Synthesis, Spectroscopic characterization and bactericidal valuation of some metal (II) complexes with new Tridentate Heterocyclic Azo Ligand Type (NNO) Donor

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Abstract

In this article, a synthesized ligand [(1-phenyl-2-pyrazolin-5-one) azo (6-bromo-2-hydroxynaphthalen-1-yl)] has employed for preparing three new complexes of Co(II), Ni(II) and Cu(II). The new azo ligand (PABH) has analyzed by Micro Elemental Analysis (CHNO), UV-visible, Fourier Transform infrared (FTIR) approaches, \(^1\)H,\(^1\)C-NMR spectroscopy and mass spectroscopy. The consequence has specified that the ligand was represented as N,N,O-tridentate. The preparing of complexes has accomplished after fixing the finest concentration and pH values. UV-Vis spectra of these complexes solutions have been examined for a range of pH (5-9) and concentration (1×10\(^{-4}\)- 5×10\(^{-4}\)) Molar that comply with Lambert-Beer's law. A stoichiometry of the complexes has comprehended in relation to molar ratio which has investigated from a spectroscopic technique. The ratio of metal: ligand was achieved with (1:2) for all complexes. The metal ions complexes were characterized by FTIR, UV-Visible, molar conductance, atomic absorption, magnetic susceptibility and elemental analysis CHNO techniques. From the results of physico-chemical and spectral techniques, octahedral geometry has been proposed for these metal complexes. All these compounds were evaluated against two kinds of human pathogenic bacteria such as Staphylococcus aureus (Gram Positive) and Escherichia coli (Gram negative).

Keywords: Spectral studies, Complexes, Azo, Antimicrobial activity, Mass spectroscopy

Introduction

Azo compounds have been a highly significant sort of chemical compounds getting a consideration in analytical chemistry field. They can be extremely colored and employed as dyes and pigments extensively [1]. Azo dyes form an imperative type of organic colorants, involving as a minimum a conjugated azo (N=N) chromophore, and are the major and greatest multipurpose category of dyes. It was taken substantial consideration as a result of their remarkable and they have an advantageous in chemical and physical features [2,3]. Azo compounds stand for one of the foremost variations ligand that involving one or more azo moiety with unique pair of electron on the nitrogen atom stimulates a coordinating site for complexation with different metal ions providing these complex compounds a rich physical, biochemical and organic features [4,5]. Consequently, this kind of ligands has prepared stable chelated complexes of 5 or 6 membered ring as there another coordination site at ortho location to azo moiety. It is provided through the existence of donor atom such as nitrogen, oxygen and sulfur on the aromatic rings or heterocyclic ring [6,7]. Pyrazolin-5-one has drawn substantial attention from scholars because of its stimulating natural activities. [8,9]. Pyrazolin-5-one and 5-Pyrazolones are very vital category of heterocycles attributable to their organic and pharmaceutical actions[10]. They are employed as main initial materials for the synthesizing viable aryl/hetarylazopyrazolone dyes [11], that are used as noble fastness dyes tuffs for wool, cotton, leather, silk, rubber and synthetic polymers (Nylons).On the other hand, many azopyrazolone dyes have been employed as indicators for complexometric titrations [12]. Within the subject of azo dyes, phenolic compounds have a foremost role for synthesizing the majority of viable dyes. Most of these commercially existing dyes...
have the naphthols bearing hydroxyl groups as an auxochrome group. [13,14]. In recent years, a significant number of tridentate azo compounds have a heteroaryl ring systems and have been developed for improving the colouring features and to accomplish more selectivity and specificity in chemical analysis[15]. Metal dicyclex complexes have a highly significant role in dye- stuff technology [16] and find uses in countless fields, particularly in analytical chemistry [17]. In continuance of studies, the interaction of coordination compounds has shown a speedy expansion in varied disciplines because of the potential use of these new compounds in biological uses. The present work explains the preparing and spectral features of [(1-phenyl-2-pyrazolin-5-one) azo (6-bromo-2-hydroxynaphthalen-1-yl)] (PABH) containing naphtholic-OH function and pyrazolin moiety. The azo dye ligand (PABH) and its metal ions Co(II), Ni(II) and Cu(II) complexes were studied by various spectral analysis and screened for their antimicrobial activity in contradiction of Staphylococcus aureus and Escherichia coli.

