Synthesis, characterization and biological evaluation of thiazolyl azo ligand complexes with some metal ions.

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Abstract

(E)-2-(benzo[d]thiazol-2-yliazenyl)-4-methoxyaniline was synthesized by reaction the diazonium salt of 2-aminobenzothiazole with 4-methoxyaniline. Identified of the ligand by spectral techniques (UV-Vis, FTIR,¹H NMR and LC-Mass) and microelemental analysis (C.H.N.S.O) are used to produce of the azo ligand. Complexes of (Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) were synthesized and identified using atomic absorption of flame, elemental analysis, infrared and UV-Vis spectral process as well conductivity and magnetic quantifications. Nature of compounds produced have been studied followed the mole ratio and continuous contrast methods, Beer's law followed during a concentration scope (1×10⁻⁴-3×10⁻⁴ mole/L), height molar absorptivity of compound solutions have been noticed. Analytical data showed that all the complexes out to 1:2 metal-ligand ratio. At the radix for physicochemical datum an octahedral structure have been described at compounds, other than the biological studies of all produced compounds was evaluation against different kinds of antimicrobial strains.

Keywords:- complexes, azo dyes, microbial studies, 2-aminobenzothiazol.

1-Introduction

Derivatives heterocyclic azo compounds have been used for dyeing industry, electrochromism, nonlinear optical elements and printing system¹. Thiazolyl azo and their derivatives are very importance uses in different fields²,³, it's have been made to determination for many metal ions⁴. Thiazole azo dyes have been used for many applications such as, biological activity, analytical reagents, clinical field and many drugs including antigrowth of germs⁵. Because of presses interesting biological activity, many studies have been done on heterocyclic azo dyes and their metal chelates⁶. Metal chelates of azo dye have been interested for uses to store molecular memory, nonlinear visual elements and printing systems⁷. Recently metal chelates containing azo dyes have attracted increasing attention into increasing electronic and structural features in connection with their application for molecular memory storage⁸. At that work, synthesis, identification and chelating of some metal
complexes containing thiazolyl azo dye as a ligand, as well biological studies of all produced compounds was evaluation against different kinds of antimicrobial strains.

2-Experimental

2-1-Instrumentation

Microelemental analysis (C.H.N.S.O) have been done in Dimashq University, Syria, employing Euro vector EA 3000, single V.3.Osingle. Conductivity for the compounds resolved at ethanol (10^{-3} \text{ mol/L}) was recorded at 25°C utilizing Philips PW- Digital Conductimeter. UV- Vis spectrum have been registered at a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. Magnetic properties have been completed through utilizing Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25°C. Atomic absorption has been recorded by employing a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. 1H-NMR spectrum have been noted at a Brucker-400 MHz Ultra Shield spectrometer on Cairo University utilizing dimethylsulfoxide like the solvent also tetramethylsaline like the reference. IR- spectrum have been taken at a Shimadzu, FTIR- 8400S Fourier Transform Infrared Spectrophotometer at the 4000- 400 cm^{-1} spectrum areas for models produced like KBr discs. Other than, melting points have been performed utilizing Stuart Melting Point Apparatus.

2-2-Materials and reagents

Following chemicals have been utilized like collected of purveyors: CoCl₂\(\text{6H₂O}\),NiCl₂\(\text{6H₂O}\),CuCl₂\(\text{2H₂O}\) and ZnCl₂ (Merck), 2-aminobenzothiazole, 4-methoxyaniline (Fluka).

2-3-Preparation of the ligand

2-aminobenzothiazole\(^{(9)}\) (0.335 gm,1mmole) melted in mixture (10ml ethanol, 2ml conc. HCl), and diazotized at 5°C with 10% solution of NaNO₂. Diazotized solution has been added collyrium wise for stirring into a cooled ethanolic solution at (0.307 gm, 1mmole) for 4-aminoaniline. Then 25 ml at (1M, NaOH) solution has been followed into dusky colored mix and precipitation for azo ligand has been noticed. This deposit have been filtrated, washed number ounces for (1:1) C₂H₅OH: H₂O, mixture subsequently left into dry. The reaction is appear at scheme 1.
2-4-Buffer solution

(0.01mol/L, 0.771 gm) for ammonium acetate was melted at one liter for doubly deionized water. For only pH scope (4-9) was the use of CH₃COOH or NH₃ solution.

2-5-Standard solution

Several standard solutions of the metal salts were made in varying concentration (10⁻⁵-10⁻³ mole/L) at pH scope (4-9). At the same time a bulk of ethanolic solutions of ligand within the extent of concentrations (10⁻⁵-10⁻³ mole/L) was also produced.

