

Synthesis and Characterization of Some Metals Complexes with New Heterocyclic Azo Dye Ligand 2-[2⁻-(Benzimidazolyl) azo]-5-DimethylaminoBenzoic Acid

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Abstract

A new chelating imidazolylazo groups were synthesis. New ligand of azo dye 2-[2⁻ (benzimidazolyl) azo]-5-dimethyl amino benzoic acid (BIABA) have been synthesized by diazotization in alkaline alcoholic solution. Complexes of this ligand were prepared with a series of metallic ions Cu (II), Co (III), Ni (II). These complexes were examined using UV-Vis spectroscopy, the surface nature, morphology and elemental composition of individual novel (BIABA) ligand particles were characterized using Field Emission Scanning Electron Microscope (FE-SEM) coupled with an Energy Dispersive X-ray system (EDX). The structures of the synthesized dyes were determined by analysis of their Mass spectrum, Fourier-transform infrared (FTIR), ¹H NMR. The physical properties of ligand have been studied via check its melting point.

Keywords: Azo dye; Benzimidazol; Benzoic acid; ¹H NMR; FESEM; X-ray system.

Introduction

Azo agents have been successfully employed in determinations of many metal ions and An important uses of these compounds by analytical reagents and they have attracted much attention in analytical field as they are sensitive chromogenic reagents [1, 3]. Imidazoles compounds are class of heterocyclic with five-member ring structure, this ring system is present in significant biological skeleton, like histidine and the associated hormone histamine Imidazole nucleus is an important the studies show that imidazole molecule is associated with a wide range of biological activities.

Also they have been used as analytical reagents and their metal complexes are known to be involved in a number of biological reactions [4]. The π -acidity of the function is largely dependent on the nature of the heterocyclic and aryl group therefor this class of azo dyes being a (π -acidic) for this reason a number of these dyes were synthesized and used as chelating ligands [5]. The metal chelates of ligands with hetero-atom donor sets have physicochemical properties and this type of molecule has several advantages. The azo group is photochromic, redox responsive, pH-sensitive; stabilizes low valent metal

oxidation states due to the presence of a low-lying azo-centred π^* -molecular orbital [6]. The imidazole derivatives characterized ligands azo dyes of hetrocyclic compounds as highly effective against most of the periodic table elements as chemistry complexes however by using to these azo ligands from a wide in different field of in practice [7]. In this paper, we report the preparation of new azo imidazole ligand and the attempt to prepare and identify some transition metal complexes of this ligand.

Experimental

Materials and Instrumentation

All solvents, organic chemicals and inorganic salts those used in this work, were all highly purified and directly used without any further purification, chemicals supplied from Sigma-Aldrich, Merck, BDH, Fluka, Scharlau Companies. Stock solutions were prepared by dissolving a required amount of chloride salt of each Ni, Co and Cu. Solutions were prepared by dissolving a required amount of acetate salt in ammonium acetate buffer solutions, and then dilution of the stock solution in double distilled water with a concentration of 1000 mg L⁻¹ for all metallic

ions, and these solutions were diluted daily to obtain working solutions, 2-[2-(benzimidazolyl) azo]-5- dimethyl amino benzoic acid (BIABA)solution was prepared by dissolving a certain weight of the organic reagent in the absolute ethanol. The ^1H NMR spectra were carried out on a Bruker model 500-Ultra Shield 300 MHZ spectrometer using DMSO-d_6 as solvent for measurement and using TMS as an internal standard reference. Mass spectra were collected on a Shimadzu Agilent Technologies model 5973C.

(FT-IR) spectra were recorded on a Shimadzu model 8400s FT-IR spectrometer scanning at range between ($4000\text{--}400\text{ cm}^{-1}$) via a KBr pellets. UV-Visible spectra were measured on a Shimadzu model UV-1650 UV-Visible spectrophotometer Double beam scanning at range of ($200\text{--}1100\text{ nm}$) using absolute ethanol as solvent for measurement. The field emission scanning electron microscope and the energy dispersive X-ray were taken on a TESCAN model MIRA3 (FE-SEM). The Melting points were taken in open capillary tube by using OMEGA Digital Melting Point apparatus model MPS10-120.