Experimental Section

Instruments, Materials and Approaches

Entirely, the chemicals have been bought from BDH and Fluka. FTIR spectra have documented based on KBr on Shimadzu- spectrophotometer in (4000-400) cm\(^{-1}\) range. Electronic spectrums in ethanol have documented by means of UV-visible spectrophotometer under (200 - 1100) nm range with quartz cell of (1cm) path length. pH measurement has been done by means of HANNA instruments pH Tester. Melting points have measured with an electro thermal Stuart apparatus, model SMP30. The measurements of electrical conductivity for complexes have noted at (25°C) for 10\(^{-3}\) mol.L\(^{-1}\) solution of the samples in dimethyl sulfoxide (DMSO) by means of WTW inolab cond 720 digital conductivity meter. Microelemental analysis (C.H.N) has gained on a(Eure EA 3000 Elemental analyzer) in Ibn Al-Haitham- College of Education For Pure Science Mass spectra in Agilent mass spectrometer 5975 quadrupole analyser. \(^1\)H NMR and \(^31\)C NMR spectrums have measured on a DRX (500-MHz) spectrometer in DMSO and Bruner DRX (500-MHz) were performed at Sharif Sainte University, Tehran, Iran. Chemical shifts are in ppm relative to internal Me\(_2\)Si. Elemental microanalyses of the ligand and their complexes have implemented through Euro Vectro-3000A. The solutions and materials are employed in a biochemical analysis sterilized based on Autoclave, Gallen Kamp. The cultivated bacteria dishes incubated via Memmert Incubator, 854 Schwach. Metal content of complexes have determined by means of atomic absorption method through Analytic Jena(A.A350) atomic absorption Spectrophotometer. Magnetic susceptibility magnitudes have gotten under room temperature via the Gouy process, Johnson Mattey Catalytic system. Thin Layer Chromatography (TLC): the (TLC) has been accomplished on Al coated plates with silica gel (Fluka), and identified through iodine. Preparation of the Ligand (PABH)

The new azo ligand was created in relation to the Gusev method [18] by dissolving (1.75 g, 0.01 mol) of 3-amino-1-phenyl-2-pyrazolin-5-one in a mixture consisting 25 mL of distilled water and 5 mL of concentrated hydrochloric acid. A solution has diazotized at (0–5 °C) 10 mL of aqueous (0.689 g, 0.01 mol) sodium nitrite. Consequently, diazonium chloride solution was added to the mixture drop by drop with stir then, 6-bromo-2-naphthol (2.23 g, 0.01 mol) was dissolved in 150 mL of alkaline ethanol and then cooled lower than 0°C. Next to effecting addition, then left the content for two hours, then 150 mL of cooled distilled water was add, the pH of the solution maintained at 6 by HCl, brown molecules were precipitated and left for 24 h. The precipitate has been filtered off and washed up many times with (1:1) ethanol : water mix then recrystallized two times from hot ethanol, and dried in a vacuum desicator.

Table (1) consist name of ligand, 83.4 % yield ,177–178 m.p from hot ethanol, and dried in a vacuum desicator.

Preparation of the Buffer Solution

Buffer solutions with pH magnitudes from 5 to 9, of acetic acid-ammonium acetate-ammonia (0.01M, 0.77gm) have been primed in one litter of deionized twice as distilled water. The requisite pH has gotten by the adding either ammonia solution or acetic acid.

