Preparation, Spectral Identification and Analytical Studies of Cu(II) Transition Metal Complex with New Imidazole Azo ligand (PADDPI) and The biological Activity Study

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ABSTRACT

In this paper, we prepared and characterized the complex of Cu(II) ion and the new organic heterocyclic azo dye 2-[(procainamide) diazenyl]-4,5-diphenylimidazole (PADDPI), which was prepared by reacting diazonium salt solution of 2-amino-5-procaine amide in alkaline ethanolic solution. The general formula of the solid complex was determined as [CuL₂Cl₂] through reacting azo imidazole ligand with metal chloride ion, and the molar ratio was (metal : ligand) [1:2]. The solid complex was characterized spectroscopically by FT-IR, electronic spectra, elemental analysis and molar conductance. The analytical data show that the ligand is a bidentate and coordinates with metal ion via nitrogen atom of azo and N₃ of imidazole. The octahedral geometry was suggested for Cu(II) ion complex.

INTRODUCTION

Azo imidazole derivatives are very important class of chemical compounds receiving attention scientific research[1,2] they are highly colored and have been used as dyes and pigments for a long time.[3,4] They are important in drugs[5], cosmetics[6], biological activities including antibacterial[7], coordination capacity[8] and participate in azo coupling reactions.[9] The coupling of diazonium salt occurs in position 2 of imidazole ring in alkaline medium to give azo imidazole dyes.[10,11] Azo imidazole molecule being the azo imine group (—N═N—C═N—), which is π-acidic and stabilized low valant metal redox state.[12] The azo imidazole ligands does not have the same interest in research and investigation because of the rarity in the preparation of this kind of ligands although the imidazole was known before 150 years.[13] A number of these azo dyes have been used as chelating ligands[4,8,14]in addition of the uses as ligands in analytical chemistry.[9,15,16] The heterocyclic azo dyes have been synthesized and proposed as highly sensitive chromogenic ligand for the determination of several metal ions[17-19].Large number of the spectro photometric methods based on these reactions were developed and used in analytical chemistry[20]. The
present study reports the preparation, spectral characterization and analytical study of new azo imidazole ligand (PADDPI) and Cu(II) metal complex.

**MATERIALS AND METHODS**

**Apparatus and materials**
All chemicals and solvents were highest purity obtained from Fluka, The Merck and BDH. The melting points were determined on a Electro thermal, melting point 9300. Elemental analysis (C.H.N) were obtained using EuRo VECTOR C.H.N elemental analyzer. IR spectra were recorded using KBr discs in the range (4000-400) cm\(^{-1}\) on FTIR Teast scan Shimaduz model 8300, while the UV-Vis. Spectra recorded in ethanol on Shimaduz model 1650PC. Molar conductance measurements were determined in DMSO (10\(^{-3}\) M) at room temperature HANNA model 214EC conductivity meter the pH measurements were carried out using pH-meter Hanna. The metal contents of the complex was measured by using atomic absorption technique by Perkin-Elmer model 2280.

**Preparation of the ligand (PADDPI)**
The heterocyclic azo ligand was prepared according to the following general procedure for diazotization of primary aromatic amine for Shibata[21]. The ligand 2-[(procainamide) diazenyl]-4,5-diphenylimidazole (PADDPI) was synthesized by dissolving (2.3533g, 0.01mol) of procaine amide in 30 ml of distilled water and 3 ml of concentrated hydrochloric acid. To this mixture a solution of (0.75gm, 0.01mol) of sodium nitrate in 15ml of distilled water was added dropwise at (0-5) °c and left to stand 20min. This diazonium solution was added dropwise into a 500ml beaker containing (2.2g, 0.01mol) of 4,5-diphenyl imidazole dissolved in 200ml of alkaline ethanol and 5 ml of 10% sodium hydroxide and 25 ml of 10% sodium carbonate at (0-5) °c, the mixture was stirred for additional 4hr in ice-bath and allowed to stand overnight and basified with dilute sodium hydroxide(0.5M) to pH > 8. The precipitate was filtered off, washed with distilled water and recrystallized ice from hot ethanol and dried in oven at 60 °c for 24 hour. The yield was (75%) of reddish orange powder (m.p = 140-143 C°)

**Preparation of complex**
The metal complex was prepared by dissolved (0.05 g, 0.00012 mole) from ligand in hot ethanol (25ml) and added drop wise with stirring to a soichiometric amounts of 1:2 (metal: ligand) molar ratio of(0.00914 g, 0.00006 mole) Cu(II) chloride salt (CuCl\(_2\).2H\(_2\)O) at optimal pH for metal ion. The solid product thus formed was filtered off from the ice-cooled reaction mixture, washed with 10ml hot ethanol to remove the remaining unreacted substances and dried at 70°C overnight.
RESULTS AND DISCUSSION

The reaction of heterocyclic azo ligand (PADDPI) with the metal ions mentioned above different color crystals depending on the nature of metal ion. The complex is stable in air and insoluble in water but soluble in most organic solvents. The analytical and physical data of the ligand and complex are given in table 1 they are consistent with the calculated results from empirical formula of compound. The ligand was seen in scheme 1.

