

SYNTHESIS, CHARACTERIZATION, STRUCTURE DETERMINATION FROM POWDER X-RAY DIFFRACTION DATA, AND BIOLOGICAL ACTIVITY OF AZO DYE OF 3-AMINOPYRIDINE AND ITS COMPLEXES OF Ni(II) AND Cu(II)

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ABSTRACT. In the present work azo dye ligand of 3-aminopyridine (L) and its complexes of Ni^{II} and Cu^{II} were synthesized, characterized and evaluated for antibacterial and antifungal activities *in vitro*. The L ligand was synthesized by reacting diazonium ion of 3-aminopyridine with 1-naphthol in presence of sodium acetate. The ligand (L) and its complexes were characterized by elemental analysis (CHN), magnetic susceptibility, molar conductivity, UV-Vis spectra, and infrared technique. The (L) azo dye exhibited high sensing for the pH changes. The color of L dye changed from red in basic medium to yellow color in acidic medium. The data of CHN, UV-Vis and magnetic susceptibility indicate that the complexes [Ni(L)₂Cl₂] and [Cu(L)₂Cl₂] are tetrahedral. The complexes of Ni(II) and Cu(II) exhibited potent activity against growth of *Staphylococcus aureus* and *Escherichia Coli* as well as against *Penicillium Sp.* And *Aspergillus niger*. Under visible irradiation (395 nm), the (L) azo dye of pyridine exhibited a significant change in the spectra under irradiation.

KEY WORDS: Pyridine, Photoisomerization, Pyridylazo, Biological activity, pH sensor

INTRODUCTION

Azo dyes are an important class of organic chemicals containing at least one azo chromophore (-N=N-) which donates the color for this famous type of dyes [1]. They play essential role in academic and applied research [2]. Electronic and geometrical features of azo metal dyes induce redox, nonlinear optical and magnetic properties and these properties lead to increase the sensitivity and stability of these compounds towards optical data storage device [3, 4].

Azo dyes consider significant analytical reagents for the micro-estimation of metal ions. 1-(2-Pyridylazo)-2-naphthol considers well-known azo dye with term PAN which forms stable complexes with many metal elements [2]. In the same time, it is sensitive for trace concentration of metal elements and trace elements [5, 6]. This kind of complexes is highly colored therefore some of them used as dyes and pigments which leads to use it as inkjet printing and toner.

The azo dyes can be exhibited trans and cis isomers depending on the present -N=N- chromophore and these dyes can exhibit the photoisomerization process in their complexes [7]. The inter-conversion between the isomers can be achieved photo-chemically and it is possible thermally or electrochemically [8]. Trans isomer is more stable than cis isomer [9]. Azo dye ligands such as aryl azophenols have low-lying p*-orbitals which lead to stabilize the low valence metal redox state in their complexes by increasing chance of charge transfer transition of metal-to-ligand [10].

Cytotoxic studies of azo dye complexes against T47D, MTLn3 and RAW tumor cell lines exhibited a satisfactory inhibitory effect on cells comparable to that of cisplatin [10]. Synthesized complexes of Mn^{II}, Co^{II}, Ni^{II} and Cu^{II} of azo dye(1-[(5-mercapto-1H-1,2,4-triazole-3-yl)diazonyl]naphthalene-2-ol) exhibited attractive biological activity against many types of bacterial and fungal strains as *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans* and *Aspergillus flavus*, and antitumor activity toward HEPG2 cell line [11]. 3-Aminopyridine derivatives exhibited antineoplastic activity *in vivo* toward the L1210 leukemia [12]. Pyridine

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ring is appear in plenty of natural products such as vitamin B6, niacins, nicotinamide adenine dinucleotide (NAD) and trigonelline [13]. Pyridine is a lot used in pesticides and drugs production because of its attractive properties such as basicity, water solubility, stability, hydrogen bond forming ability beside its small molecular [14].

The drugs of pyridine such as sulfapyridine and salazosulfapyridine used as antiviral, antimicrobial, antioxidant as well as anti-malarial agents [15]. Sulfasalazine is azo dye of pyridine which called under the trade name Azulfidine in pharmacy. It widely employed for treatment of rheumatoid arthritis, Crohn's disease and ulcerative colitis [16, 17]. Therefore, we hereby report to synthesis and characterization of azo dye of 3-aminopyridine and its synthesizing complexes of Ni^{II} and Cu^{II} as well as screening their biological activity against number of pathogenic bacteria and fungi.

