Synthesis and spectral studies of heterocyclic azo dye complexes with some transition metals

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Abstract. 6-(2-benzathiazolyl azo) -3,5-dimethylphenol was formed by grouping the 2-benzothiazole diazonium chloride with 3,5-dimethylphenol. Azo ligand(L) was resolved on the origin by ¹H and ¹³C NMR, FTIR and UV-V is spectral analysis. Complexation of tridentate ligand (L) with Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ in aqueous of ethyl alcohol with a 1:2 metal:ligand, and at ideal pH. The formation of metal chelates are assigned using flame atomic absorption, FTIR and UV-Vis spectral analysis, other than conductivity and magnetic estates. The nature of the metal chelates were carried out by mole ratio and continuous variation mechanism, Beer’s law followed the rate (0.0001 - 3×0.0001 M) concentration. High molar absorptivity for the complex solutions were observed. On the origin data an octahedral geometry were described for the metal chelates. Biological activity of the ready compounds were assayed.

Keywords:- heterocyclic azo dyes, complexes, spectral studies, biological activity

1-Introduction
Azo dyes have been widely used in the textile industrial and highest versatile group of produced organic dyes [1]. Heterocyclic azo dyes have been studied highly applications in thermal, optical and medicinal estates, such as antiviral, anti-fungal and antioxidant properties [2-5]. Because of heterocyclic azo dyes colorist, this dyes have been used to evaluate of many elements. Recently, many workers developed a model mechanism for the evaluation of metal ions with heterocyclic azo dyes [6]. Most of metal chelates of azo dyes have been highly studied in the antimicrobial, anti-cancer and analytical application [7-9]. In the last years, the azo dyes and their metal chelates have been extensively used in deying industries [10]. In this work, we produced azo ligand derived from 2-benzothiazole diazoniumchloride with 3,5-dimethylphenol, the metal chelates of azo dye were prepared and identified using different spectral studies.
2-Experimental

2-1-Instrumentation
$^{13}$C,proton-NMR spectra were recorded on a Brucker-300 MHz Ultra Shield spectrometer at the Al- al- Bayt University using DMSO-d6 as solvent and trimethylsilane as a reference. Electronic spectra were taken on a Schimadzu UV- 160A UV-Vis Spectrophotometer. Fourier transform spectra were registered on a Shimadzu, Fourier transform -IR-8400S in the rate 4000- 400 cm$^{-1}$ with KBr discs. Conductivity was recorded for 0.001 M solutions of complexes, in ethylalcohol at 25°C using Philips PW-Digital Conductimeter. Magnetic properties were completed by using Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25°C. Atomic absorption was obtained from using a Shimadzu A.A-160A Atomic Absorption, Flame Emission Spectrophotometer. Other than, m.p were quantities using Stuart Melting Point device.

2-2-Reagents and Materials

Obeying chemicals were used, as collected from provider; CoCl$_2$.6H$_2$O (Fluka); NiCl$_2$.6H$_2$O, CuCl$_2$.2H$_2$O, ZnCl$_2$(Merck); 2-aminobenzothiazole and 3,5-dimethylphenol (Merck).

2-3-synthesis of 2-(benzo[d]thiazol-2-yl diazenyl)-3,5-dimethylphenol(ligand)

(1 mmole, 0.272 gm) of 2-aminobenzothiazol [11] was melted in (10ml) of ethanol formed (2 ml) conc. HCl was diluted in water 10 ml, and diazotized at 5°C and 10% NaNO$_2$ solution, then added gradually and stirring to a cooled of ethyl alcohol (1mmole, 0.345 gm) of 3,5-dimethylphenol. On other hand, (20 ml) of 1M of solution of NaOH was appended to the color dark mixture and precipitation of azo ligand was noticed. This product was filtered and washed number ounce with (1:1) ethylalcohol: water, and dry. The reaction steps were shown in scheme 1.

![Scheme 1. Preparation of 2-(benzo[d]thiazol-2-yl diazenyl)-3,5-dimethylphenol(ligand).](image-url)
2-4- Buffer Solution series
(0.771gm, 0.01M) of ammonium ethanoate was melted in 1000 milliliter of doubly distilled water for rate pH rate (4-9) was used ethanoic acid or ammonium hydroxide.

