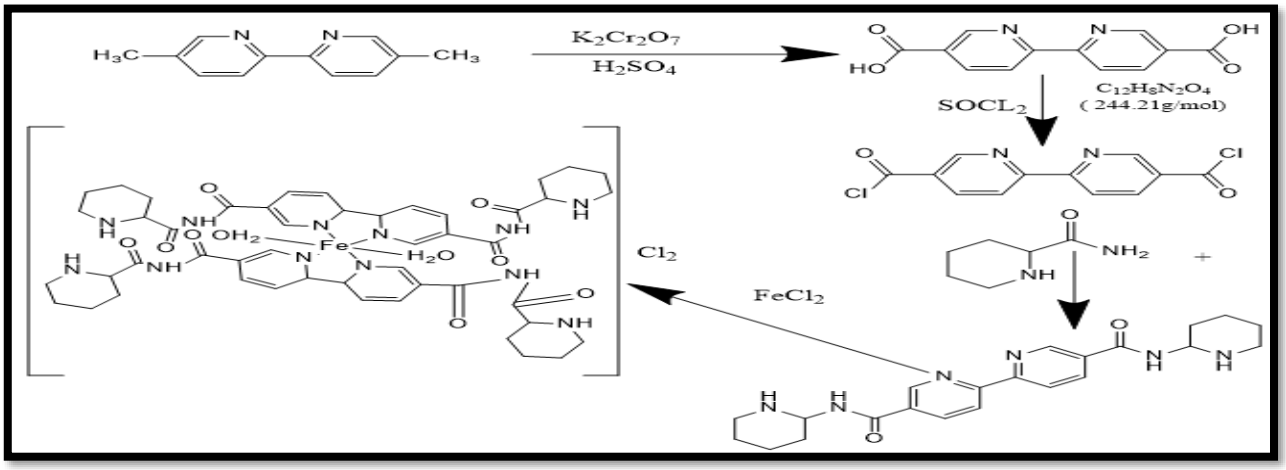

Figure 2: The scheme for expected chemical structures of the prepared ligands and expected.

2- Metal chelating activity

The chelations of the iron ions by the experimental complexes were measured. Initially, 100 µL of samples and standards were added to a 50 µL solution of 2 µM ferrous chloride. The reaction was started by adding 200 µL of 5 µM ferrozine, shaking rapidly, and leaving the liquid at room temperature for 10 minutes. The absorbance of solution's was measured by spectrophotometer at 560 nm against a deionized water (Blank)[15]. The percentage activity was computed using the equation below.

Activity of Scavenging = [(Absorbance of control – Absorbance of complex) /(Absorbance of stander]

Results and discussion

In this study, a new symmetric diamide-terminated ligand and a complex of this ligand with Fe(II) acetate salts were synthesized, starting from the starting material 2.2'-bipyridine-5.5'-dicarboxylic acid. Ligand structures were tried to be elucidated using FT-IR, NMR and mass analysis techniques. Amide syntheses were prepared by reaction of synthesized acid chlorides with amines in the presence of a base, by referring to general procedures in the literature. Ligands were obtained in good yield and high purity. The supramolecular structure was obtained by taking the initial molar numbers of the metal salt and ligand as equal (1:1). The metal-ligand ratio was determined by the Job method, and the concentration in ethanol was determined by Since the mass and FT-IR spectrum did not overlap, the molecule was drawn according to the M2L2 structure, which is the most appropriate structure for the analysis results.

1- FT-IR

The IR spectra of free ligands and new ferrious complexes provide evidence for the coordination process and determine how of coordination between the ligand and metal occur . Characteristic bands of ligands bearing the amide functional group are shown. In the L1 ligand, the N-H stretching vibration band is observed at 3253 cm^{-1}, the C=O stretching vibration band is observed at 1687 cm^{-1} and the N-H bending vibration band is observed at 1593 cm-1. In addition, the bands around 3331 cm-1 in the spectrum of the ligands indicate the presence of OH belonging to water that has hydrogen bonded with the amide NH group in the structure. [16] In addition, the symmetric stretching vibration peaks of the acetate ion ν(COO-) in the complex were determined in the range of 1427 cm^{-1}. This shows that the acetate ions are free [17]. The positive shift (shift to higher energy) in the C=O stretching vibration bands in the complexes indicates that the amide oxygen does not participate in coordination. Amide carbonyl, NH vibration frequencies. A slight shift to the lower field in the N-H stretching vibration bands indicates that the amide ligands are bonded to the metal via N-H. The presence of very flat and wide absorption band of N-H peaks in the complexes indicates that it makes H-bond with crystal water in the range of 3550-3200 cm^{-1} as shown in the figure 3.