Synthesis of azo dye ligand

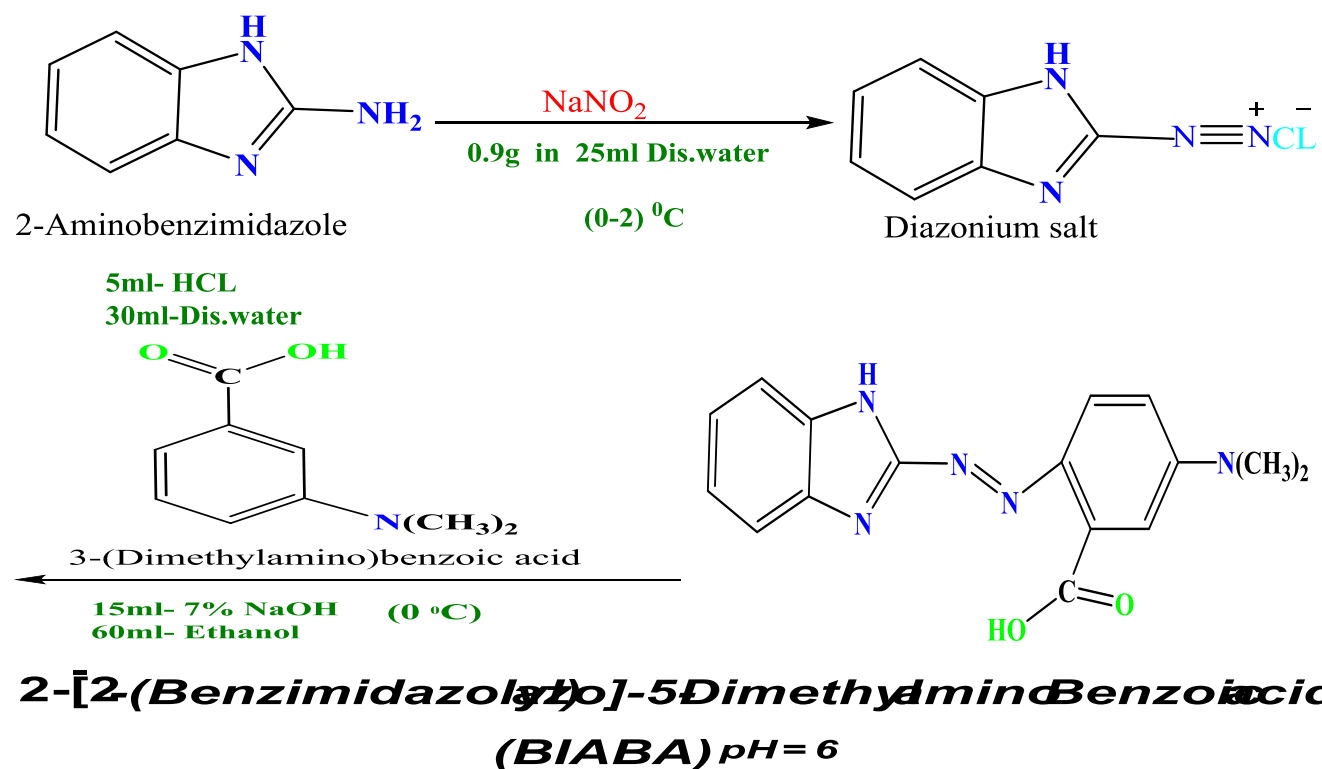
2-[2⁻ - (Benzimidazolyl) azo]-5- Dimethyl amino Benzoic acid (BIABA)

Synthesis of the novel azo ligand was applied according to the method proposed by Al-Adilee et al.[8-9], with some modification via

the diazotization coupling reaction (Scheme 1). This method of action included dissolving (1.33g, 0.01mol) from 2-Aminobenzimidazole mixture contain (5ml of concentrated HCl) and (30ml of distilled water) then the all mixture was cooled to ($0\text{--}2^\circ\text{C}$), then to this solution was added drop wise a solution of sodium nitrite prepared by dissolving (0.9g, 0.013mol of NaNO_2) in 25ml of distilled water, and stirred for (30min) at ($0\text{--}5^\circ\text{C}$).

The mixture of diazonium chloride solution was added also drop wise while maintaining temperature at ($0\text{--}5^\circ\text{C}$), with stirring continuously into a 500 mL beaker containing (1.65g, 0.01mol of 3-Dimethylaminobenzoic acid in the mix contains on 60ml of absolute ethanol and 15ml of 7% NaOH) and coolant to ($0\text{--}5^\circ\text{C}$), after completion of the add-on process the final mixture was stirring at least for (2h) then complete the precipitate of the ligand by modifying the acidic function of the solution to $\text{pH}=6$ and allowed to stand overnight. The precipitate was filtered off, washed with distilled water and finally recrystallized.

