Synthesis and Spectroscopic study of some transition metal complexes with 2-(4-Iodo Phenyl Azo)-4,5- Diphenyl Imidazol

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Abstract. This work deals with the preparation and identification of azo dye ,2-(4-Iodo phenyl azo)- 4,5-diphenyl imidazole (4-IPAI). The characterization of this ligand was done by elemental analysis is (C.H.N) mass spectra , Uv-vis. and IR techniques. The complexes of Co(II), Ni(II), and Cu(II) with (4-IPAI) have been prepared. The preparation were performed after fixing the optimum conditions of pH and molar concentration using Uv-Vis spectra of mixed solutions of the above ions with (4-IPAI). A wide range of pH and molar concentration in the ranges obeyed Lambert-Beers law were studies, and the stability (stability constant) were studied at optimum conditions of pH, molar concentration and mole ratio for all complex. The structure of these complexes were deduced according to the mole ratio method which were obtained from the spectroscopic studies of the complex solutions of the above ions. However ratio 1:2 metal: ligand were obtained. Uv-Vis absorption spectra of ethanol solution of the studied complexes showed bathochromic shift in the visible region compared with that of the ligand. The IR. Spectra of these complexes showed some changes in the band shape and density compared with those of the free ligands. New bands have been observed which may indicate that the coordinated with the metal ions. The elemental analysis (C.H.N) agreed with our results, the flame atomic absorption spectroscopy has also been used to determine the metal ion percentages. The percentages of metal ions were determined using flame atomic absorption spectroscopy, good agreement were obtained between the found and calculated percent values. Conductivity measurements have shown non-ionic character of complexes in ethanol and DMF solution. From all above observations the proposed geometrical structures of these complexes were octahedral [M(4-IPAI)2Cl2].

Keyword: Azo compounds ,Complexes , spectrophotometric studying, imidazole.

Introduction :

Heterocyclic azo ligands are the recent ligands relatively, that’s give many uses in the chemical analysis due to contain more from function group ,have high tendency towards many metal ions to formation chelating complexes of five- or six-member ring , which are characterized by their colors and solubility in the different solvents [1],[2].The colored solutions of this complexes have been studied extensively in the field of inorganic and analytical chemistry[3]-[4]-[5]-[6], and widely used for spectrophotometric determination of metal ions in trace concentration by UV-Vis spectra [7],[8]. Interested have been
concentrated on the heterocyclic azo ligands by different methods of the preparation by different primary materials [10], [11], [12], [13], solvents [14] and medium [16], [15]. In this work we describe the preparation and characterization of imidazole azo ligand and some of their transition metal complexes.

Materials and Methods:

All chemicals were from Fluka, and B.D.H with high purity. Melting points of ligand and it's complexes were determined on a Stuart capillary point apparatus. Electronic spectra in ethanol were recorded by (Cintra 5) GBC Scientific Equipment UV-Visible Spectrophotometer, IR spectra recorded on (Pye Unicam SP3-300) Infrared Spectrophotometer using CsI disk. Elemental analysis was carried out by Perkin-Elmer 2400 (C.H.N) Elemental analyzer. Atomic absorption were calculated using (Shimadzu-AA-160) Atomic Absorption/spectra were measured by Shimadzu – Gas Chromato-graphy Mass Spectrometer QP 1000 in the range m/z (10 to 1000) with a voltage of 70 e.v and vacuum pressure < 1 pa. Electrical conductivity and pH measurements measured by HANNA pH meter model HI 9321.

Synthesis of 4,5- diphenyl imidazole [17]:

the synthesis procedure of imidazole derivative compound was summarized as follows: (0.02) mole of benzil, (0.004) mole of Hexamethylenetetramine, (0.15) mole of ammonium acetate and 100 mL glacial acetic acid were placed in 100 mL Erlenmeyer flask, The reaction mixtures were stirred well, and reflexed for one hour and then the solution was transferred to Baker (1 liter) after cooling and diluted with 400 mL of distilled water. The imidazole derivative was adding ammonium hydroxide (0.88). The White solid product was filtered, washed several times with distilled water, and dried. Its melting point (230-229 °C).