2-6-Preparation of metal chelates

EtOH solution of the ligand (0.284 gm, 2mmole) was added drop wise with stirring to the 0.118, 0.118, 0.085 and 0.064 gm of CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O and ZnCl₂ dissolved in the pH solution with the needed pH. The mixture was cooled until dark color precipitate was contained, filtered, and washed number ounces with 1:1 H₂O: C₂H₅OH mixture. The preparation technique is shown in scheme-2, other than the physical estates and (C,H,N,S,O) analysis are listed in Table 1.
Scheme 2: Suggested structure of the metal (II) complexes for azo ligand (L).
Table 1: Physical properties to the azo ligand and metal chelates.

| Compounds      | Color     | M.P°C | Yield % | Analysis Calc (Found) |
|----------------|-----------|-------|---------|-----------------------|
|                |           |       |         | M%    | C%    | H%    | N%    | O%    | S%    |
| Ligand(L)      | Deep brown| 300 > | 82      | -     | 59.15 | 4.22  | 19.71 | 5.63  | 11.26 |
| [Co(L)₂] Cl₂   | Reddish brown| 205  | 85      | 8.45  | 48.13 | 3.43  | 16.04 | 4.58  | 9.16  |
| [Ni(L)₂] Cl₂   | Yellow    | 225   | 80      | 8.32  | 48.20 | 3.44  | 16.06 | 4.59  | 9.18  |
| [Cu(L)₂] Cl₂   | Brown     | 145   | 83      | 9.10  | 47.79 | 3.41  | 15.93 | 4.55  | 9.10  |
| [Zn(L)₂] Cl₂   | Brown     | 142   | 82      | 9.23  | 47.72 | 3.40  | 15.90 | 4.54  | 9.09  |

2-7- Antimicrobial activity

The ligand and all the synthesized compounds were evaluated to examine their in vitro antibacterial activities against (*Staphylococcus aureus, Staphylococcus epidermidis* and *Pseudomonas aeruginosa*) as gram positive bacteria and (*Streptococcus sp.*, *Escherichia coli* and *Klebsiella sp.*) as gram negative bacteria and antifungal activity such as *Candida albicans* (Yeast) by employing disk diffusion method. The solvent utilized for working exam samples and level was DMSO and sample of (1- 200 μg/ml) were utilized. Antibacterial and antifungal activity of any compound were estimated by means of the well-diffusion method. 1cm³ at a 24h broth the culture including 106CFU/cm³ was placed in sterilized Petri-dishes. Molten nutritio us agar (15cm³) was kept in ca.45 °C and teeming in the Petri-dishes and pliable into stiffen. Other holes of 6mm diameter were punctured accurately employing a sterilized cork borer and these were perfectly stuffed for the exam solutions. The dishes were brood into 24h. within 37 °C.

3-Results and Discussion

Rudy for azo ligand (L) a joined of 4-methoxyaniline with the suitable diazetized in alkaline solution was performance. Synthesized ligand was identified by spectral studies (¹HNMR, FT-IR, UV-Vis and LC-Mass) and microelemental analysis.
(C.H.N.S.O). Aqueous-ethanol solutions were constantly obtained into study of the interaction of metal salts with the produced ligand.

3-1. $^1$HNMR spectra

Spectrum for azo ligand at dimethylsulfoxide (Fig. 1) display many signals at $(\delta=7.00-7.857)$ ppm assigned to aromatic protons$^{11}$. Signals obtained at $(\delta=7.908)$ ppm and $(\delta=3.426)$ ppm due to $\delta$(NH$_2$) and $\delta$(CH$_3$) for methoxy group sequences$^{12}$, the signal observed at $(\delta=2.50)$ ppm lead to DMSO-d6.

![Fig. 1: $^1$HNMR spectrum for azo ligand (L).](image)

3.2. Mass spectra

Mass spectrum for azo ligand (L) showed peak centered at $m/z = 284$ due to the formula C$_{14}$H$_{12}$N$_4$OS. The general pattern of fragmentation are summarized in Scheme- 3, see Fig. 2. Mass spectrum for Co$^{2+}$ complex displays peak centered at $m/z = 698$ due to the formulas C$_{28}$H$_{24}$N$_8$O$_2$S$_2$Cl$_2$Co. The general pattern of fragmentation are summarized in Schemes- 4, see Fig. 3.
Fig. 2: Mass spectrum for azo ligand (L).
Scheme - 3: Fragmentation pattern for azo ligand (L).