![Scheme 1: Preparation of (PADDPI) ligand](image)

Table 1: Analytical data and physical properties of the ligand (PADDPI) and complex.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Molecular formula of ligand</th>
<th>Color of complex</th>
<th>M.P °C of complex</th>
<th>Yield% of complex</th>
<th>Optimal pH of complex</th>
<th>Found (Calc.)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L=(PADDPI)</td>
<td>C_{28}H_{30}N_{6}O (466.58)(Mol.Wt)</td>
<td>brwon-red</td>
<td>196-197</td>
<td>94</td>
<td>8</td>
<td>72.103 *(72.36) 6.437 *(6.46) 18.025 *(17.97) 13.635 *(13.25)</td>
</tr>
</tbody>
</table>

L=ligand
* = the practical value
M=metal
Absorption spectra
The absorption spectra in aqueous ethanolic solution 50% (V/V) were studied for ligand fig.1 and the prepared complex showed a bathochromic shift about (77) nm fig.2

![Absorption spectra of free Ligand (L) and Cu(II) complex with (PADDPI)](image)

Effect of pH
The effect of acidity on Cu(II) complex formation was studied in the 50%(v/v) ethanolic by changing the pH value of the solution and the result is shown in figs.3. where fig.3 demonstrated that the best absorbance of Cu(II) PADDPI system is in the range (7.8-8). The ligand formed a stable complex with metal ion Cu(II) at pH(8).

![Effect of acidity on Cu(II) complex formation](image)

Effect of time
Also the reaction is complete in 5 min at room temperature and remains stable for about 180 min. This shows (PADDPI) ligand strong coordination with metal ion in this time. The result are shown in fig.4.
Metal: ligand ratio
Composition of chelate complexes were investigated by mole ratio method[22] at fixed concentration of metal ion (4x10^{-5}M) and increasing concentration of ligand (1x10^{-5}-14x10^{-5}M) at optimum pH and $\lambda_{\text{max}}$. This method indicated that the more probable structure of complex was 1:2 for Cu(II) ion as shown in fig.5 the results are given.

Determination of the metal complex stability constants
Stability constant ($\beta$) values are obtained spectrophotometrically by measuring the absorbance of a mixture of ligand and metal solution at fixed wavelength ($\lambda_{\text{max}}$) and optimum pH values. The degree of formation of the complex are obtained from the relationship[23] $\beta = (1-\alpha/4\alpha^3c^2)$ for 1:2 metal complex and $\alpha = \text{Am-As} / \text{Am}$ where As and Am are the absorbance of the partially and fully formed complex respectively at optimum concentration. The calculated $\beta$ and log $\beta$ values for the prepared complex are given in table2.

Molar conductivity
The data obtained from the measurement of molar conductance of the complexes are shown in table 2 were carried out in DMSO(10^{-3}M) at room temperature. The value indicate that the chelate complex of Cu(II) ion is non-electrolyte nature, where the value suggest that no anions outside the coordination spheres[24,25].
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Table 2: metal :reagnt stability constant value (β) molar conductivity, optimal concentration and wave length with molar absorptivity (Є) of chelate complex

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Metal Ion</th>
<th>Metal: Ligand</th>
<th>Optimal molar conc. x 10^5 M</th>
<th>Optimal wave length (λ max) nm</th>
<th>Molar absorptivity (Є)x10^4L.mol^-1.cm^-1</th>
<th>β L².mol^-2</th>
<th>Logβ</th>
<th>Molar conductivity s.mol^-1.cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PADDPI , λmax= 431 nm</td>
<td>Cu(II)</td>
<td>1:2</td>
<td>4</td>
<td>508</td>
<td>1.53</td>
<td>42x10^11</td>
<td>28.50</td>
<td>58.0</td>
</tr>
</tbody>
</table>

Infrared spectra

Infrared spectra data (KBr disk) of ligand (PADDPI) and its complex are summarized in table3. The comparison between spectrum of the ligand with this of the coordination complex have revealed certain characteristic differences. Azo ligand spectrum show strong band at 3446cm^-1 due to υ(N-H) group [26]. The unchanged of this band in complex means that the υ(NH) group does not participate in coordination[27]. There are weak peaks appear at positions 3853 cm^-1, 3075 cm^-1 to (C─H) aliphatic and aromatic[28]. These bands are stable in position and intensity in both ligand and its metal complex. Another strong band appeare at 1543cm^-1 in the ligand spectrum which is due to υ(C=N) [29] to imidazole ring. In this spectra of complexes this band was shifted to a different frequencies at (1500-1543)cm^-1 with a little change in shape. These differences suggest a coordination of the metal ion with nitrogen atom N₃ of imidazole ring.[30]. The free ligand shows a strong band at 1689cm^-1 due to υ(C=O) of carbonyl group.[31] This band is change in position in both ligand and complex . The υ(N=N) stretching vibration appears band at 1506cm^-1 in the free ligand spectrum. This band appearing at (1442)cm^-1 with different in shape and reduced in intensity in prepared complex spectra. Both bands shifted and reduced intensity due to complex formation.[32] Some other new bands appeared in the region of (466) cm^-1 in the complexes spectra which are not present in the spectrum of the ligand may attributed to the υ(M-N) band.[33] Thus the above IR spectra data lead to suggest that ligand behaves as a bidentate chelating agent and the coordination sites are the nitrogen atom of azo group nearst to phenyl ring and N₃ atom of the imidazole ring to give five-membered chelat ring. Representaive example for their spectra are given in figs. 7 and 8.
Figure 6: FT-IR Spectrum of (PADDPI) ligand