EXPERIMENTAL

Materials and methods

The solvents and materials were used without further purification. Sodium nitrite, 3-aminopyridine, hydrochloric acid, 1-naphthol, sodium acetate were got from Sigma-Aldrich. NiCl₂·6H₂O and CuCl₂·2H₂O were got from Alfa Aesar.

The UV-Vis spectra of the synthesized compounds were done by using UV-1650 PC UV-Visible Spectrophotometer from Shimadzu. The infrared spectra of synthesized compounds were done by using Shimadzu FT-IR 8400S spectrophotometer. ¹H NMR spectrum of (L) ligand was done by using Bruker 400 MHz spectrophotometer in DMSO-d₆. Mass spectrum of (L) ligand was done by Shimadzu Agilent Technologies 5973C. The elemental analysis (CHN) of the L ligand and its synthesized complexes of Ni^{II} and Cu^{II} were done by using EURO EA 3000. The magnetic susceptibility was done by balance magnetic susceptibility model-MSB auto. The molar conductivity measurements for complexes of Ni^{II} and Cu^{II} were done by using Cond720 (WTW) in DMSO solvent at room temperature. X-ray diffraction measurements were done by using Bestic Germany Aluminum for (L) ligand.

Synthesis of azo dye of 3-aminopyridine (L)

3-Aminopyridine (0.94 g, 0.0099 mol) was dissolved in 40 mL of distilled water. 5 mL of concentrated hydrochloric acid was added to solution of 3-aminopyridine, then the solution was cooled at 0 °C. 5 mL aqueous solution sodium nitrite (0.683 g, 0.0099 mol) was cooled to 0 °C. The cold aqueous solution of sodium nitrite was added gradually to cold the acidic solution of 3-aminopyridine to form diazonium salt of pyridine. The diazonium salt of pyridine was let under stirring for 30 min at 0 °C. Sodium acetate (2 g, 0.02 mol) was dissolved in 8 mL of distilled water then the solution of sodium acetate was added to 30 mL ethanolic solution of 1-naphthol (1.427 g, 0.0099 mol). The basic solution of 1-naphthol was put under cooling at 0 °C. The solution of diazonium salt was added gradually to basic solution of 1-naphthol under cooling. The new solution of azo dye of 3-aminopyridine was red and the solution was let overnight. The solution of dye was filtrated and it washed many times with water to remove the salts. It was red powder with yield 90%. ¹H NMR (ppm in DMSO-d₆): 11.31 (1H, s), 9.169 (1H, s), 8.92 (1H, 6.5Hz, d), 8.70 (1H, 2.4Hz, d), 8.27 (2H, 9.4Hz, d), 7.93 (1H, 6.4Hz, d), 7.24 (1H, 11.2 and 5.6 Hz, t), 7.61 (2H, 5.2Hz, d), 7.05 (1H, 6.8Hz, d). C₁₅H₁₁N₃O C: 72.20, H: 4.41, N: 16.85; experimental: C: 72.05, H: 4.30, N: 16.81.

Synthesis of Ni^{II} and Cu^{II} complexes of (L) azo dye ligand

Ni^{II} complex. (0.249 g, 0.001 mol) of (L) ligand was dissolved in 20 mL of ethanol under heating to 60 °C. Nickel chloride (0.12 g, 0.0005 mol) was dissolved in 10 mL of buffer solution

(pH = 8). The solution of (L) ligand was added to hot solution of nickel chloride. The reaction mixture was refluxed under 60 °C for three hours. The solution of reaction was filtrated, washed by distilled water many times, red powder was put in desiccators to dry. The yield of nickel(II) complex was 60%. Theoretical $C_{30}H_{22}N_6O_2NiCl_2$, C: 57.36, H: 3.53, N: 13.38., experimental: C: 57.25, H: 3.42, N: 13.31.

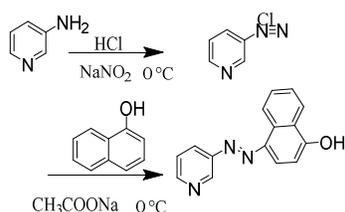
Cu^{II} complex. We used the same procedure of nickel(II) complex to synthesise Cu^{II} complex excepting we used (0.15 g, 0.0005 mol) of copper(II) chloride. $C_{30}H_{22}N_6O_2CuCl_2$ C: 56.92, H: 3.50, N: 13.28., experimental: C: 56.83, H: 3.33, N: 13.17.