Fig. 3: Mass spectrum for [Co(L)₂] Cl₂ complex.
3-3 Calibration curve

Varied molar concentration (10^{-5}–10^{-3} \text{ M/L}) for mixed aqueous-ethanol ligand and metal ions, only reach (1-3×10^{-4} \text{ M/L}) concentration followed Beer’s law as well showed obvious intensive color. The best straight lines fit have been taken for correlation factor $R>0.9980$ like assigned at Fig. 4.

![Fig. 4: Linear relationship between molar condensation and absorption.](image)

3-4-Model conditions

For search out interaction between produced ligand and metal ions beneath education at the preparation of compounds, the spectrum from combining solutions at ligand and metal ions into attain for optimum pH and concentration, as well firm wave length ($\lambda_{\text{max}}$) were the first studies .As well as mole ratio metal to ligand (M:L) has been defined into prepare compounds. Perfect concentration was option of compound solution based on that solution gives highest absorbance in fixed ($\lambda_{\text{max}}$) with various pH, and outcomes are described at Table 3. Trial outcomes proof such the absorbance for all prepared compounds are extreme and steady at a buffer solution from $\text{NH}_4\text{OOCCH}_3$ at the pH extent (4-9). All prepared compounds were found to have a perfect pH like is shown at Fig. 5.
3-5. Metal to ligand ratio

Appoint for the complexes in solutions have been tested by mole ratio and job techniques. At both situations outcomes spread 1:2 (metal to ligand) ratio. Picked plot is shown at Fig. 6. Table 3 synopsizes outcomes gated, and specification into making compounds.
3-6- Physical estates

Interaction of the ligand melted in ethanol with the metal ions melted in perfect pH and in a (Metal:Ligand) ratio of (1:2) have been produced to solid complexes. The outcome of elemental analysis and the metal import from compounds were in real identical as well calculated values. Conductivity from ligand and metal chelates melted at ethanol (10^{-3} mole / L) display electrolytic type(13) ratio (1:2), data are recorded at Table 3.

3-7-Determination of stability constant and gibbs free energy

The constant (K) of stability to the (1:2) metal to ligand compound can be computed according to the equations.

\[
K = \frac{1 - \alpha}{4\alpha^2 C^2} \quad \alpha = \frac{A_m - A_i}{A_m}
\]

Where \( c \) = condensation to the compound solution at mole/ L \( \alpha \) = degree for dissociation, \( A_s \) = Absorption in solution containing same amount of ligand and metal ion and \( A_m \) = the absorption of solution containing the selfsame quantities for metal and surplus for ligand. High values for (K) refers to high constancy for produced complexes(14). Thermodynamic parameters of Gibbs free energy (\( \Delta G \)) were also studied. The \( \Delta G \) data have been reckoned from the equation(15).

\[
\Delta G = -RT \ln k
\]

Where; \( R \) = gas constant = 8.314 J.mol^{-1}.K, T = absolute temperature (Kelvin). Negative value of (\( \Delta G \)) due to the reaction between azo dye ligand (L) and metal ions understudy are spontaneous, see Table 2.

Table 2 : Stability constant and Gibbs free energy of the prepared complexes.

| Complexes     | \( A_s \) | \( A_m \) | \( \alpha \) | \( k \)     | Lin k | \( \Delta G \)  |
|---------------|----------|----------|-------------|------------|------|--------------|
|               |          |          |             | \( k \)    |       | kJ.mol^{-1}  |
| [Co(L)\(_2\)] Cl\(_2\) | 0.085    | 0.147    | 0.421       | 32.166\times10^6 | 17.286 | -42.827      |
| [Ni(L)\(_2\)] Cl\(_2\) | 0.098    | 0.188    | 0.478       | 19.333\times10^6 | 16.777 | -41.656      |
| [Cu(L)\(_2\)] Cl\(_2\) | 0.117    | 0.206    | 0.432       | 29.894\times10^6 | 17.213 | -42.646      |
| [Zn(L)\(_2\)] Cl\(_2\) | 0.104    | 0.162    | 0.358       | 58.363\times10^6 | 17.882 | -44.303      |