Figure 7: FT-IR Spectrum of Cu(II) complex with (PADDPI)

Table 3: Characteristic IR absorption bands of the ligand (PADDPI) and its complex in cm\(^{-1}\) units (KBr disk)

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>(\nu(N-H))</th>
<th>(\nu(C-H)Ar).</th>
<th>(\nu(CH)Alip.)</th>
<th>(\nu(C=O))</th>
<th>(\nu(C=N))</th>
<th>(\nu(N=N))</th>
<th>Imid.r.d.</th>
<th>PH-ind.</th>
<th>(\nu(M-N))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R=(PADDPI)</td>
<td>3446br.</td>
<td>3057w</td>
<td>3853w</td>
<td>1689s</td>
<td>1543s</td>
<td>1506m</td>
<td>1087m</td>
<td>771s</td>
<td>694s</td>
</tr>
<tr>
<td>2</td>
<td>[Cu R_2Cl_2]</td>
<td>3437br.</td>
<td>3059w</td>
<td>1701m</td>
<td>1500w</td>
<td>1442w</td>
<td>1103m</td>
<td>773s</td>
<td>698s</td>
<td>466w</td>
</tr>
</tbody>
</table>

W=weak; s=strong; br.=broad; m=medium
**Electronic spectra**

The electronic spectra data of prepared ligand are three peaks, one for electronic transition \((\pi - \pi^*)\) (223nm), the second (289nm) refer to \((n - \pi^*)\) [34], the third peak (431nm) for donor atoms such as azo group C.T transition (charge transfer).

**Biological Activity**

The biological activity of (PADDPI) ligand and its synthesized complex Cu-PADDPI were studied against a four diagnosed fungi samples (penecillium, A.orizea, A.terrus and A.niger) . Antifungal activity of (PADDPI) ligand and its synthesized complex were determined by the agar (PDA) dilution method [35]. Four different final concentrations of (PADDPI) ligand and complex in the agar (0, 5, 10, and 15µg/ml). Each experiment was repeated three times. The activity of each concentration in the inhibition of fungus growth was estimated by the mean of inhibition percentages and mean inhibition concentrations. The results showed effective inhibition of growth of the fungi especially at higher concentration of synthesized complex. (PDA) which is dissolved in 500ml of water and cooled at 50°C and purified with autoclave for (20min) at (121°C). The result show in table 4.

### Table 4: Effect a different concentration of Cu(II) complex in the inhibition of the radial growth of fungi isolated

<table>
<thead>
<tr>
<th>Fungi</th>
<th>Concentration (µg/ml)</th>
<th>Growth rate of fungi</th>
<th>Inhibitor ratio %</th>
</tr>
</thead>
<tbody>
<tr>
<td>penecillium</td>
<td>0</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8.0</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.8</td>
<td>20.8</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.7</td>
<td>58.3</td>
</tr>
<tr>
<td>A.niger</td>
<td>0</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.2</td>
<td>53.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.0</td>
<td>77.2</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.0</td>
<td>88.8</td>
</tr>
<tr>
<td>A.orizea</td>
<td>0</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.4</td>
<td>62.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.4</td>
<td>73.3</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.3</td>
<td>85.5</td>
</tr>
<tr>
<td>A.terrus</td>
<td>0</td>
<td>9.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7.1</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.0</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>5.4</td>
<td>40.2</td>
</tr>
</tbody>
</table>

The biological activity of prepared ligand showed low activity and sensitivity against all fungi and its complex showed high activity and sensitivity against all fungi.

**CONCLUSIONS**

In this present study we report the preparation characterization and spectroscopy study of new azo ligand derived from imidazole and its complex with Cu(II) metal ion. The isolated complex was characterized
by available techniques. The aryl azo imidazole ligand (PADDPI) behaves as a bidentate chelating agent and coordinating through the N₃ atom of imidazole and another nitrogen atom of azo group which is the farthest of imidazole ring to form five-memberd metalo ring. The coordination of the metal ion Cu(II) with ligand(PADDPI) are to give hexa coordinated show octahedral stereochemistry. The biological activity of prepared ligand showed low activity and sensitivity against all fungi and its complex showed high activity and sensitivity against all fungi.

REFERENCES