Preparing the Standard Solution

The metal salt solutions (1x10\(^{-3}\)-1x10\(^{-6}\) M) have organized through dissolving the fitting weights of every of these salts [CoCl\(_2\).6H\(_2\)O, NiCl\(_2\).6H\(_2\)O and CuCl\(_2\).2H\(_2\)O] in the equipped buffer solutions. Simultaneously, the range of concentration has employed for preparing the ligand solutions obtained via dissolving (0.04 g, 0.001 mole) from the ligand (PABH) in (100) mL of ethanol. The solution was diluted to obtain concentrations (1x10\(^{-3}\)-1x10\(^{-6}\) M).

Determination of Optimum Concentrations

The optimum concentrations for the mixing process, the solutions ranged between (1x10\(^{-2}\), 1x10\(^{-6}\) M) were determined for both the ligand and metal ions. Equal volumes were mixed for both the ligand and metal ions at rang of acidity functions (5-9) and measured the absorption.
value for these solutions. The high-ranged concentrations (1x10^{-3} and 6x10^{-4} M) showed complex precipitation for instant mixing of these solutions. So the concentrations between (1x10^{-4}-5x10^{-4} M) were chosen because it gave acceptable absorption and some of them comply with the Beer-Lambert law, as for the minimum concentrations (1x10^{-5} and 1x10^{-6} M), they gave a weak measured.

**Determination of Optimum Acid Function**

The effect of acidic function change was studied at a range of pH (5-9) to reach the optimum acidic function of the metal ions after the optimal conditions were established, which included the determination of the optimal concentrations of ligand and metal ions.

**Determination of Standard Calibration Curve of the Metal Complexes**

A solutions ranged between (1x10^{-5}-5x10^{-4} M) for both the ligand and the metal ions studied, the equal volumes of same concentration of metal salts solutions and ligand solutions were mixed at optimal acidic function and the wavelength that gives the highest absorbance (λmax). The absorption values of these solutions in practical experiments showed that the optimal concentrations for complexes prepared and suitable for spectral measurements fall within the range (1x10^{-4} - 5x10^{-4} M) were obeyed the Lambert-Beer's law.

According to the graphs plotted of the standard calibration curve for the metal ions complexes solutions, the relationship between the ligand and metal ions concentrations was obeyed the Lambert-Beer's law.

**Synthesis of Complexes**

The complexes have equipped through adding dropwise based on hot stirring ethanolic solution of (2 mmole) ligand to stoichiometry amount of M:L ratio of (1:2) of [Co(II), Ni(II) as well as Cu(II)] that dissolved in a primed buffer solution at finest pH. A mix has heated up under (60°C) and stirred up to (1 hour). After that, at room temperature, they have left to cool. A colored precipitate has filtered, washed many times with a (1:1) (water:alcohol) mix then left to desiccated in vacuum desiccator. A recommended stoichiometry structure for the complexes has been illustrated in scheme (2), Figure (1) 3D. Table (1) presents, the suggested formula, color, m.p, and yield ratio of formed solid complexes.
Antimicrobial Activity Study

Antibacterial activities of the new Azo ligand and its metal complexes were screened by Kirby-Bauer disk diffusion method [19]. This paper employs dual strains for pathogenic bacteria first, a *Staphylococcus aureus* (Gram Positive) and the other strain, *Escherichia coli*. (Gram Negative). The used biochemical solutions were organized through dimethyl sulfoxide (DMSO) as solvent, where a single concentration (C) 1x10\(^{-3}\)M is joined. The dishes have been incubated under 37°C for a complete day. Based on the inhibition zones, the diameter (Inhibition area) mm has formed after a complete day as a principle for an intensity of the influence of synthetic chemical compounds on a growth of specific cultivated bacteria strains

Consequences and Discussion

General

The Azo ligand (PABH) is pale brown crystal, which is not soluble in water and soluble in common organic solvents. The reaction of this ligand with the metal ions gives different color crystals. All complexes are quiet water - insoluble, stable in air, while they are soluble in most organic solvents such as DMSO, DMF, acetone…etc.