Synthesis of azo ligand (2-(4-Iodo Phenyl azo)-4,5- diphenyl imidazole) (4-IPAI) :

The azo ligand (4-IPAI) was prepared according to the following general procedure [3]. The azo ligand was prepared by dissolving the amine ( P-iodo aniline) (0.01 mole) in mixture of 2 ml HCl Conc. and 10 ml distilled water and stirred for (15) min in ice bath then ice cold solution of NaNO₂ (10 % ) 25 ml was add drop wise on a period of (30) min, then add drop wise to another ice cooled solution of 4,5-diphenyl imidazole (0.01 mole) in 25 ml of alkaline ethanol, with continuous stirring at 0-5°C, and left over night. The mixture was natural with dilute hydrochloric acid and ammonia solution until (pH=7). The solid product was filtered, washed with cold distilled water, and dried.
Preparation of Buffer Solutions:

Buffer solutions, covering the pH values from 5 to 10, of ammonium acetate (0.01M) were prepared by dissolving (0.7708g) of CH₃COONH₄ in one liter of distilled water. The required pH was obtained by the addition of either ammonium hydroxide solution or glacial acetic acid.

Preparation of Metal Salts and ligand Solutions:

The metal salts solutions were prepared by dissolving the appropriate weight of each of the following salts CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O in distilled water, and ligand solutions were prepared by dissolving the appropriate weight of ligand in ethanol. These solutions were prepared in concentrations ranging between (1×10⁻³ - 1×10⁻²) M.

Synthesis of Metal Complexes:

The metal complexes were prepared by dissolving (2 mmol) from ligand in 25 ml ethanol and drop-wise with stirring to a stoichiometric amounts of (1:2) (metal : ligand) molar ratio of Cu(II), Co(II) and Ni(II) chloride dissolving in 20 ml hot distilled water, the pH of the reaction mixture was adjusted at optimum pH for complex. The resulting mixture solution was stirred under reflux for 2h. The solid product of the complex was flattened, washed with distilled water, recrystallized from absolute ethanol, and dried at 50 °C over night. The general reaction for the preparation of the metal complexes of azo ligand is shown below:

\[
\text{MCl}_2 + 2L \rightarrow [\text{ML}_2\text{Cl}_2]
\]

M = Co(II), Ni(II) and Cu(II)

Results and discussion:

Mass Spectrum of (4-IPAI) Ligand:

paths the first one by loose (N₂) of azo group at m/z (422) while the second bath was started by cleavage double bond of azo group, then continue with the mass fragmentation as shown in scheme (2) and fig.(1).

Mass spectra show a peak at m/z (447) represents the molecular ion peak of the free ligand 4-IPAI at Relative abundance=20% , the primary fragmentation of ligand take place in two

Scheme (2): Mass fragmentation of 4-IPAI ligand.
Study of the UV-Vis Spectra of Ligand and Complex Solutions:

Electronic spectra of ligand display mainly three absorption bands in ethanol within the range 200-800 nm. The first and second bands (244-296 nm) due to $\pi-\pi^*$ transitions of aromatic rings, this band appeared also approximately in the same potions in complexes spectra. Another band at (428) nm assigned to $n-\pi^*$ transitions [18],[19] in Vis. region which is shifted to high wave lengths in complexes spectra as a result of charge transfer transition. The data of transitions is summarized in table (1), and figures (2 - 5) represent the electronic spectra of the free ligand and Co(II), Ni(II) and Cu(II) complexes.

Figure (2): UV-Vis Spectrum of 4-IPAI Ligand.

Figure (3): UV-Vis Spectrum of [Ni(L)2Cl2] complex.

Figure (4): UV-Vis Spectrum of [Cu(L)2Cl2]

Figure (5): UV-Vis Spectrum of [Co(L)2Cl2]
**Effect of pH and Concentration:**

The UV-Vis spectra were measured for a set of mixed solutions containing equal quantities of same concentrations of metal ion and ligand. The studied molar concentration of the prepared solutions were within the range $10^{-5}$–$10^{-3}$ molar, while the pH range was between 5 to 10. The high concentrations are not all suitable in regard to the spectroscopic measurements, while the solutions sited within the $(10^{-4}-10^{-5})$ molar concentration obey Lambert-Beer's law and showed a clear intense color. A calibration curve was plotted on absorbance against molar concentration. The Fig. (6) show the linear relationship of the calibration curve of the concentrations of the mixtures of these ions with the ligand at wavelength of maximum absorption ($\lambda_{\text{max}}$) for all complex solutions. The influence of the pH of the complex solutions were also studied at pH range 5 to 10, Fig. (7) Tables (1). It is observed that the intensity of the complexes increases at optimum pH for all complex solutions. On the whole, it is appear that the complexes of Co (II) and Cu (II) ions are formed in weak base medium. While, the Ni(II) complex formed in base medium [20]-[21]-[22].