2-5- Standard Solution
Series of standard solutions of metal chloride were produced in variant concentration (10^-5-10^-3 M) at pH rate (4-9). On other hand, a series of ethyl alcholic solutions of ligand within the rate (0.00001-0.001 M) concentrations were also produced.

2-6- synthesis of Metal Complexes
(0.268 g, 2 mmole) of the ligand dissolved in ethanol was appended gradually with stirring to the 0.118, 0.118, 0.085 and 0.068 gm (1 mmole) of CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O, CuCl$_2$.2H$_2$O, ZnCl$_2$, continuously melted in the buffer solution with the required pH. The mixture reaction was cooled and kept dark color precipitate was formed, filtered, then washed number ounces with (1:1) of H$_2$O: ethylalcohol solution. The preparation technique is shown in scheme-2.

Scheme 2: The expected geometry of the metal chelates.

2-7- Biological Activity Studies
The ligands and Metal chelates were test in vitro for their three types antibacterial activity against bacteria: Staph. aureus, E-coli and Pseudomonas using the paper disc method. The produced compounds in DMSO solution were applied in vitro by paper disc method. All materials used were sterilized in a hot air oven and colony of each of the tested microorganisms were subculture and
incubated about (8 hours) before introducing into agar plates. The discs (7 mm diameter) were drenched with variant test samples (concentration 1000 ug/ml) drained and then put on the agar plate using sterilized forceps. The plates were kept in incubated under 37°C for (48 hours), finally of the incubation period; the zones of inhibition of the different bacteria were carried out [12]. The values of which are listed in Table (1).

**Table 1.** Diameters (mm) of deactivation of bacteria for ready compounds.

| Compounds     | Staphylococcus aureus | E-coli | Pseudomonas |
|---------------|-----------------------|--------|-------------|
| Ligand(L)     | 10                    | 20     | 18          |
| [Co(L)₂]      | 14                    | 18     | 17          |
| [Ni(L)₂]      | 17                    | 21     | 20          |
| [Cu(L)₂]      | 15                    | 18     | 18          |
| [Zn(L)₂]      | 15                    | 20     | 20          |

3-Results and discussion
The readying of the ligand (HL) a linkup compound 4-nitroaniline with the diazotized derivative in basic medium was carried out. Performed ligand was verified by ¹H and ¹³CNMR, Fourier transform infrared and Ultraviolet-Vis spectral.

3-1-NMR Spectrum
The ¹H NMR spectrum of the 2(2-benzothiazolyl azo)-3,5-dimethylphenol (L) in dimethylsulfoxide (Figure 1) show resonance at δ=7.283-8.937 ppm described to phenyl protons [13]. Peak at δ=6.278 ppm assigned to proton of phenol [14]. The resonance at δ=2.598 ppm is assigned to proton of (methyl) groups and the gesture at δ=2.50 assigned to dimethylsulfoxide-d₆ [15]. The ¹³CNMR spectrum of ligand (Figure 2) appeared signals at δ=162.549 and δ=158.537 ppm described to (C-OH) and carbon of thiazole group. The various symbol at (δ=139.829, 133.393, 126.848, 126.586, 123.808, 122.732 and 116.943 ppm lead to carbon atoms of aromatic rings. The signals at δ=34.283 and 21.231 ppm attributed to δ(CH₃) groups of phenol. The gesture at δ=39.225 ppm due to DMSO-d₆ [16].
**Figure 1.** $^1$HNMR spectrum of the ligand.

**Figure 2.** $^{13}$CNMR spectrum of the ligand.
3-2-Physical properties
Metal chelates have been readied by immediate reaction of ethanolic and ligand (L) solution with the aqueous solution of the metal ions at the perfection pH and in a M:L proportion of (1:2). The product of metal content of these complexes were in a good agreements with the calculated values, data recorded in Table 2. The molar conductance of (0.001 M) in ethylalcoholic solutions for these complexes lead to non-electrolytic type [17] data are formed in Table 2. Magnetic estates Table 2 of the produced metal chelates have been happened to a paramagnetic that was accounted for octahedral geometry [18].