Physical Properties and Elemental Analyses

Reacting the organized ligand (PABH) with a selection of metal ions [Co(II), Ni(II) and Cu(II)] at finest concentration and pH, that causes formed complexes with formula [Co(PABH)\(_2\)], [Ni(PABH)\(_2\)] and [Cu(PABH)\(_2\)]. The ligand has performance as N,N,O⁻-chelator, in which N (azo), N (2-pyrazolin-5-one) and O’ hydroxyl (6-bromo-2naphthol). The physical features and consequences gotten from C.H.N.O examinations and metal contents of the organized compounds are explained in Table (1). The analytical data have been well accepted with the computed magnitudes. The molecular formula of the ligand and its metal complexes have been suggested according to the data which were resulted from spectral and magnetic susceptibility of metal complexes. In all cases (1:2) metal to ligand solid complexes are isolated.

Table 1: Physical details and analytical information of the made Azo ligand (PABH) besides its complexes

<table>
<thead>
<tr>
<th>Empirical formula (M, Wt) gm/mol</th>
<th>pH</th>
<th>Color</th>
<th>Mp, °C</th>
<th>Yield, %</th>
<th>Found(Calc.)(%)</th>
<th>M(II)</th>
<th>μ(\text{eff.}), B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>Ligand C(<em>{19})H(</em>{13})BrN(<em>{2})O(</em>{2})</td>
<td>-</td>
<td>Pale Brown</td>
<td>177-178</td>
<td>83.4</td>
<td>55.76 (56.02)</td>
<td>3.2</td>
<td>13.69 (13.82)</td>
</tr>
<tr>
<td>[Co(C(<em>{19})H(</em>{13})BrN(<em>{2})O(</em>{2}))(_2)]</td>
<td>8</td>
<td>Reddish-Brown</td>
<td>196-197</td>
<td>76</td>
<td>52.13 (52.34)</td>
<td>2.76</td>
<td>12.8 (12.71)</td>
</tr>
<tr>
<td>[Ni(C(<em>{19})H(</em>{13})BrN(<em>{2})O(</em>{2}))(_2)]</td>
<td>8</td>
<td>Yellowish-Green</td>
<td>188-189</td>
<td>74.1</td>
<td>52.15 (52.41)</td>
<td>2.76</td>
<td>12.8 (12.89)</td>
</tr>
<tr>
<td>[Cu(C(<em>{19})H(</em>{13})BrN(<em>{2})O(</em>{2}))(_2)]</td>
<td>9</td>
<td>Pale Green</td>
<td>207-208</td>
<td>76.19</td>
<td>51.86 (52.05)</td>
<td>2.74</td>
<td>12.73 (12.65)</td>
</tr>
</tbody>
</table>

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Influence of pH

The pH magnitudes intended for metallic ions complexes solutions have been investigated for detecting a finest pH medium for preparing the metallic complexes, the best concentration of complexes has reserved as provided an ascension to study (λmax) at numerous pH magnitudes. The pH influence has been as well examined within (5-9) range. Figure (2) depicted an absorbance for pH curves that had completed at (λmax) and some concentrations under study for every metal ion solution. The huge band of the curves for pH which was reflected as a reference of complex formation and acceptance as finest pH for preparing complexes. Hence, we deduce that all equipped chelate complexes with a selection of metal ions have been prepared in basic medium [20,21].

Mole Ratio [Metal:Ligand] Ratio

The mole ratio technique was adopted with the intention of identifying spectrophotometrically of a composition of metal chelate complexes and for conclusion of potential structural formula of organized metallic ions complexes, this technique has been in accordance with an range measurement for every complexes solution under fixed finest pH and concentration at a supreme absorbance wavelength. The colors intensity for the solution of equipped metallic ions complexes has raised based on intersection point for [M:L] ratio approach. The continual stability of color beyond an intersection point signifying the formed metallic complexes [21]. The structure of formed complexes in solutions was proven by mole ratio method. Accordingly, the consequences show a mole ratio [M:L] [1:2] for entire metal ions to ligand ratio. The method supports the complexes formation, as explained by Figure (3).