The ligand is spectrally studied and checks of purity via TLC techniques. The azo ligand found to be decomposed at (238°C) and the yield was of about 84% of (dark orange crystals) very fine powder. The following diagram illustrates the method of preparation of azo dye (BIABA):



Scheme 1: Synthesis of azo dye ligand (BIABA)

General Method for the Preparation of Metallic ions Complexes

The metallic ions complexes were prepared using corresponding metal chlorides for Ni (II), Co (III), Cu (II). Amount of 0.6 g (0.002mol) from azo ligand, dissolved in 50 mL of absolute ethanol was gradually added in drops wise with stirring a stoichiometric to (0.001mol) amount of [1:2] M:L for Ni(II), Co(III), Cu(II), chloride salt dissolved in 30 mL hot buffer solution (ammonium acetate)

(pH=7). The mixture was heated to (50-60) °C at 35-40 min until the precipitated product, then left over night. The separated solid complexes were filtered off, washed with distilled water. Little warm ethanol to be added to remove any traces of unreacted materials. The complexes obtained were finally dried under vacuum desiccators over combined CaCl_2 dehydrated. The analytical and electronic spectra (nm, cm^{-1}) data of ligand and its metal complexes are collected in Table-1.

Table 1: Electronic spectra (nm, cm^{-1}), & Analytical Data of (Biaba) & Their Complexes

Compound	Color	Maximum Wavelength	Absorption bands
HL=BIABA	Orange	486 nm	20576 cm^{-1}
[Co (L) ₂]	Dark Indigo	605 nm	16529 cm^{-1}
[Ni (L) ₂]	Blue	567 nm	17637 cm^{-1}
[Cu (L) ₂]	green bluish	600 nm	16667 cm^{-1}

Result and Discussion

Physical and Chemical Properties of azo dye ligand (BIABA)

The azo ligand (BIABA) is characterized by the fact that his amorphous look is on the form of a very fine dark orange crystals powder, giving the color orange when dissolved with ethanol, but the obtained metal complexes were found to be vary in color crystals depending on the nature metal ion. This synthesis azo ligand is easily soluble in most solvents [Acetone, THF, DMSO, DMF, Methanol, Ethanol] and sparingly soluble in water. The obtained metallic ions complexes and azo (BIABA) ligand were stable in air at room temperature.

¹H NMR Spectra

The ¹H NMR spectra for novel ligand (BIABA) [10-12] was obtained in DMSO-d₆ as solvent with TMS as an internal reference (300MHZ). The spectrograph which is illustrated in Figure.1 is interpreted as follows: a Singlet at $\delta=9.908$ ppm (s,1H) due to the presence of O-

H group of the carboxylic acid (COOH), while the multiple peak at 6.905-7.323 ppm which are assigned to protons of the aromatic and hetero-aromatic rings, the multiple peaks at $\delta=2.943$ ppm due to methyl groups in N-(CH₃)₂ and the single peak at $\delta=2.517$ -2.528 ppm (s,1H) due to NH group in imidazole molecule.

Mass Spectra

The mass spectral of free novelty ligand (BIABA) are presented in Figure.2, the mass spectra show a molecular ion peak M⁺ at M/Z= (309.1) correspond to the original molecular weight of ligand (309.32), [C₁₆H₁₅N₅O₅] with high stability where the mass spectrum was given to ligand a number of fragmentation and these fragmentation represented in the mass spectra in term of relative abundance compared to M/Z⁺, and the main peak show via mass spectrum is relatively to molecular weight of ligand molecular ion [C₁₆H₁₅N₅O₅]⁺, the explains the proposed mass fragmentation products for ligand (BIABA) [13, 14].