Table 2. Physical properties of ligand and metal chelates.

| Products       | Color           | Melting points °C | Percentage products % | M% Calculate (found) | $\Lambda_m$(S.cm$^2$.mol$^{-1}$) in ethanol | $\mu_{eff}$ (B.M) |
|----------------|-----------------|-------------------|-----------------------|----------------------|---------------------------------------------|------------------|
| Ligand(L)      | Reddish orange  | 175               | 75                    | -                    | -                                           | -                |
| [Co(L)$_2$]    | Brown           | 194               | 70                    | 9.91 (8.88)          | 7.54                                        | 4.53             |
| [Ni(L)$_2$]    | Reddish brown   | 220               | 77                    | 9.76 (9.31)          | 11.73                                       | 3.07             |
| [Cu(L)$_2$]    | Deep brown      | 230               | 75                    | 10.66 (9.78)         | 3.42                                        | 1.77             |
| [Zn(L)$_2$]    | Orange          | 210               | 70                    | 10.81 (9.77)         | 14.32                                       | Di               |

3-3-Calibration Curve
Variant molar concentration (0.00001–0.001) M of mixed aqueous-ethanol of ligand and metal ions, only the rate (1-3×10$^{-4}$M) concentration followed Beer’s law and produced obvious intense color. Best excellent straight lines were happened together with correlation factor R>0.9980 as showed below (Figure 3).
3.4 Perfect Conditions

To work out coordination between the ready metal ions and ligand under searching for the synthesis of the metal chelates, the spectra of combining solutions for the metal ions and ligand to attain to perfect pH and concentration, as well as firm ($\lambda_{\text{max}}$) were studied first. Then mole ratio metal to ligand (M:L) was defined to prepare the metal chelates. Perfect concentration was selection for complex solution based on which solution gives the highest absorbance at constant ($\lambda_{\text{max}}$) at variant pH, and results are assigned in Table-3. The probation results proof that the absorbance of all produced complexes are high and constant in a buffer solution of ammonium ethanoate in the pH extent (4-9). It was found that ready metal chelates had perfect pH as is showed below in Figure (4).
3.5-Ratio of Complexes
Mole ratio and job mechanisms are used to appoint the complexes in solutions. In both procedures the products disclose a (metal:ligand)1:2 ratio. A picked plot is shown in Figure (5). Table 3 outlines the results contained, other than specification for the making complexes.

![Figure 5](image)

**Figure 5.** Mole ratio and Job mechanisms for complexes solutions.

3.6-Electronic spectra
Ultraviolet-Vis spectra of the ready azo ligand and their metal chelates mixed in ethanol (0.001 M) were studied and the dataset included in Table 3. The spectrum of the ligand (L) (Figure 6) display peaks at 262 and 408 nm described to (\(\pi-\pi^*\)) electronic transition [19]. The spectrum of Co\(^{3+}\) complex shows peaks at 270 and 416 nm related to ligand field, other peak at 893 nm lead to electronic transition [20] \(^4T_{1g(F)} \rightarrow ^4T_{2g(F)}\) The spectrum of Ni\(^{2+}\) complex refers peaks at 268 and 418 nm due to ligand field, than peaks at 892 and 980 nm were assigned to electronic transition [21] \(^3A_{2g(F)} \rightarrow ^3T_{1g(F)}\) and \(^3A_{2g(F)} \rightarrow ^3T_{2g(F)}\). The Cu\(^{2+}\)complex (Figure 7) display peaks at 268 and 420 nm lead to ligand, the peak at 892 nm described to electronic transition [22] \(^2E_g \rightarrow ^2T_{2g}\). The electronic spectrum of Zn\(^{2+}\)complex do show the charge transfer, because d-d transition is not possible hence electronic spectrum did not give any fruitful information [23].
Table 3. Conditions for the produced metal chelates and UV-Vis data.