![Fig. (6): Linear Relationship Between Molar Concentration and Absorbance for 4-IPA1-Metal Ion Complex.](image1)

![Fig.(7): Effect of pH on Absorbance at ($\lambda_{\text{max}}$) for Complex Ion Solutions at Optimum Concentrations.](image2)

**Metal: ligand ratios:**

The metal : ligand ratio (M:L) of complexes were determined by the molar ratio method [23], [24] at the wavelength of maximum absorption ($\lambda_{\text{max}}$), optimum pH and concentrations. The figure (8-10) shows the relationship between absorbance and (metal : ligand ) ratio while the data were given in Table (1). The molar ratio at the sharp break indicates the composition of the complex. The results indicates the formation of ( 1:2 ) ( metal : ligand ) ratio for all complexes.
Fig. (8): Mole ratio Plot for Co(II)-Complex Solution.

Fig. (9): Mole ratio Plot for Cu(II)-Complex Solution.

Fig. (10): Mole ratio Plot for Ni(II)-Complex Solution.

Table (1): UV-Vis Spectral Data of 4-IPAI-Complex Solutions.

| Complexes  | Conc. (mol.L⁻¹) | λ_max (nm) | ε × 10⁵ (L.mol⁻¹.cm⁻¹) | Mole ratio (M:L) | Optimum pH |
|------------|----------------|------------|--------------------------|------------------|------------|
| [Co(L)₂Cl₂] | 1 × 10⁻⁴       | 504        | 2.16                     | 1:2              | 8.0        |
| [Ni(L)₂Cl₂] | 1 × 10⁻⁴       | 480        | 5.234                    | 1:2              | 9.5        |
| [Cu(L)₂Cl₂] | 1 × 10⁻⁴       | 506        | 4.642                    | 1:2              | 8.0        |

Effect of Time on Absorbance:

The figures (11-13) show the effect of time on the development and stability period of the colored complex solutions under optimum experimental conditions described before. It can be noticed that the formation of most of the colored complexes being completed at room temperature and remains stable for long time. This indicates the strong coordination and high stability of the ligand with the metal ions Co(II), Ni(II), and Cu(II).
Fig.(11): Effect of Time on Stability of Co(II) Complex.

Fig.(12): Effect of Time on Stability of Ni(II) Complex.

Fig.(13): Effect of Time on Stability of Ni(II) Complex.

(d) Determination of Stability Constant of the Metal Complexes:
Stability constants [25] are obtained by measuring the absorbance of solutions of ligand and metal ion mixture at $\lambda_{\text{max}}$ and pH values. The degree of formation of the complexes are obtained from the relation $\beta = (1-\alpha)/(4\alpha^2c^2)$ for 1:2 metal complexes, metal chelates and $\alpha=A_{\text{m}}-A_{\text{s}}/A_{\text{m}}$. Where $A_{\text{m}}$ and $A_{\text{s}}$ are the absorbance's of the fully and partially formed complex respectively at optimum condition. The calculated (log$\beta$) values for each complex are given in Table (2). The results obtained for $\beta$ and Log $\beta$ values, shown in Table 2, show that the $\beta$ values of the complexes increase from cobalt(II) to copper(II), this result is agreement with the results of the Irving-Williams series of stability [26], Co < Ni < Cu.
Table (2): Stability constant \( \beta \) values of Co(II), Ni(II) and Cu(II) complexes at optimum conditions.

| Metal Ion Complex       | \( A_i \) | \( A_m \) | \( \alpha \) | \( \beta \) \( \times 10^8 \) | Log \( \beta \) |
|-------------------------|-----------|-----------|-------------|-----------------|-------------|
| \([\text{Co(L)}_2\text{Cl}_2]\) | 0.216     | 0.305     | 0.2918      | 7.12 \( \times 10^8 \) | 8.85248    |
| \([\text{Ni(L)}_2\text{Cl}_2]\) | 0.521     | 0.715     | 0.2713      | 9.11 \( \times 10^8 \) | 8.959518   |
| \([\text{Cu(L)}_2\text{Cl}_2]\) | 0.461     | 0.603     | 0.2520      | 1.46 \( \times 10^9 \) | 9.1643528  |

Elemental analysis (C.H.N):

The complexes were identified and metal ions concentrations were calculated using the atomic absorption technique. Table (3) shows some of the physical properties of these complexes and the results of elemental analysis.