3-8- Electronic spectra
UV-Vis spectra to the produced compounds melted at ethanol (10⁻³ M/L) were gauged as well the datum formed are listed at Table 3. UV-Vis spectrum for azo ligand shows peaks in 240 and 354 nm were appointed into mild energy (π-π*) transition and peak in 412 nm due to (n-π*) transition. Co II spectrum appears three peaks at 245, 352 and 457 nm caused by intra ligand and charge transfer, peaks at 632, 730 and 868 nm described to electronic transition type 4T_{1g(F)}→ 4T_{1g(P)}, 4T_{1g(F)}→ 4A_{2g} and 4T_{1g(F)}→ 4T_{2g(F)} respectively, also the value of the magnetic moment at 4.85 B.M may be taken as additional evidence for octahedral geometry. Ni II complex exhibited three absorption peaks at 244, 355 and 457 nm which were assigned to intra ligand and charge transfer. Other peaks at 624, 688 and 724 nm were assigned to electronic transition type 3A_{2g}→ 3T_{1g(P)}, 3A_{2g}→ 3T_{1g(F)} and 3A_{2g}→ 3T_{2g(F)} respectively. Magnetic moment of this complex was found at 2.96 B.M which was very close to the octahedral environment. Cu II complex shows peaks at 245, 353 and 480 nm due to intra ligand and charge transfer, while peak at 680 nm described to electronic transition type 2E_{g}→ 2T_{2g}, the magnetic moment of this complex was found at 1.73 B.M which was very close to the octahedral environment. Zn II complex show the charge transfer, and the magnetic susceptibility shows that the complex has diamagnetic moments, because d-d transition are not possible hence electronic spectra did not give any fruitful information, in fact this result is a good agreement with previous work of octahedral geometry.

Table 3: Conditions of the produced compounds and UV-Visible, magnetic susceptibility as well as conductance mensuration's datum.

| Compounds          | Optimum pH | Optimum Molar Conc. x 10⁻⁴ | M:L Ratio | (λ_{max}) nm | ABS     | €_{max} (Lmol⁻¹cm⁻¹) | Lam(S.cm².mol⁻¹) | In ethanol | μ_{eff} (B.M) |
|--------------------|------------|-----------------------------|-----------|---------------|---------|-------------------|-----------------|------------|--------------|
| Ligand(L)          | -          | -                           | -         | 240           | 1.891   | 1891              | -               | -          | -            |
|                    |            | 354                         | 1.850     | 412           | 1.75    | 1175              |                 |            |              |
| [Co(L)₂Cl₂]       | 7          | 2.5                         | 1:2       | 548           | 1.698   | 1698              | 74.67           | 4.85       |              |
|                    |            | 352                         | 2.120     | 457           | 0.231   | 2120              |                 |            |              |
|                    |            | 630                         | 0.005     | 730           | 0.008   | 231               |                 |            |              |
|                    |            | 688                         | 0.090     | 868           |         | 5                 |                 |            |              |
|                    |            |                             |           |               |         | 8                 |                 |            |              |
| [Ni(L)₂Cl₂]       | 7          | 2.0                         | 1:2       | 244           | 1.480   | 1480              | 83.23           | 2.96       |              |
|                    |            | 355                         | 1.768     | 457           | 0.246   | 1768              |                 |            |              |
|                    |            | 624                         | 0.019     | 688           | 0.003   | 246               |                 |            |              |
|                    |            | 688                         | 0.025     | 728           |         | 19                |                 |            |              |
|                    |            |                             |           |               |         | 3                 |                 |            |              |
|                    |            |                             |           |               |         | 25                |                 |            |              |
3-9- FTIR spectra

FTIR spectra to the azo ligand and their metal chelates have been collated, and the data was scheduled in Table 4. Spectrum of the ligand exhibited bands at 3441 and 3387 cm\(^{-1}\) which were assigned to stretching vibration of \(\nu(\text{NH}_2)\), at the spectra of all produced compounds these bands has been removed to lower frequency implying the coordination with metal ion\(^{(21)}\). Strong band at 1604 cm\(^{-1}\) described to \(\nu(\text{C=N})\) of thiazole ring, at the spectra of metal chelates this band has been removed to lower frequency implying the coordination with metal ion\(^{(22)}\). Bands at 1568 and 1535 cm\(^{-1}\) attributed to \(\nu(\text{C=C})\), and the bands at (1404, 1387 and 1309) cm\(^{-1}\) lead to bending vibration of \(\delta(\text{CH}_3)\) group\(^{(23)}\). Band of the azo group at 1504 cm\(^{-1}\) displaced into lower wave number for change during shape at spectra for all produced compounds\(^{(24)}\). Stretching frequency bands to metal-nitrogen more\(^{(25,26)}\) assured by the existence to the bands at rate 432-536 cm\(^{-1}\). Pursuant to the results protected, an octahedral geometry has been offered for the produced metal chelates.