Biological activity

The antimicrobial activity of (L) ligand and its synthesizing complexes of Ni^{II} and Cu^{II} were examined against two types of pathogenic bacteria (*Escherchia coli* and *Staphylococcus aureus*) and two types of fungi (*Penicillium Sp.* and *Aspergillus niger*) by using agar well diffusion method. Here we used Mueller-Hinton agar for bacterial strains and sabouraud dextrose agar for fungal strains. The autoclaved molten media (20 mL) was poured in each 90 mm sterilized Petri plate and allowed to solidify. Three circular well of diameter 6 mm were made in each Petri dish by using cork borer and each well was filled with 0.1 mL of the test solution at three different concentrations 50, 75, 100 mg/mL for (L) ligand, Ni^{II} and Cu^{II} complexes and inhibition zones were measured in mm after 24 h of incubation period.

RESULTS AND DISCUSSION

The azo dye ligand 4-(3-pyridyl azo)- α -naphthol of 3-aminopyridine (L) was synthesized by coupling α -naphthol with diazonium ion of 3-aminopyridine in present of sodium acetate as shown in Scheme 1. The yield of synthesized dye (L) was 90% with red powder.



Scheme 1. Coupling reaction of α -naphthol with diazonium ion of 3-aminopyridine.

The mass spectrum is consistent with the existence of m⁺ of the (L) dye (Figure 1) which is in agreement with elemental analysis (CHN) of the (L) dye.

Test of pH sensing effect on (L) ligand was evaluate by UV-Visible spectra in basic and acidic mediums in acetone at 10⁻⁵ molarity at room temperature which are depicted in Figure 3. The synthesized dye (L) exhibited decreasing in intensity of π - π^* transition at pH = 10 compared to parent azo and arising a new band at 550 nm which is due to ICT from OH (donor) to pyridine ring (accepter) during the azo functional (bridge) that meaning that the electronic transition involves the overall electronic system of the azo dye (L) ligand [19]. The spectrum of hydrazone form of (L) dye at pH = 2 appears little bit red shift and increasing in intensity for π - π^* transition compared to parent azo form which is in agreement with the literatures [20-23]. These dramatic changes candidates this ligand a good example on the analytical indicators of acid-base like methyl orange which is azo dye.

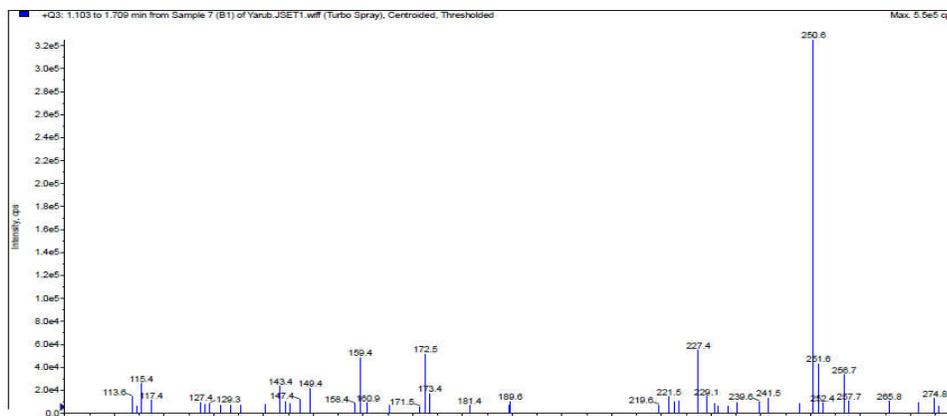


Figure 1. Mass spectrum of azo dye ligand of 3-aminopyridine (L).

The geometry optimization of (L) dye was done by DFT using (Gaussian 09, B3LYP functional) with (LanL2DZ) basis set [18] which is depicted in Figure 2.