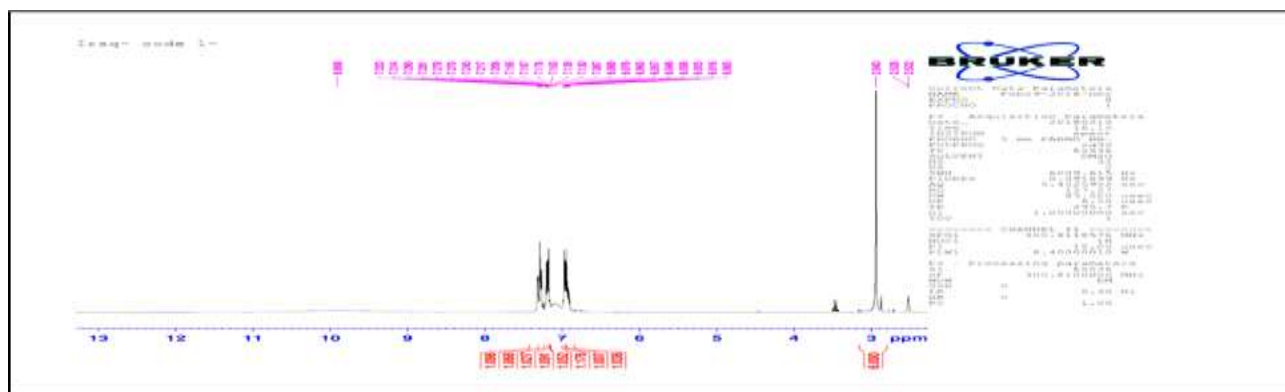


Figure.1: ¹H-NMR spectrum of ligand (BIABA)

Electronic Spectra Measurements

The electronic absorption spectra of imidazole azo dye ligand (BIABA), and its' chelates complexes are studied via used absolute ethanol as solvent to them, the ligand and its chelates appearing many of specific absorbance bands at differ wavelength due to the electronic transitions for them[15-17]. The free ligand spectrum gives three absorption bands were detected first band located at 486 nm (20576cm^{-1}) for $n\text{-}\pi^*$ transition of the azo

group (-N=N-), this band shows a red shift on coordination with ametal ions around range at (567-605) nm. The second band observed at 370 nm (27027cm^{-1}) due to $\pi\text{-}\pi^*$ transition to the $\text{C}=\text{C}$ group in heterocyclic benzimidazole and aromatic carboxylic acid rings, while the third band at 241 nm (41494cm^{-1}) for $\pi\text{-}\pi^*$ transition to the $\text{C}=\text{N}$ group in the ligand structure. The U.V spectrum of (BIABA) and its' chelates complexes were obtained in absolute ethanol solution are given in Figures (3, 4, 5 and 6).

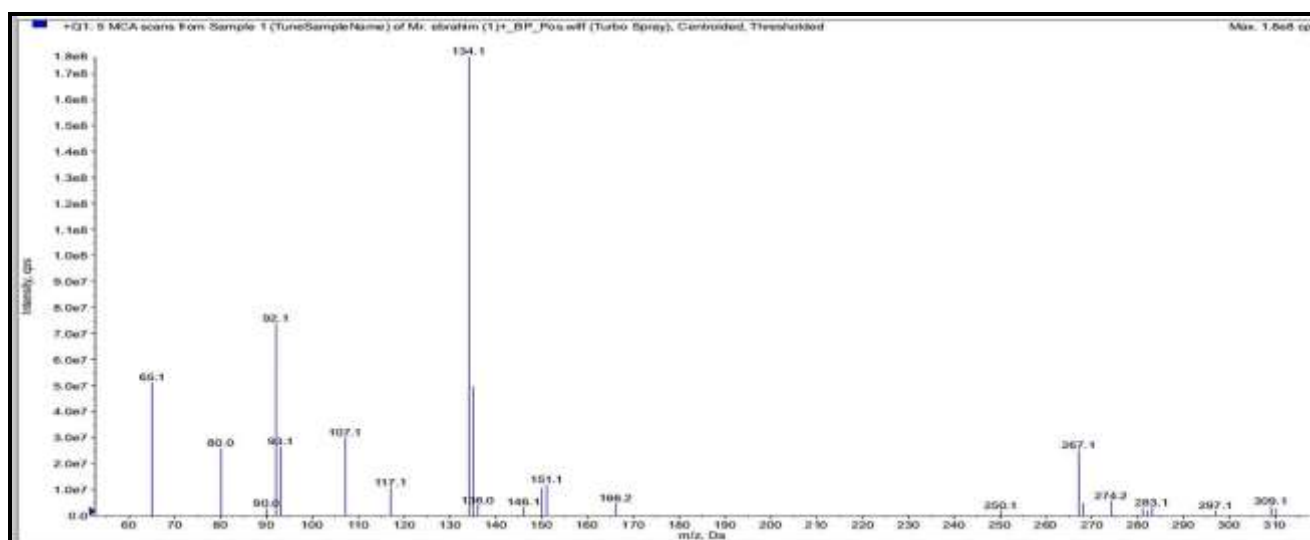


Figure 2: Mass spectrum of azo dye ligand (BIABA)