| Products | Perfect pH | Perfect Molar Concentration. \( \times 0.0001 \) | M:L Ratio | \( \lambda_{\text{max}} \) nm | ABS | \( C_{\text{max}} \) |
|----------|------------|-----------------------------------------------|-----------|----------------------|-----|----------------|
| Ligand(L) | -          | -                                             | -         | 262                  | 0.510 | 510  |
|          |            |                                               |           | 408                  | 1.267 | 1267 |
| [Co(L)\(_2\)] | 7          | 2                                             | 1:2       | 270                  | 0.433 | 433  |
|          |            |                                               |           | 416                  | 1.189 | 1189 |
|          |            |                                               |           | 893                  | 0.022 | 22   |
| [Ni(L)\(_2\)] | 7          | 2                                             | 1:2       | 268                  | 0.358 | 358  |
|          |            |                                               |           | 418                  | 1.249 | 1249 |
|          |            |                                               |           | 892                  | 0.004 | 4    |
|          |            |                                               |           | 980                  | 0.023 | 23   |
| [Cu(L)\(_2\)] | 7          | 2                                             | 1:2       | 268                  | 0.3151 | 315  |
|          |            |                                               |           | 420                  | .218  | 1218 |
|          |            |                                               |           | 892                  | 0.023 | 23   |
| [Zn(L)\(_2\)] | 7          | 2.5                                           | 1:2       | 266                  | 0.322 | 322  |
|          |            |                                               |           | 423                  | 1.124 | 1124 |

Figure 6. spectrum UV-Vis of the ligand (L).
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**Figure 7.** spectrum UV-Vis of the \([\text{Cu}(\text{L})_2]\) complex.

3.7-**Fourier transforms infrared spectra**

FTIR spectra of ready compounds have been formed, data was scheduled in Table (4). Broad band in FTIR spectrum of the ligand (Figure 8) at 3396 cm\(^{-1}\) due to \(\nu(\text{OH})\) phenol, in the metal chelates spectra, disappearance of this band (Figure 9) indicated to coordinate with metal ion [24]. The spectrum show band at 1608 cm\(^{-1}\) ascribed to \(\nu(\text{C} = \text{N})\), on chelates a shifted to higher frequency may be lead to coordinate with metal ion [25]. Band at 1461 cm\(^{-1}\) due to azo bridge, this band shifted to higher frequency may be result to coordinate with metal ion [26]. The bands at (1454, 1435, 1377, 1311 and 1570 cm\(^{-1}\)) due to bending frequency of (\(\delta(\text{CH}_3)\)) and vibration of \(\nu(\text{C} = \text{C})\) [27]. Bands for metal-nitrogen and metal-oxygen [28-29] at the rate (442-572) cm\(^{-1}\). Other than, results protected an octahedral geometry has been offered for the metal chelates.
### Table 4. The main frequencies of the ready compounds (cm\(^{-1}\)).

| Compounds | \( )\text{OH}\nu(\ ) | \( \nu(\text{C}=\text{N}) \) + \( \nu(\text{C}=\text{C}) \) | \( \nu (\text{N}=\text{N}) \) | \( \text{CH}3\text{as,}\delta \) | \( )\text{M-N( }\nu + \text{M-O)(}\nu \) |
|------------|----------------------|---------------------|---------------------|----------------|-------------------------------|
| Ligand(L)  | 3396 br.             | 1608 sh. 1570 sh.   | 1461 sh.            | 1454 sh. 1435 sho. 1377 sh. 1311 sh. | - |
| \([\text{Co(L)}2]\) | -                   | 1630 sh. 1570 sh.   | 1477 s.             | 1453 sh. 1432 sho. 1375 sh. 1310 sh. | 530 w. 471 w. |
| \([\text{Ni(L)}2]\) | -                   | 1635 sh. 1571sh.    | 1477 s.             | 1450 sho. 1430 sho. 1370 s. 1311 sh. | 572 w. 442 w. |
| \([\text{Cu(L)}2 ]\) | -                   | 1633 sh. 1570 s.    | 1473 sh.            | 1455 sh. 1431 sh. 1370 sh. 1310 sh. | 570 w. 472 w. |
| \([\text{Zn(L)}2 ]\) | -                   | 1637 sh. 1570 sh.   | 1473 s.             | 1454 sh. 1435 sho. 1377 sh. 1311 sh. | 516 w. 493 w. |

br = broad, sh = sharp, s = strong, w = weak, sho = shoulder
Figure 8. FT-IR spectrum of the ligand (L).

Figure 9. FTIR spectrum of the [Zn(L)₂] complex.
4-Conclusion
In this paper, metal chelates have been produced with the azo ligand (L). The willing compounds are described by melting point, flame atomic absorption, FT-IR and UV-Vis spectral, other than, conductivity and magnetic moment mechanisms. Exploration of antimicrobial activities was lifted out opposite the experimented organism. Other than, analytical data an octahedral structure offered for metal chelates.

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