NMR Spectra for the Azo Ligand

The 1H-NMR spectrum of ligand (PABH) in DMSO-d6 Figure (4) was shows a single peak appeared at δ(10.458) ppm which was attributed to chemical shift of OH proton in the 2-naphthol [13],[20]. A multiplet peak at δ (8.461 - 6.884) ppm that have been as a result of chemical shifts of aromatic protons for aromatic rings of 2-naphthol and phenyl moieties [22,23,24]. The doublet signal observed at δ (3.561 - 3.514) ppm were assigned to H-C-H protons on the pyrazolin ring moiety in the ligand [22],[25].

13C-NMR spectrum Figure (5) displayed a peak at δ (178.22) ppm which is due to pyrazolin carbonyl group[23], while the C=N pyrazolin moiety carbon signal is showed at δ (168.26) ppm [25]. The multiplet peaks at δ (162.16 - 122.23) ppm are due to aromatic carbons of 2-naphthol and phenyl moieties [26]. A peak at δ (167.13) ppm which is assigned to C=C-CH and a signal at (121.81) duo to C=C-Br carbons in 2-naphthol rings [13]. The peak at δ (163.74) ppm is due to C=C-N site linked of 2-naphthol with azo group for pyrazolin ring [20],[27]. The signals at δ (47,34) ppm are assigned to the middle and terminal C-C carbon atoms of diaminobutane moiety in the ligand [12],[25],[27].
Mass Spectrum for the Azo Ligand (PABH)

The mass spectrum data for azo ligand Figure (6) showed a molecular ion peak at (m/z = 409.6) [25,27]. The molecular ion peak corresponds to (C\textsubscript{19}H\textsubscript{13}BrN\textsubscript{4}O\textsubscript{2}). Other fragments and relative abundance are summarised in Scheme (3).

![Fig. 4: 1H-NMR spectrum of the azo ligand (PABH)](image1)

![Fig. 5: 13C-NMR spectrum of the azo ligand (PABH)](image2)

![Scheme 3. The fragmentation and relative abundance data of the azo ligand (PABH)](image3)
UV-Vis Spectral Studies

The electronic absorption bands along with the conductivity values have briefed in Table (2). The UV-Visible spectrum of azo ligand Figure (7) in ethanol (5x10⁻⁴ M) within the range (200-1100) nm appeared two absorptions at (244 and 295) nm (40983 and 33898) cm⁻¹, which is due to π-π* transition and a broad low intensity band at (420) nm (23809) cm⁻¹, which was attributed to n → π* transition of (C.T) intermolecular charge-transfer taken place through the azo group (-N=N-), Fig. (1). [16,28,29].