Infrared Spectra Measurements

The FT-IR spectra data for imidazole azo dye ligand (BIABA) are shown in Figure 7. Free ligand shows a number of variable absorbance bands in them is due to this transitions responsible for FT-IR bands are due to molecular vibrations, these absorbance bands that appeared on FT-IR spectrum were due to active functional groups present[18-20]. The spectrum of the azo dye ligand showed a broad absorption around 3309.62 cm^{-1}

assignable to the amine hydrogen and hydroxyl of carboxylic group. The medium band at 3093.61 cm^{-1} and weak band at 2931.60 cm^{-1} in the ligand spectrum which is due to γ (C-H) aromatic and aliphatic respectively. The spectrum of ligand shows a single strong absorption band at 1589 cm^{-1} assignable to the γ (COOH) group. The infrared spectrum of azo dye ligand (BIABA) revealed a medium band at 1689.53 cm^{-1} due to γ ($\text{C}=\text{N}$) of imidazole molecule. The azo group, γ ($\text{N}=\text{N}$) appear at 1473.51 cm^{-1} .

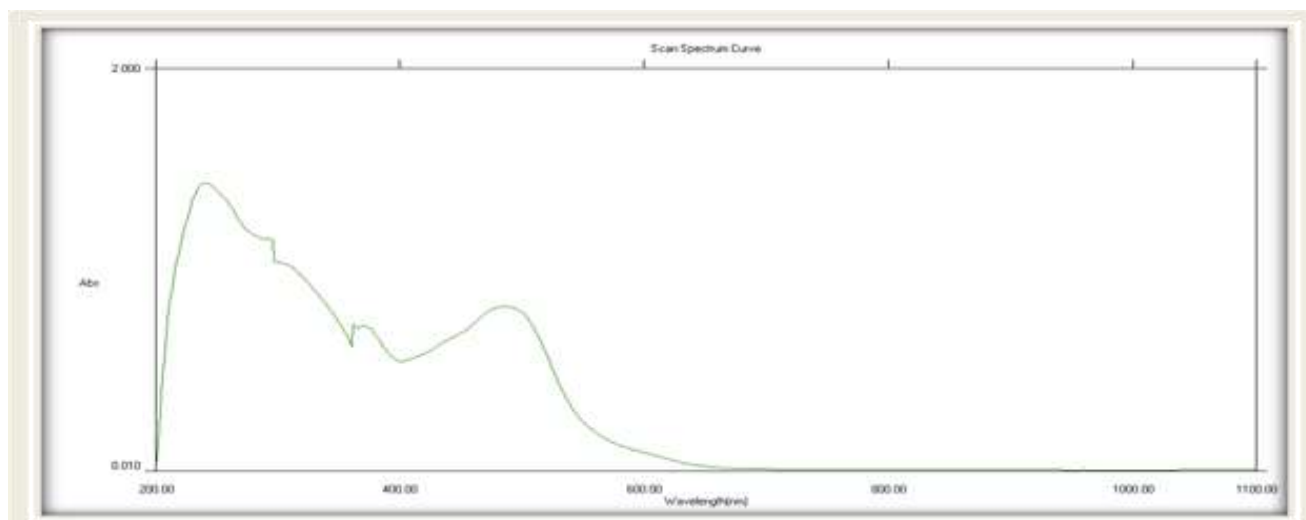


Figure 3: UV-Vis spectrum of ligand BIABA

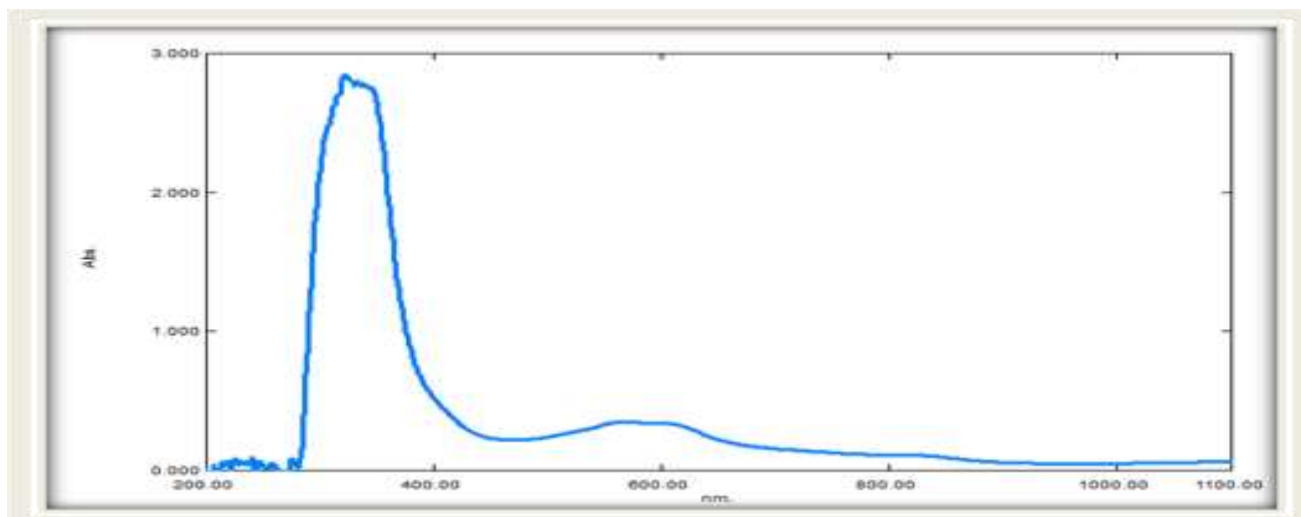


Figure.4: UV- vis spectrum of Ni (II)-Complex

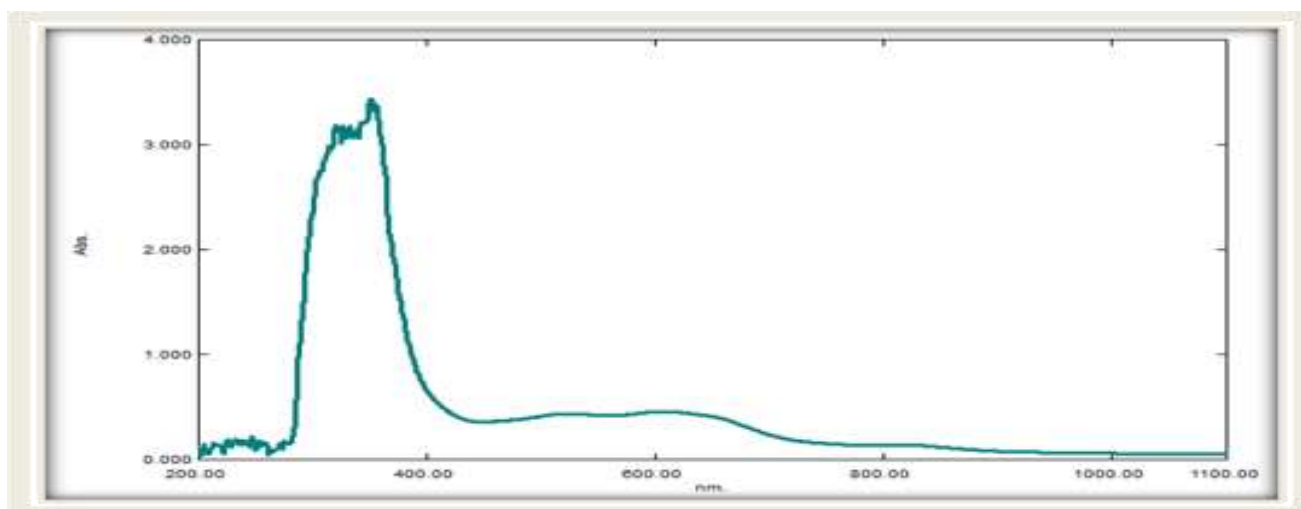


Figure.5: UV- vis spectrum of Co (II)-Complex

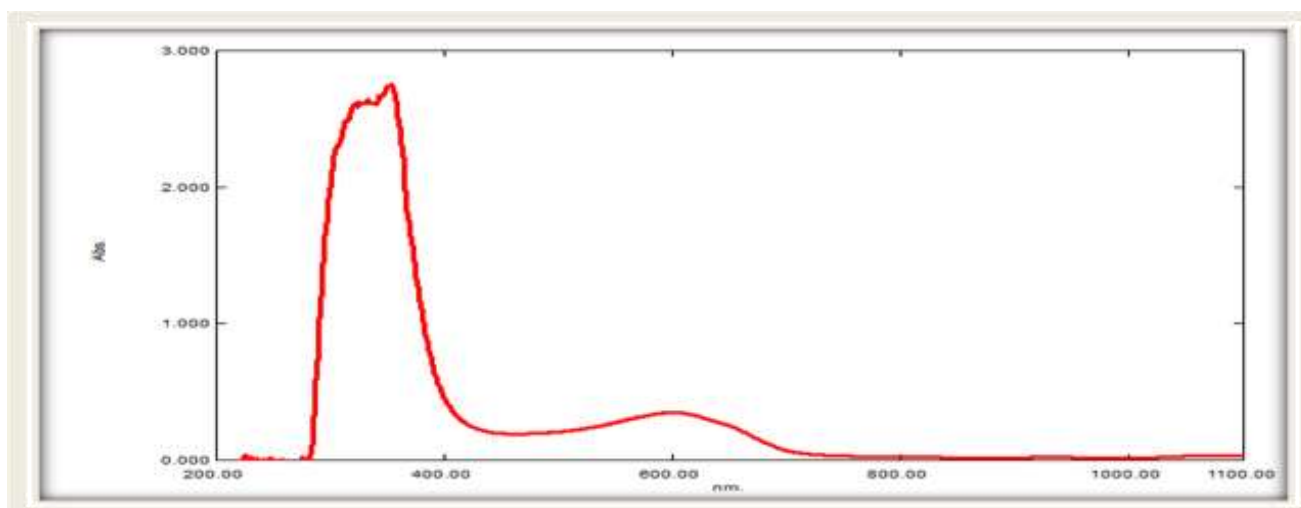


Figure.6: UV- Vis spectrum of Cu (II)-Complex

EDX and FE-SEM Analysis

The morphology and the Topography for ligand (BIABA) is identified using FE-SEM, the Figures.8 (a, b). Show FE-SEM