Table (3): Some physical properties and elemental analysis for 4-IPAI and its complexes.

| Metal Complex | Colour          | m.p (ºC) | % C     | % H     | % N     | % Metal |
|---------------|-----------------|----------|---------|---------|---------|---------|
| Co(C\(_2\)H\(_{15}\)N\(_4\)I\(_2\))\(_2\)Cl\(_2\) | Black brown     | 270-271  | 48.69   | 2.77    | 10.68   | 5.46    |
| Ni(C\(_2\)H\(_{15}\)N\(_4\)I\(_2\))\(_2\)Cl\(_2\) | Brown           | 277-278  | 48.75   | 3.11    | 10.66   | 6.05    |
| Cu(C\(_2\)H\(_{15}\)N\(_4\)I\(_2\))\(_2\)Cl\(_2\) | Deep brown      | 265-266  | 49.03   | 2.73    | 11.03   | 6.54    |
| C\(_2\)H\(_{15}\)N\(_4\)I* | Light orange    | 174-176  | 55.81   | 3.14    | 12.93   | ---     |

The IR spectra of the ligand and complexes:

The IR spectra of the free ligand (4-IPAI) and its complexes with Co(II), Ni(II) and Cu(II) are given in Fig.(14-17) and Table (4). The IR spectra of heterocyclic azo compounds are complicated due to extensive overlap especially within the range (200-1700) cm\(^{-1}\) arising from \( \nu(N-H) \), \( \nu(N=N) \) and the bands belong to the phenyl and imidazole rings [27],[28],[29],[30],[32].

Table (4): Characteristic IR absorption bands of the ligand (4-IPAI) and its complexes.

| Compound          | \( \nu(N-H) \) | \( \nu((C=N) + \nu(C=C)) \) | \( \nu(N=N) \) | \( \nu(C=N-N-C) \) | \( \nu(M-N) \) | \( \nu(M-Cl) \) |
|-------------------|----------------|----------------------------|----------------|-------------------|---------------|---------------|
| C\(_2\)H\(_{18}\)N\(_4\)I(L) | 3350w          | 1635                      | 1400m          | 1240vsh           | ---           | ---           |
|                   | 1610msh        | 1480                      | 1260m          |                   |               |               |
| [Co(L)\(_2\)]\(_2\)Cl\(_2\) | 3355w          | 1625m                     | 1420           | 1240              | 320           | 260 w         |
|                   | 1590vsh        | 1480m                     | 1250           |                   |               |               |
| [Ni(L)\(_2\)]\(_2\)Cl\(_2\) | 3350w          | 1630                      | 1420w          | 1215w             | 390 vs        | 290 vw        |
|                   | 1615           | 1470sh                    | 1260sh         |                   |               |               |
| [Cu(L)\(_2\)]\(_2\)Cl\(_2\) | 3350w          | 1625m                     | 1440           | 1205sh            | 360s          | 250           |
|                   | 1600w          | 1495                      | 1260           |                   |               |               |
Fig.(14): IR spectra of (4-IPA1) ligand.

Fig.(15): IR spectra of Co(II)- complex.

Fig.(16): IR spectra of Ni(II)- complex.

Fig.(17): IR spectra of Cu(II)- complex.
Conductivity measurements:

The molar conductance values of $10^{-3}$ M of complexes in methanol and DMF solvent at 25 C were found to be the range (3-6) S.mol$^{-1}$.Cm$^2$, which indicated nonionic structure of these complexes [33],[34].

Table (5): Conductivity measurements of 4-IPAI- Complexes

| No | Complexes   | $\Lambda m$ (S. mol$^{-1}$.Cm$^2$) |
|----|-------------|----------------------------------|
|    |             | In Methanol                      |
| 1  | [Co(L)$_2$Cl$_2$] | 3.616                            |
| 2  | [Ni(L)$_2$Cl$_2$] | 4.872                            |
| 3  | [Cu(L)$_2$Cl$_2$] | 5.470                            |
|    |             | In DMF                           |
| 1  | [Co(L)$_2$Cl$_2$] | 5.187                            |
| 2  | [Ni(L)$_2$Cl$_2$] | 6.162                            |
| 3  | [Cu(L)$_2$Cl$_2$] | 3.526                            |

Suggested structure:

On the basis of measurements, spectroscopic studies and molar conductivity for the ligand 4-IPAI and its complexes, we suggest that the ligand acted as a bidentate chelating ligand joint to Co(II), Ni(II) and Cu(II) metal ions through the azo nitrogen and the N atom of imidazole, and Chloride ion was presented in all complexes as coordinated ion. This will give rise to the central metal ion to displays the coordination number 6 in these complexes leading to octahedral structure (Fig.18).

Fig. (18): The proposed structural of Co(II), Ni(II) and Cu(II) with the ligand (4-IPAI).

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