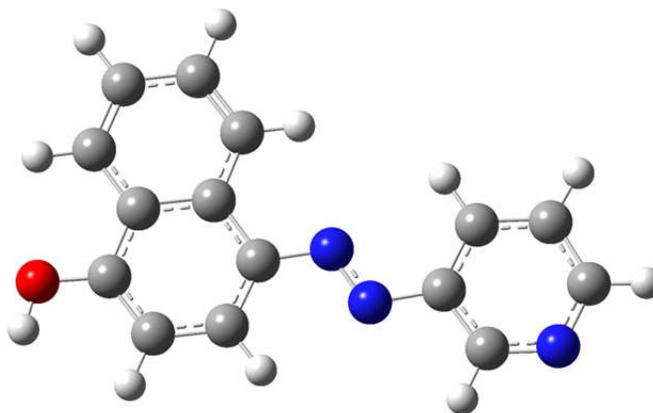


Figure 2. Optimization structure of (L) ligand using B3LYP functional with (LanL2DZ) basis set.

Beside to use photoisomerization of azo dyes for high optic data storage, recently this process gets large attention and applications in biological system [24]. For that, we are interested in controlling the photoisomerization of our ligand (L) which exhibited interesting absorbance in visible region. We evaluate the photochromic changes of (L) dye by UV-Visible spectra in acetone before irradiation, under irradiation and after irradiation at room temperature (Figure 4). The UV-Vis spectrum of (L) dye before irradiation presents trans isomer which is a planer and stable more than cis isomer which exhibits under irradiation. The intensity of $\pi \rightarrow \pi^*$ of (L) dye exhibited low intensity under irradiation with light of 395 nm for 3 min while under 7 min of irradiation, the intensity of $\pi \rightarrow \pi^*$ gone more down and appearing a new band at 650 nm having low intensity which is due to $n \rightarrow \pi^*$ [25, 26]. The last transition is more allowed in cis isomer than trans isomer which is planer. When we remove the source of light, the spectrum

of cis isomer vanished with time and we got same spectrum of trans isomer. Which means that the (L) azo dye possess real photochromic behavior [27] and a good candidates for optical data storage devices.

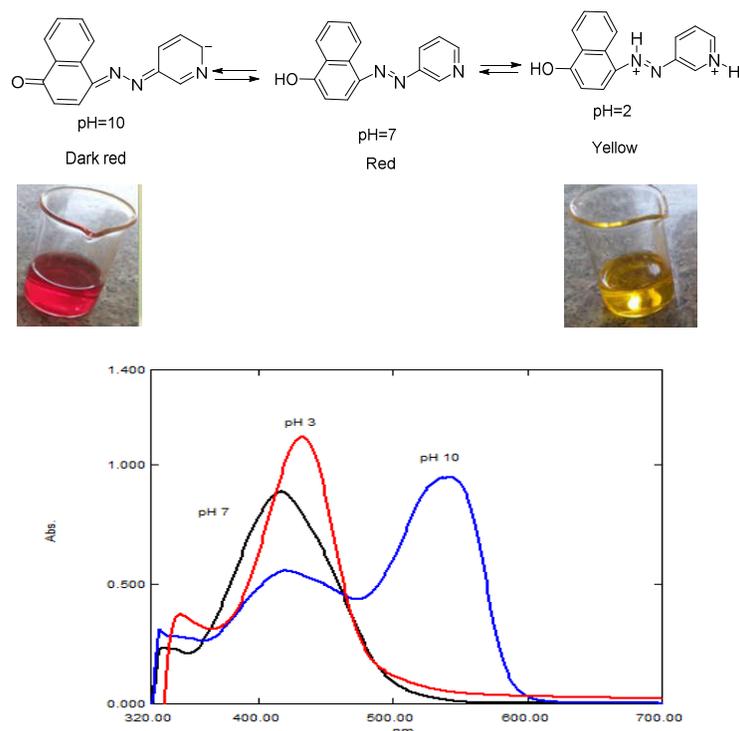


Figure 3. UV-Vis spectra of ligand (L) in basic, neutral and acidic media.

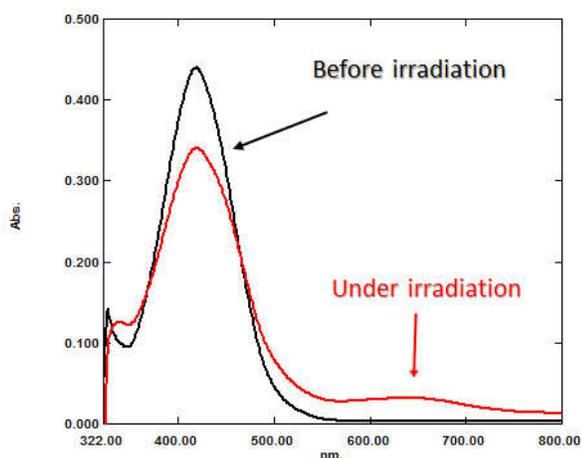


Figure 4. Evaluation of photochromic behavior of (L) dye under irradiation at 395 nm at 25 °C in acetone.