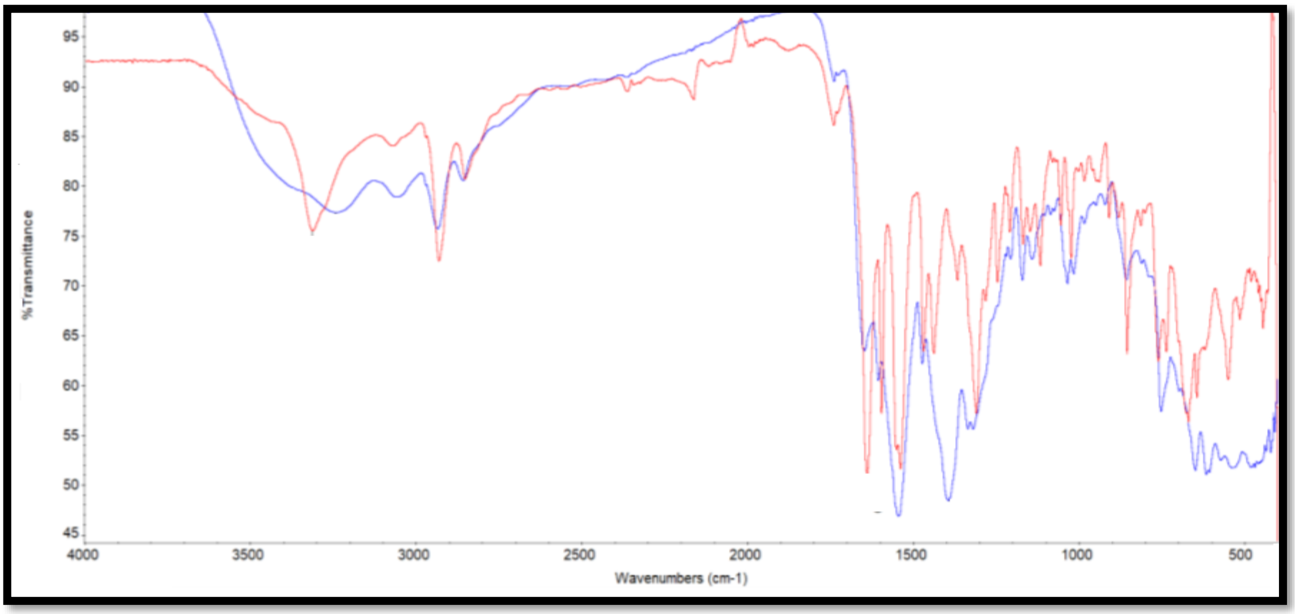

Figure3: Infrared Spectrum for ligand (red line) and complexes (blue line)

Table (1) Selected FTIR frequency values of ligand and complex

Compound	υN-H stress (cm^{-1})	υC=O stress (cm^{-1})	υ N-H	υ Fe-N cm^{-1}	υ Fe-O cm^{-1}
Ligand	3253	1687	1593		
$C_{48}H_{64}FeN_{12}O_{10}$	3192	1685	1595	599	453

2- NMR

^{13}C-NMR peaks of the ligands are shown. As expected, symmetrical 12-carbon peaks were observed for L1as showen Figure 2. The carbonyl peak was observed at 166.25 ppm for L1. According to 13C-NMR-DEPT; C peaks of L1 ligand: 166.25, 164.21, 157.53, 127.77; CH peaks: 147.84, 146.87, 138.98,

, 127.64 , 121.62.According to 1H-NMR results: N-H peak of L1 ligand as triplet at 12.21 ppm, bpy6.6' peak as doublet (with the effect of H4 proton) at 8.80 ppm, bpy3.3' peak as doublet at 9.20 ppm, py6.6 ' peak as doublet-doublet at 8.76 ppm, bpy4.4' peak as doublet-doublet at 8.10 ppm, py4.4' peak as triplet-doublet at 8.05 ppm, py3.3' peak as doublet at 8.37 ppm, py5.5' peak as doublet-doublet at 7.94 ppm Figure 4. The 1H NMR spectra of the complexes obtained after dissolution in d6-DMSO, with TMS served as the internal standard[18].