The spectra of the metal ions complexes within (5x10⁻⁴ M) at optimum pH showed bathochromic transfers of ligand band. The assigned bands to intraligand π→π* for the Co(II), Ni(II), and Cu(II) complexes were observed at (38055, 32172), (37811, 31523) and (37535, 31014) cm⁻¹ respectively. The changing in a color of free ligand solutions and high shift in the (λmax) offers a worthy sign for coordinating and complex forming [28],[30]. The spectra of complexes depicted added low intensity bands in the perceptible regions associated with ligand field d-d transitions [20],[26]. Co-complex spectrum in ethanol solution in Figure (8), revealed dual bands at (510) nm (19607.84) cm⁻¹ and (590) nm (16949.15) cm⁻¹, which were attributed to the ¹T₁g→²T₁g(P) (υ₁) and ⁴T₁g→⁴A₂g (υ₂) transitions corresponding of octahedral geometrical structure [31],[31]. Based on a ratio of υ₁/υ₂ (1.15), a magnitude of Dq/B (1.73) has been gotten. The magnitude of B' (688.53) in addition to a position of υ₁(10Dq) (12447.36) cm⁻¹ have analyzed by means of Tanaba-Sugano diagram for d⁸ structure for octahedral configuration geometry[31,32]. The value of β (0.67) indicates some covalent character. The conductivity measurement in ethanol as solvent, specifies that the Co-complex is non-ionic. Spectrum of Ni(II) complex Figure (9), depicted two bands in a visible region at (573) nm (17452) cm⁻¹ and (446) nm (22421.52) cm⁻¹ which are due to ⁴A₂g→⁵T₁g(F) (υ₁), ⁴A₂g→⁵T₁g(P) (υ₁) respectively. The ratio of υ₁/(1.28) has applied on Tanaba-Sugano diagram regarding d⁶ octahedral complexes,[31,32,33]B(complex) (774) and β (0.73), Dq/B (1.17), 10Dq(υ₁) (9053.61) cm⁻¹ have computed hypothetically. The conductivity has depicted that the Ni(II)-complex has been non-electrolyte. The Cu(II) complex spectrum in Figure (10), has depicted broad band at (650) nm (15384.61) cm⁻¹ assigned to ²Eg→²T₂g transition that signifies Jahn-Teller distortion of octahedral geometry[27],[31]. A measurement of conductivity for the complex signposts in which a complex has been non-ionic.

![Fig. 7: UV-Vis spectrum of Ligand (PABH)](image)

![Fig. 8: UV-Vis spectrum of Co(PABH)₂ complex at pH =8](image)

![Fig. 9: UV-Vis spectrum of Ni(PABH)₂ complex at pH=8](image)

![Fig. 10: UV-Vis spectrum of Cu(PABH)₂ complex at pH =9](image)

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The UV-Vis spectra for complexes were studied within the concentration range of (1×10⁻³-1×10⁻⁶) molar, whereas the pH sequence has been (5-9). Not each concentration is appropriate for spectral measurements, while a solution in (1×10⁻⁵ M) concentration go along with Lambert-Beer’s low with an obvious color indication. Figure (11) has depicted the finest fit straight lines, as the absorbance plotted vs. molar concentration under (1×10⁻⁴- 5×10⁻⁵) molar range.

**IR Spectra of Azo Ligands and Complexes**

The infrared spectral data of azo ligand and its complexes have illustrated in Figures (12-15) and Table (3). The IR spectra for complexes have compared with those of the free ligand with the intention of determining the coordination sites that can be included in chelation.

The IR spectrums offer worthy facts about the nature of functional groups in a ligand and some of which involved to the metal ion [22],[26]. The IR spectrum of the free ligand (PABH), exhibited a wide and strong intensity band at (3397 cm⁻¹), which was attributed to the stretching vibration of the hydroxyl group in the naphthol[23,34], this band disappear in the complex spectrum, that indicating the oxygen atom of the hydroxyl group in the 2-naphthol was attached with the metal ions in the complexes. The ligand showed a strong band at (1628 cm⁻¹) due to (N=N) this band undergo change to lower frequency in the spectrum of the complex signifying an engaged one of the two nitrogen atoms of the azo group in the coordinating with the metal ions[24,32]. The band shoulder at 1725 cm⁻¹ in a spectrum of a free ligand, attributed to v(C=O) on pyrazolin ring [25],[28] the position of this band remained at approximately the identical frequency in spectrums of metal complexes, signifying the noncoordination of this group [35]. The band appearing at 1650 cm⁻¹ in the free ligand pyrazolin ring , assignable to v(C=O) on pyrazolin ring[24,35], is shifted to lower wave numbers with a Δν at range (30-19) cm⁻¹ in the complexes spectra, this indicating the involvement of pyrazolin nitrogen atom in coordination[22,25]. A medium intensity band at (1153cm⁻¹) showed in the ligand spectrum returning to the (C-N) (carbon 2-naphthol - nitrogen azo), when compared to the spectrum of the complex, a slight change in its position and shape was observed due to the coordinate the metal ion with the close azo nitrogen atom[35,36]. The presence of dual new bands in the region 482-468 and 444-423 cm⁻¹ in the complexes spectra, as a result of v(M−N) and v(M−O) stretching vibrations respectively[23,27,36], also confirmed the formation of metal complexes.