X-ray diffraction of powder

The X-ray pattern of synthesized azo dye ligand (L) has been presented by using software Materials Studio. We have done the simulated XRD pattern of azo dye with its experimental XRD pattern. The result was perfect match between them which are depicted in Figure 5. The unit cell of (L) azo dye is monoclinic and the data of unit cell is depicted in Table 1.

Table 1. Cell data and crystal parameter of (L) azo dye.

Space group	P-1
Crystal system	Triclinic
a (Å)	7.4343
b (Å)	8.3073
c (Å)	22.4717
Alpha	79.8675
Beta	94.8902
Gamma	65.2226
Wavelength (Cu Ka) (Å)	0.71073

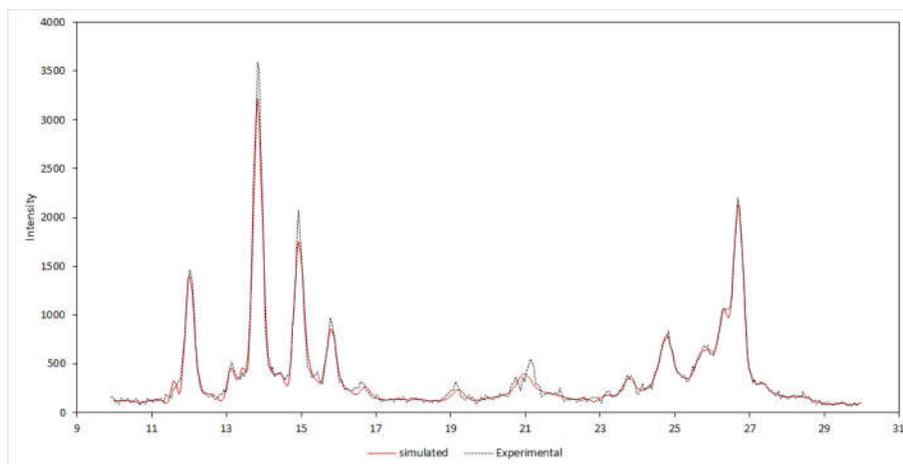
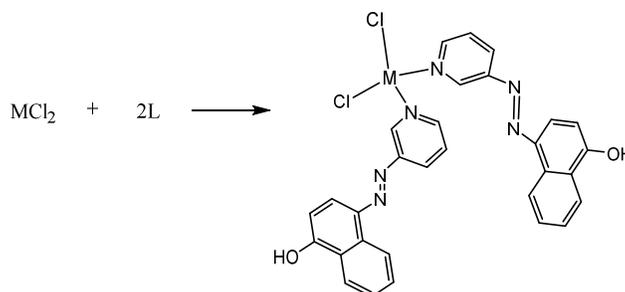


Figure 5. The X-ray diffraction patterns of experimental and simulated of synthesized azo dye (L) of 3-aminopyridine.

The complexes of Ni^{II} and Cu^{II} were synthesized in same procedure by mixing nickel(II) chloride or copper(II) chloride with (L) ligand at pH = 8 under 60 °C for 3 h. The synthesized complexes were characterized by CHN analysis elements, molar conductivity, magnetic susceptibility, UV-VIS and infrared spectra. Molar conductivity of Ni^{II} and Cu^{II} were 6 and 10 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively, that means that the complexes are nonelectrolytes. The mole ratio for both complexes was 2:1 ligand:metal (Scheme 2).

The infrared spectrum of the azo dye ligand (L) showed important characteristics peaks in the range of 4000-400 cm^{-1} such as OH (3200 cm^{-1}), CH (3050 cm^{-1}), C=N (1580 cm^{-1}), N=N (1505 cm^{-1}), C=C (1403 cm^{-1}), O-H bend (1390 cm^{-1}), C-O (1290 cm^{-1}), CH bend (1080, 700 cm^{-1}). Ni^{II} and Cu^{II} complexes exhibited infrared spectra similar to the free ligand (L) excepting the C=N functional undergo red shift 23-34 cm^{-1} , respectively [28, 29].