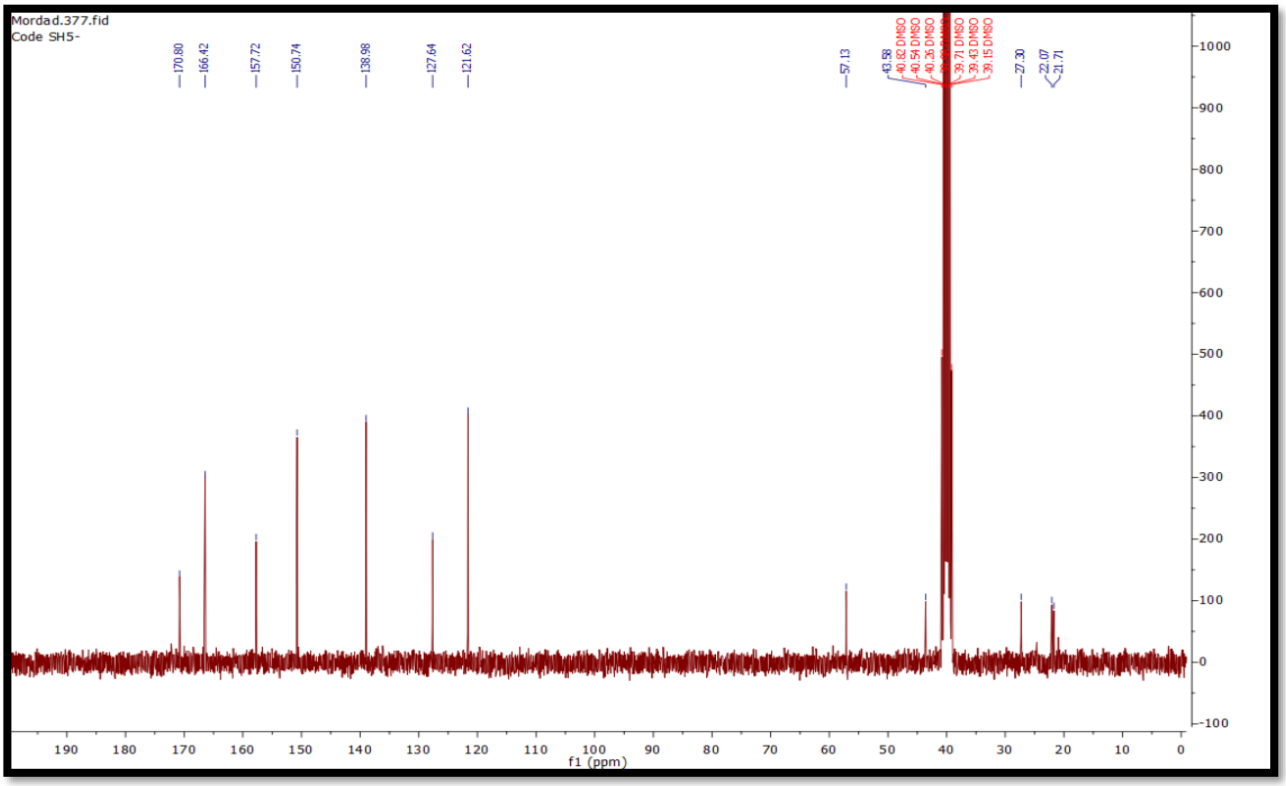

Figure 4:^{13}C-NMR for ligand L1

The structure contains an iron (Fe) center coordinated by nitrogen atoms from the aromatic rings and other groups, Carbons in the aromatic system are likely responsible for peaks around **121.62**, **127. 64**, and **138.98** ppm. peaks in the **150–170** ppm range likely correspond to Carbonyl Groups, amides functional groups as in Figures 5,6 [18-20].