![Fig. 11: The linear relationship between absorption and the range of selected concentrations for metal ions complexes at optimum pH and λ_max](image)
Table 3: Most Imperative FTIR spectral bands and their Assignments of the azo ligand and its Complexes (cm⁻¹)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ν (O-H) 2-naphth</th>
<th>ν (C=≡) pyrazolin</th>
<th>ν (N=N) azo</th>
<th>M-N(ν)</th>
<th>M-O(ν)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{19}H_{13}BrN_{4}O_{2}(PABH)</td>
<td>3397,b</td>
<td>1650,m</td>
<td>1629,m</td>
<td>1594,m</td>
<td>468,w</td>
</tr>
<tr>
<td>[Co(PABH)₂]</td>
<td>1620,m</td>
<td>1594,m</td>
<td>468,w</td>
<td>425,w</td>
<td></td>
</tr>
<tr>
<td>[Ni(PABH)₂]</td>
<td>1639,m</td>
<td>1596,m</td>
<td>474,w</td>
<td>423,w</td>
<td></td>
</tr>
<tr>
<td>[Cu(PABH)₂]</td>
<td>1631,m</td>
<td>1591,m</td>
<td>482,w</td>
<td>444,w</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 12: FTIR spectrum of azo ligand (PABH)

Fig. 13: FTIR spectrum of [Co(PABH)₂] complex
Fig. 14: FTIR spectrum of [Ni(PABH)₂] complex

Fig. 15: FTIR spectrum of [Cu(PABH)₂] complex

**Thin Layer Chromatography (TLC)**

A solution of azo ligand besides its complexes in ethanol as solvent, shown as one spot each, ratifying that these compounds, entirely, have been pure and possess only single isomer[31]. Table (4) explains the Rf for complexes and the ligand.

Table 4: Shows the Rf for the azo ligand (PABH) and its complexes in ethanol solvent

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g/mol)</th>
<th>Rf eth. solv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand C₁₉H₁₂BrN₄O₂</td>
<td>409.6</td>
<td>0.41</td>
</tr>
<tr>
<td>[Co(C₁₉H₁₂BrN₄O₂)₂]</td>
<td>875.39</td>
<td>0.28</td>
</tr>
<tr>
<td>[Ni(C₁₉H₁₂BrN₄O₂)₂]</td>
<td>875.15</td>
<td>0.3</td>
</tr>
<tr>
<td>[Cu(C₁₉H₁₂BrN₄O₂)₂]</td>
<td>880.00</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Antimicrobial Activity**

The response of selected bacteria, we observed the excessive biochemical effect of the azo ligand and its complexes studied at concentration (1x10⁻³ M) with dual varieties of pathogenic bacteria (Staphylococcus aureus), its Gram Positive and either with the germ (Escherichia coli), Gram negative bacteria, have depicted lower response to ligand besides its complexes investigated from the other category of bacteria, categorized it’s resistant to numerous chemical compounds and antibiotics[19],[29],[35]. The cause for this resistant is the colon bacteria that are found in a distinct bacilli having thick casing surroundings of its cell, this casing has an excessive amount of lipid works to oppose these materials from inflowing a cell, whereas the Staphylococcus aureus bacteria don’t have this feature. Accordingly, it will
be in lower resistance in an arrival of chemical and antibiotic substances to inner bacterial cell [30,31],[36]. Normally, the prepared complexes have explained biochemical effect more as compared with the ligand (PABH), while the ligand contain nitrogen and oxygen atoms biological retardant[22],[31],[37]. The positive charge ion in the chelated complex has been partly shared with the donor atoms orbital in a ligand and there has been \(\pi\)-electron delocalization over the entire chelate ring, which decrease in the polarity of the metal ion to a greater level, this in turn increases a lipophilic character of a metal chelate and favors its permeation via the lipid layers of the membrane the microorganisms[31],[37]. The consequences presented in previous activity Tables (5) and figures (16,17).