Scheme 2. Synthesis of Ni^{II} and Cu^{II} complexes.*Electronic spectra of azo dye ligand (L) and its synthesized complexes*

In general, azo dye ligands exhibit strong $\pi\text{-}\pi^*$ and weak $n\text{-}\pi^*$ bands, but in our case the azo dye (L) exhibits $\pi\text{-}\pi^*$ overlaps with $n\text{-}\pi^*$ to form large and strong band in visible region at 420 nm because there is donor group (OH) and acceptor functional pyridine ring which leads to overlap $\pi\text{-}\pi^*$ transition with $n\text{-}\pi^*$ transition [19].

Nickel(II) complex exhibited 10820 and 15215 cm^{-1} , which are due to ${}^3T_1(F) \rightarrow {}^3A_2(F)$ and ${}^3T_1(F) \rightarrow {}^3T_1(P)$, respectively, with magnetic susceptibility equal to 2.81 B.M., which is in agreement with tetrahedral configuration [29, 30]. On the other hand, the strength of chloro and azo dye ligands are low to medium depending on the spectrochemical series therefore the complex prefers the tetrahedral than square planer configuration.

Copper(II) complex exhibited charge transfer at 21276 cm^{-1} , and d-d transition due to ${}^2T_2(D) \rightarrow {}^2E(D)$ at 12468 cm^{-1} beside the electronic transition $\pi \rightarrow \pi^*$ of (L) ligand with magnetic susceptibility equal to 1.92 B.M., which is in agreement with tetrahedral configuration [30, 31].

Biological activity

The global emergence of antimicrobial resistance is increasingly decreases the effectiveness of many antibiotics, especially in immune-compromised patients. Drug resistance, especially by bacteria and fungi, is consider one of the major concerns to public health and scientific communities' worldwide [32]. Many azo dye complexes consider important biological species [33]. In our study we investigated the biological activity of our synthesized compounds against two types of bacteria gram positive bacteria (*S. aureus*) and gram negative bacteria (*E. Coli*) and two types of fungi (*Aspergillus niger* and *Penicillium Sp.*) by agar well diffusion method. The results depicted in Table 2, revealed that the Ni^{II} and Cu^{II} complexes exhibited interestingly high inhibition zone against tested *E. coli* and *S. aureus* while the (L) ligand did not show interesting antibacterial activity against screened strains and moderate activity against fungal strains. This activity may be attributed to our complexes are amphiphilic nature which may facilitate the penetration through the bacterial cell membranes which is rich in polysaccharide fraction and also passes through the cell walls of fungi [34, 35]. The Ni^{II} complex exhibited higher inhibition zone against *E. coli* than *S. aureus*. The Cu^{II} complex exhibited high inhibition against *E. coli* and *S. aureus*.

The synthesized ligand (L) and its synthesized complexes of Ni^{II} and Cu^{II} showed significant action against both *Aspergillus niger* and *Penicillium Sp.* In the same time, the inhibition zone of synthesized compounds increased against *Penicillium* with increase in their concentration.

Table 2. Antimicrobial action of tested compounds against pathogenic microorganism in culture media.

Compound	Concentration (mg/mL)	Pathogenic bacteria		Pathogenic fungi	
		<i>S. aureus</i>	<i>E. coli</i>	<i>A. niger</i>	<i>Penicillium sp.</i>
L ligand	50	-	5	12	13
	75	-	-	16	15
	100	-	-	14	17
Ni ^{II} complex	50	4	17	16	13
	75	8	17	18	13
	100	-	17	15	16
Cu ^{II} complex	50	8	10	14	8
	75	16	12	15	10
	100	16	12	18	17

Values represent zone of inhibition in mm.

CONCLUSION

In the present work, we have reported the synthesis and characterization of Ni^{II} and Cu^{II} complexes having general formula [M(L)₂Cl₂]. We have also demonstrated that UV-Vis spectra of azo dye ligand (L) change on altering the pH values and under irradiation therefore these properties made the synthesized ligand an interesting candidate for its applications in storage device and analytic indicator. Both synthesized complexes of Ni^{II} and Cu^{II} are nonelectrolyte having tetrahedral environmental and exhibited considerable antibacterial and antifungal activities against both *S. aureus* and *E. Coli* as well as against *A. niger* and *Penicillium Sp.*

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