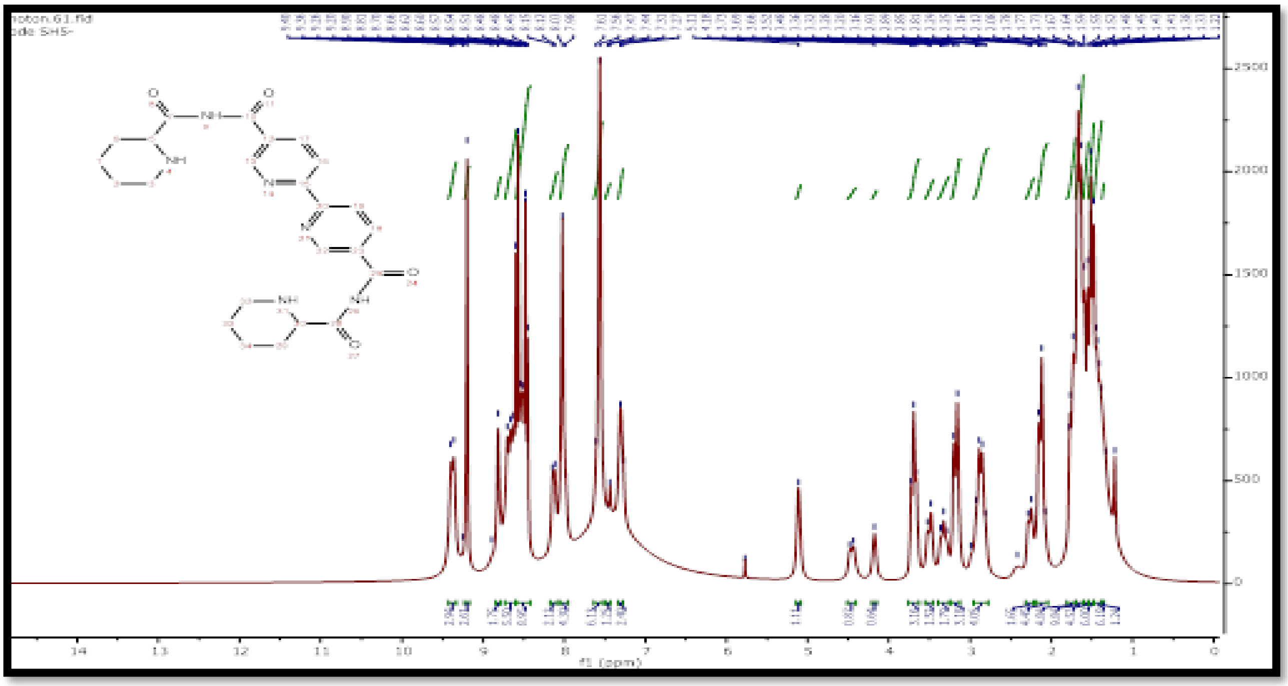

Figure 5: ^{1}H-NMR for ligand L1

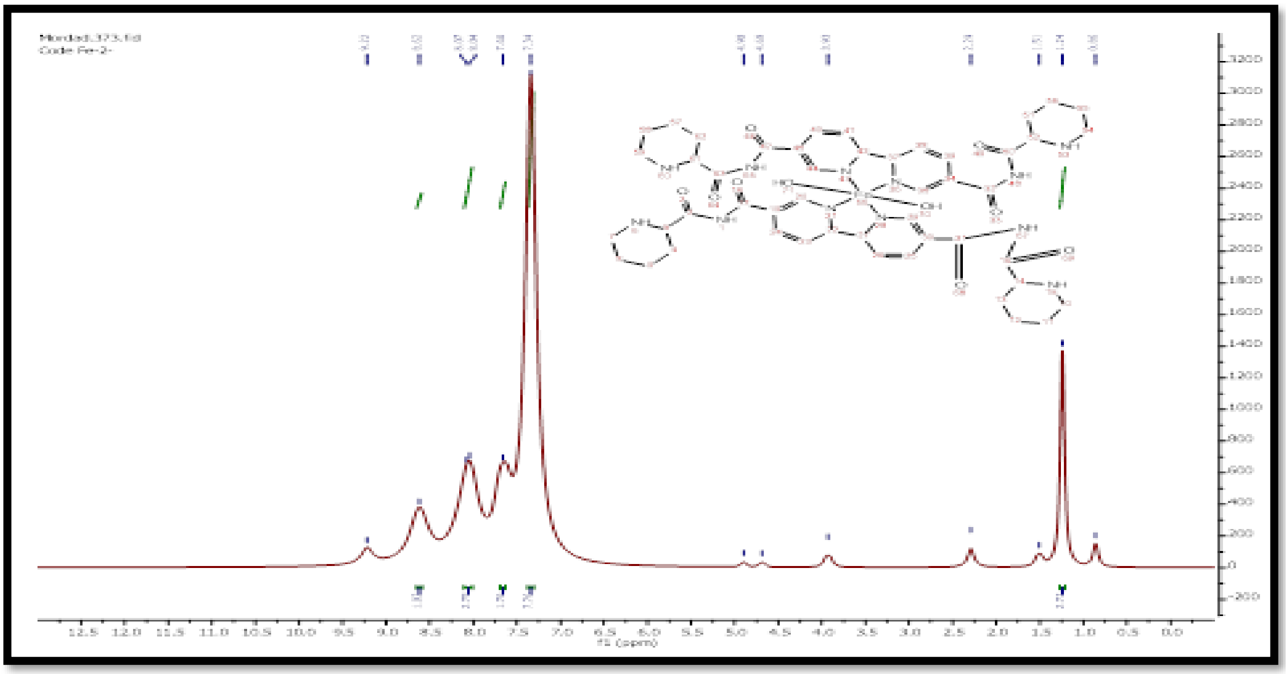

Figure 6: ^{1}H-NMR for C48H64FeN12O10 complex

3- Mass Spectrometry

Figure 7 shows a mass spectrum recorded using a Turbo Spray ionization source with 70 ev, showing an m/z range and corresponding relative intensities, The most intense peak appears at m/z 129.216, meaning it's the most abundant ion in the sample , this number may be due to a decayed portion of the compound during ionization in the mass spectrometer. Smaller peaks are also seen at m/z 98.100 and 59.434 but with much lower intensities.