and EDX spectra analysis of ligand. FE-SEM image shows the ligand (BIABA) where the nature of homogeneity of the surface and the distribution of particles and collected in an unregularly order, and illustrated the surface

shape of the ligand on it as huge Micro-Flowers with a giant block appearance. The EDX image shows that the prepared ligand includes only carbon, nitrogen, and oxygenis similar to the chemical composition for azo ligand. This indicates a match in the atomic structure and to the purity of the synthesis azo ligand (BIABA). The EDX spectrum referred to weight percentage of each element within the composition of the ligand.

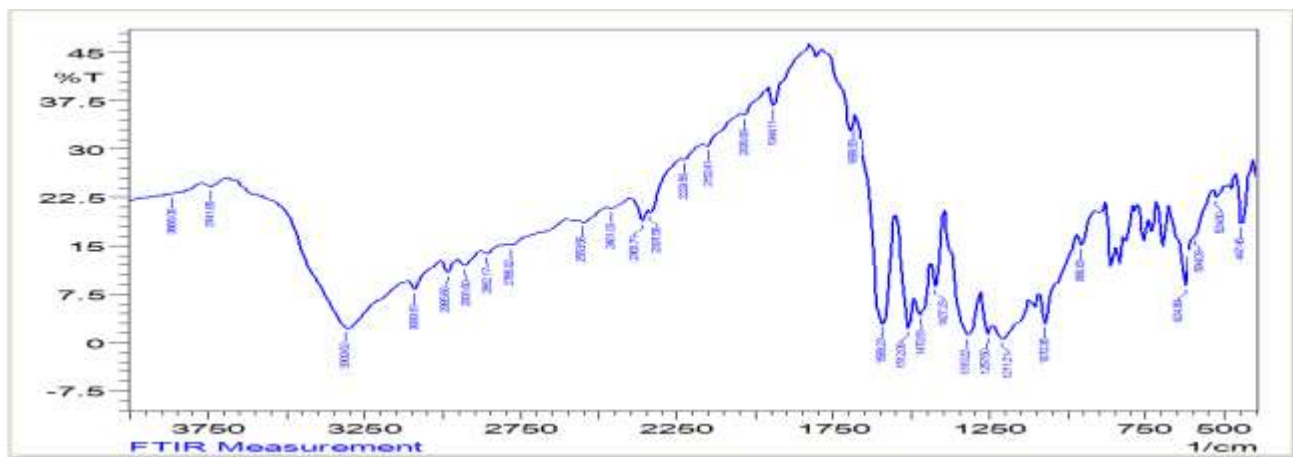


Figure.7: FTIR analysis of ofofazo dye ligand (BIABA)