Table 4: The main frequencies to the ligand and compounds (cm\(^{-1}\)).

| Compounds    | \(\nu(\text{NH}_2)\) | \(\nu(\text{C=N})\) | \(\nu(\text{C=C})\) + \(\nu(\text{N=N})\) | \(\delta\text{CH}_3\) as,s | \(\nu(\text{M-N})\) |
|--------------|----------------------|---------------------|---------------------------------|---------------------------|---------------------|
| Ligand(L)    | 3441 sh. 3387 sh.    | 1604 sh.            | 1568 s. 1535 s. 1504 sh.        | 1404 sho. 1387 sho. 1309 s. | -                   |
| [Co(L)\(_2\)]Cl\(_2\) | 3419 sh. 3367 sh.    | 1593 sh.            | 1568 s. 1535 s. 1448 sh.        | 1404 sho. 1369 sho. 1303 s. | 511 w. 464 w.       |
| [Ni(L)\(_2\)]Cl\(_2\) | 3402 sh. 3370 sh.    | 1592 sh.            | 1571 sho. 1565 sh. 1448 sh.     | 1430 sho. 1375 sho. 1328 s. | 472 w. 432 w.       |
|              | 3431 sh. 1569 sh.    | 1535 s.             | 1404 sho.                        | 534 w.                    |                     |
As = asymmetry, s = symmetry, sh = sharp, s = strong, w = weak, sho = shoulder

3-10- Antimicrobial screening result

Azo ligand (L) and its complexes reported here were evaluated for antibacterial activity against \( \textit{Staphylococcus aureus} \), \( \textit{Staphylococcus epidermidis} \) and \( \textit{Pseudomonas Aeruginosa} \), \( (G+ev) \) and \( \textit{Steptococcus sp.}, \textit{Escherichia coli} \) and \( \textit{Klebsiella sp.} \), \( (G-ev) \) and antifungal activity such as \( \textit{Candida albicans} \) (Yeast) by employing disk diffusion method. The data of antibacterial and antifungal activities of zone inhibition were measured in millimeter of ligand and its complexes with are given in Table(5). As can be seen from the antibacterial activity and antifungal activity of ligand and metal complexes, among all these complexes the Zn$^{II}$ complex showed the higher antibacterial activity with inhibition zone of 15 mm against \( \textit{Staphylococcus epidermidis} \), \( \textit{Steptococcus sp.} \) and \( \textit{Escherichia coli} \) compared with ligand and other metal complexes. In case of Zn$^{II}$ compound the antifungal activity of \textit{Candida albicans} shows higher inhibition area of 18 mm is higher activity from ligand and rest metal complexes.

Table 5: Biological activity results of Ligand (L) and its complexes showed the inhibition circle diameter in millimeter for the bacteria after 24h.

| Compounds       | \textit{Staphylococcus aureus} \( (G+ev) \) | \textit{Staphylococcus epidermidis} \( (G+ev) \) | \textit{Pseudomonas Aeruginosa} \( (G+ev) \) | \textit{Steptococcus sp.} \( (G-ev) \) | \textit{Escherichia coli} \( (G-ev) \) | \textit{Klebsiella sp.} \( (G-ev) \) | \textit{Candida albicans} \( \text{(Yeast)} \) |
|-----------------|---------------------------------|---------------------------------|---------------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|
| Control (DMSO)  | -                               | -                               | -                               | -                          | -                          | -                          | -                           |
| Ligand(L)       | 15                              | 10                              | 10                              | 16                         | 10                         | 13                         | 10                          |
| \([\text{Co(L)}_2]\text{Cl}_2\) | 16                              | 14                              | 11                              | 13                         | 10                         | 15                         | 12                          |
| \([\text{Ni(L)}_2]\text{Cl}_2\) | 19                              | 10                              | 12                              | 10                         | 8                          | 12                         | 6                           |
| \([\text{Cu(L)}_2]\text{Cl}_2\) | 16                              | 11                              | 14                              | 16                         | 11                         | 11                         | 11                          |
| \([\text{Zn(L)}_2]\text{Cl}_2\) | 13                              | 15                              | 12                              | 15                         | 11                         | 12                         | 18                          |

4-Conclusion
In this work, the metal chelates complexes have been readied with the ligand. The willing compounds are described by melting point, atomic absorption of flame, IR and UV-visible spectral, as well conductivity quantifications. Exploration of antimicrobial activities was lifted out opposite the experimented organism. According result data an octahedral structure suggested for readied complexes.

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