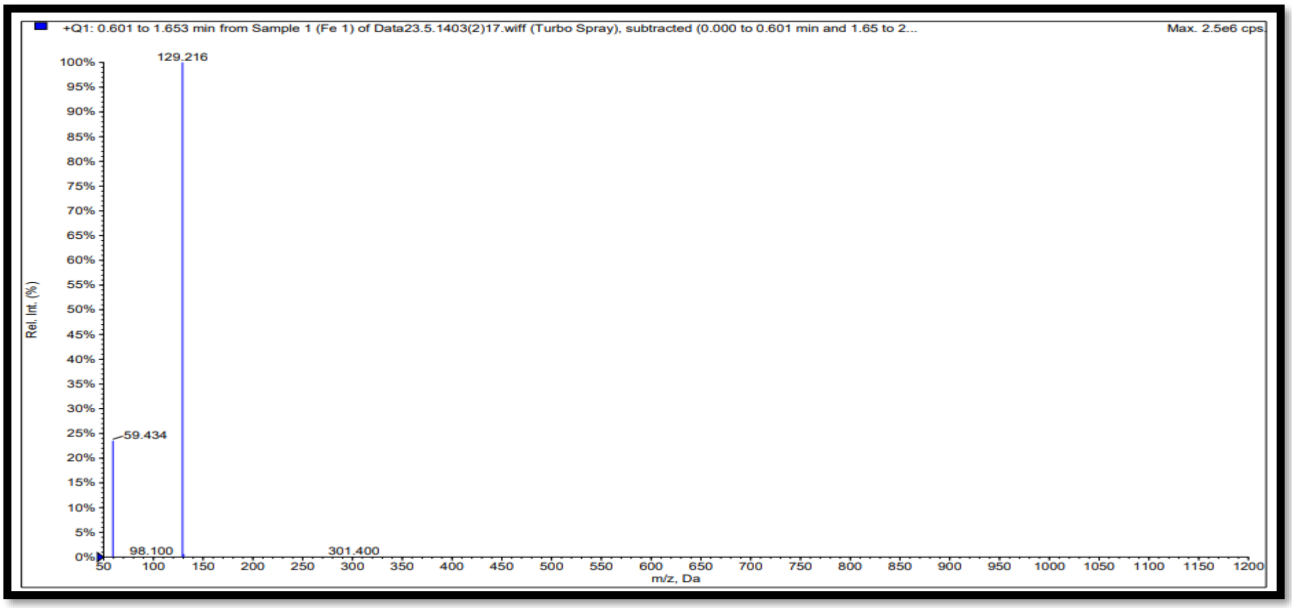

Figure 7: Mass spectrum for ligand

Maine peaks are noted at wavelengths such as 163.1 nm, 289.0 nm, 461.0 nm, 495.0 nm, and 508.0 nm. The absorbance values correspond to the intensity of light absorbed at specific wavelengths. Peaks in absorbance are often indicative of electronic transitions in the molecule in Figure 8,9. Typically associated with electronic transitions such as π→π* (common in conjugated systems) or n→π* (from non-bonding electrons to π* orbitals) [21]. The 289 nm peak might indicate the presence of a chromophore or conjugated system. These correspond to d-d transitions in metal complexes or charge-transfer transitions, if present. Peaks like 461 nm, 495 nm, and 508 nm suggest the molecule may have color due to these transitions. σ→σ*: Transitions typically occur in saturated compounds and require high energy, observed in the far UV region (e.g., below 200 nm). π→π*: Common in unsaturated systems (e.g., double bonds, aromatic systems), observed around 200–300 nm. n→π*. From non-bonding orbitals (e.g., lone pairs on oxygen or nitrogen) to anti-bonding π orbitals, observed in 250–350 nm [22].Charge Transfer Transitions Occur in complexes where an electron moves between a ligand and a central metal ion (or vice versa), often in the visible region, explaining peaks like 461 nm or 508 nm in your spectrum .Absorption Peaks and Color:Peaks in the visible region (400–700 nm) correspond to colors observed due to complementary absorption. [23-24].