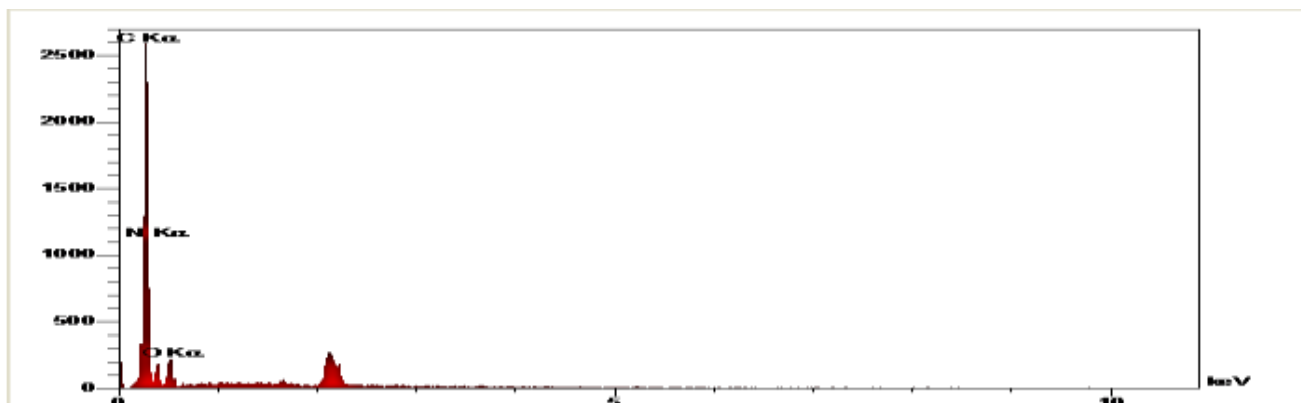


Figure.8: (A) EDX spectra of ligand (BIABA)

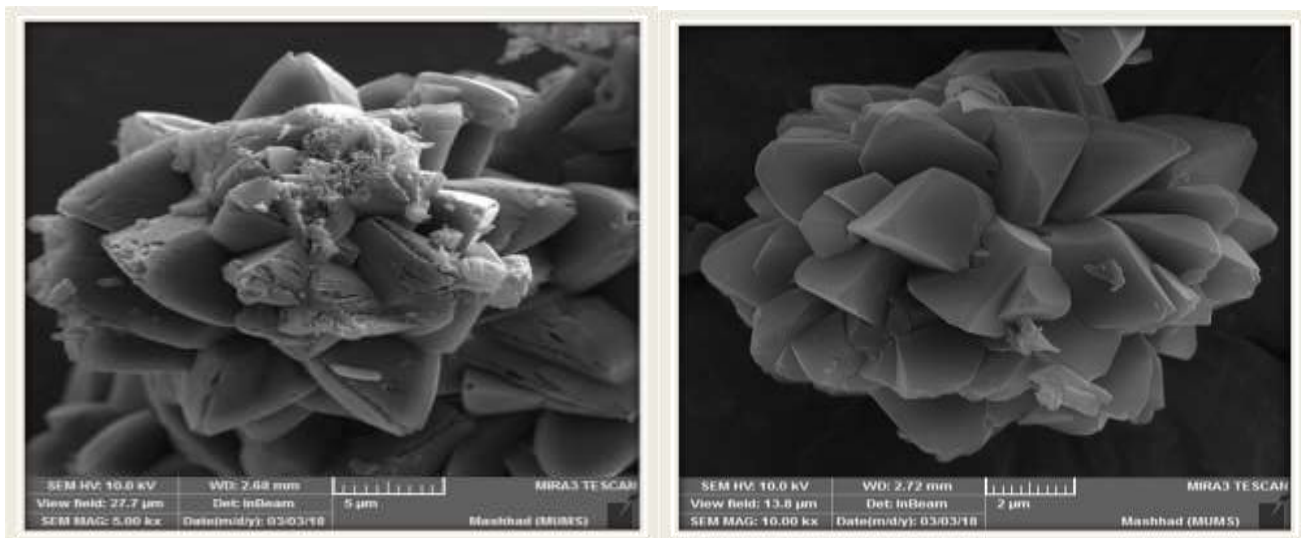


Figure.8: (b) FE-SEM images of ligand (BIABA)

Conclusions

Based on this experimental study, the following conclusions were reached: we have prepared and structurally characterized of new azo chelating ligand (BIABA) derived from imidazole. The structure of analytical reagent has been confirmed by the analytical

data (EDX), mass spectrum, ^1H NMR, FT-IR and electronic spectra. The azo ligands have different morphologies as appeared in SEM. The ligand characterized solid metal complexes are stable in air and moisture, and high melting point gives further proof of the stability of ligand.

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