Table 5. The data of antibacterial activity (zone of inhibition) (mm) of azo ligand (PABH) and its complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>G-(E.coli)</th>
<th>G+(St.aureus)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (S) DMSO</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Ligand (PABH)</td>
<td>11.5</td>
<td>14</td>
</tr>
<tr>
<td>[Co(PABH)(_2)]</td>
<td>12.3</td>
<td>15.8</td>
</tr>
<tr>
<td>[Ni(PABH)(_2)]</td>
<td>13</td>
<td>16.2</td>
</tr>
<tr>
<td>[Cu(PABH)(_2)]</td>
<td>14.7</td>
<td>19.4</td>
</tr>
</tbody>
</table>

Fig. 16: The biological effects of azo ligand (PABH) and its complexes

Fig. 17: Photograph of antibacterial activities of the ligand (PABH) and its complexes

Conclusion

The azo ligand (PABH), coordinates with Co(II), Ni(II) and Cu(II) ions based on a tridentate nitrogen atom of the azo, nitrogen atom of pyrazolin ring and oxygen atom of the hydroxyl in the 2-naphthol groups resulting in six-coordinated metal ion, this behavior with M:L mole ratio of 1:2. Each complex has been of octahedral geometry and categorized by numerous physio-chemical techniques, the analysis ratified the composition and structures for the gained complex jointly. Biological activity results have depicted that all the compounds have variety of antibacterial activities.

Acknowledgment

I would like to state my sincere gratitude to the Department of Chemistry, College of Education,
References


[26] Gholamhassan I.; Alireza B.; Taurof F. and Zahra S., Green synthesis of novel isatin thioketal derivatives

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*Egypt. J. Chem.*, 64, No. 3 (2021)


Some metal (II) complexes with new tridentate heterocyclic azo ligand type (NNO)...

**SOME METAL (II) COMPLEXES WITH NEW TRIDENTATE HETEROCYCLIC AZO LIGAND TYPE (NNO).**

Translating and translating to the doctorate of some metal complexes with new Schiff base amine ligands.

**In this research,** we have synthesized a new Schiff base ligand through the condensation of anthranilic acid with benzoin using the oxidative method of polycondensation. The Schiff base ligand was synthesized using the condensation of benzoin with anthranilic acid. The ligand was then treated with metal ions to form metal complexes. The metal complexes were characterized using various spectroscopic techniques, including UV-Vis, IR, NMR, and mass spectrometry. The antibacterial activity of the metal complexes was tested against a range of bacterial strains. The results showed that the metal complexes had good antibacterial activity, with MIC values ranging from 50 to 100 μg/mL. The complexes were also tested for their cytotoxicity against mammalian cells. The results indicated that the complexes were relatively nontoxic, with IC50 values ranging from 200 to 500 μg/mL. Overall, the study demonstrated the potential of the new Schiff base ligand for the development of new metal complexes with antibacterial and cytotoxic properties.

**Notes:**

1. The ligand was synthesized by condensing benzoin with anthranilic acid.
2. The metal complexes were characterized using UV-Vis, IR, NMR, and mass spectrometry.
3. The antibacterial activity of the complexes was tested against a range of bacterial strains.
4. The complexes showed good antibacterial activity, with MIC values ranging from 50 to 100 μg/mL.
5. The complexes were relatively nontoxic, with IC50 values ranging from 200 to 500 μg/mL.

**References:**


**Egypt. J. Chem.** **64**, No. 3 (2021)