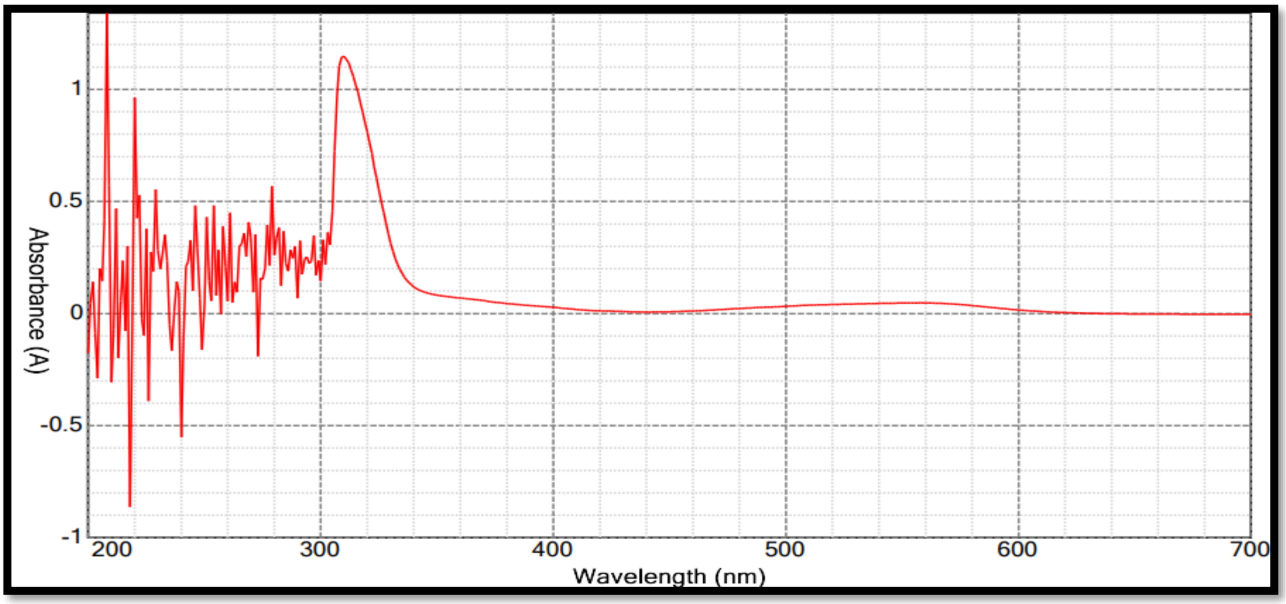

Figure 8: Electronic spectra for ligand

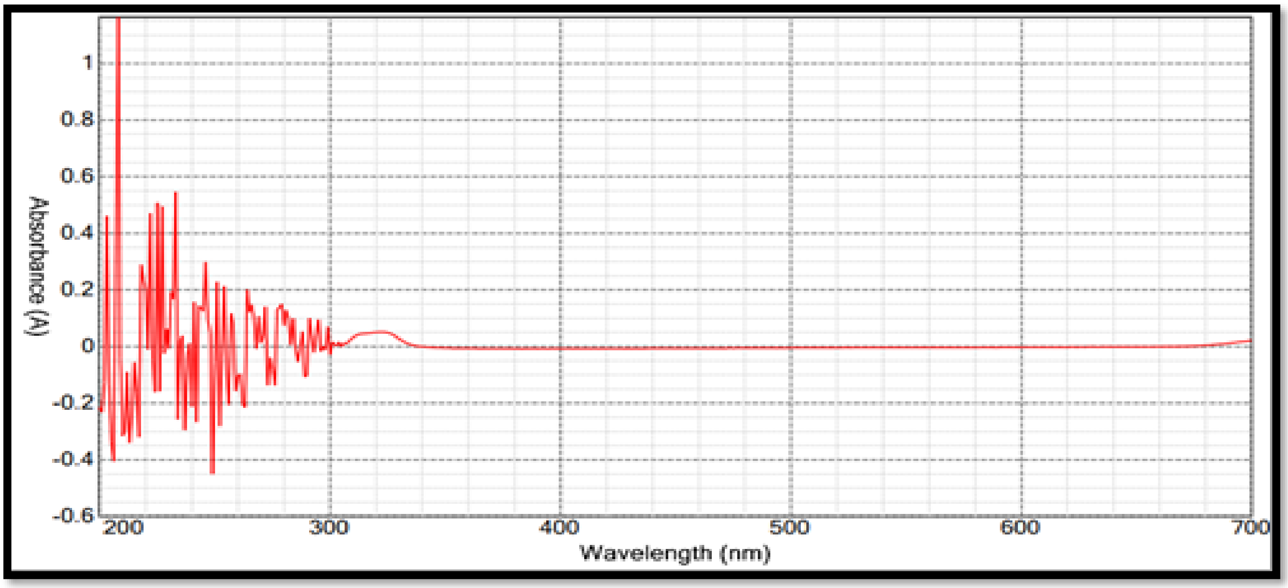

Figure 9: Electronic spectra for C48H64FeN12O10 complex

5- Antioxidant Activity

The complexes demonstrated moderate to high metal-chelating activity, likely due to the interaction of Fe^{+3} ions with the electron-rich anionic amine and uncoordinated carbonyl groups. However, no notable radical scavenging activity was observed in any of the tests, including those involving ferric precursor complexes and ligands, under identical experimental conditions. The data suggest that precursor complexes and free ligands exhibit significantly weaker scavenging effects compared to their Fe(II) complexes, primarily due to the organic ligand's chelation with Fe(II). While the radical scavenging mechanism of these complexes remains unclear, the experimental results provide valuable insights for the development of more potent antioxidants[26].

Conclusion

A novel multidentate ligand based on 2,2′-bipyridine derivatives incorporating diamide functional groups can be successfully synthesized and characterized. The ligand can be prepared through the oxidation of 5,5′-dimethyl-2,2′-bipyridine to its acid derivatives, followed by conversion into acid chloride derivatives using thionyl chloride, and subsequent treatment with amines, such as pyridine-2-carboxamide, to yield the diamide-functionalized ligand. The corresponding transition complex with iron(II) can be synthesized, showcasing the ligand's ability to coordinate effectively with transition metals.The structural and chemical properties of the ligand and its iron(II) complex were confirmed using various advanced techniques, including elemental analysis, NMR spectroscopy, FTIR, UV-Vis spectroscopy, and mass spectrometry.

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