Synthesis, Spectral Identification and Biological Activity of Chelate Complexes Derived from New Azo Naphthresorcenol.

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Abstract. A new azo compound is prepared by coupling the diazonium salts of (2- Cyananiline) with 1,3-dihydroxynaphthalene to form (E)-2-(2,4-dihydroxynaphthalen-1-yl)diazencylbenezonitrile. The azo ligand was identified by Mass, ¹H-NMR, C¹³NMR, UV-Vis, and IR spectra, in addition to elemental analysis measurement. The chelate complexes were characterized by elemental analysis, magnetic susceptibility, Molar conductance, UV-Vis, and IR spectra. The geometry of metal complexes were proposed based on analytical and spectral data. Analytical data revealed that all the complexes exhibited 1:2 metal–ligand ratio. On the basis of magnetic susceptibility measurements, suitable geometry was proposed for each complex. IR spectra of complexes show that the ligand is coordinated to the metal ions in bidentate manner with Oxygen and Nitrogen donor sites of hydroxynaphthalene (OH) and azo Nitrogen, which suggest octahedral geometry for all complexes. Also, biological evaluation of all synthesized compound shows moderate to good activity against Candida albicans, as antifungal.

Keywords: Azo ligand; Metal Complexes; Dihydroxynaphthalene; NMR; Antifungal Activity.

1.Introduction

Azo compounds are considered to be one of the most common compounds used as ligands, and have attracted much attention in both academic and applied researches. The N=N group is called an azo group and the name of azo comes from azote, the French name for nitrogen that is derived from the Greek a (not) + zoe (to live) such as dyeing textile fiber, biomedical studies, advance application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical devices and ink-jet printers[1-3]. A large number of (N,N')- donor ligands in azo imine family have been prepared in the last few years[4,4]. Many azo-compounds have been applied as chromogenic reagents for the determination of several metal ions[7,8]. The use of such reagents was found to depend essentially on their UV–vis spectral properties. Many articles have been published concerning the spectral characteristics of azo compounds[9,10], which dealt with spectral-structure correlations as well.
as the effects of the medium on the band position. However, it seems that no studies were carried out concerning azo-compounds based on dihydroxynaphthalenes.

The coordination complexes of transition metals with azo-ligands are of current attraction due to the interesting physical, chemical, photophysical and photochemical, and their properties. The p-acidity and metal binding ability of azo nitrogen have drawn attention to the exploration of the chemistry of metal complexes incorporating azo-ligands [11-13]. Coordination chemistry of transition metal complexes with azo ligands are an important and fascinating branch of chemistry, and plays a pivotal role in industry, technology and life processes [14,15,16]. In this work, we synthesized new azo-dyes by bringing together two important chemical compounds, 1,3-dihydroxynaphthalene, 3-aminopyridine. The chemical structures of both azo dyes and azo metal complexes have been studied in detail.

2. Experimental

2.1. Materials: All chemicals used in the preparation of azo ligand and metal complexes A. R. products from BDH and Merck.

2.2 Measurement: Melting points is determined by open capillary tube method and are uncorrected by using Stuart melting point model 9300. Elemental analyses (C, H, N) were carried out using a C.H.N.S EA-3000. mth instrument. The metal contents of the complexes was measured using atomic absorption technique by Shimadzu AA-6300. IR spectra were recorded on a Shimadzu 8400S FTIR spectrophotometer in the (4000-400) cm\(^{-1}\) range using KBr discs. Electronic spectra were obtained on a Shimadzu 1700 UV spectrophotometer using ethanol as solvent in the (1100-200) nm range. Magnetic susceptibilities are determined by faraday method at room temperature using Balance Model Sherwood Scientific, at Chemistry Department, College of Science, University of Al – Mustansiriyah, apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constant. And Mass Spectra were recorded on AB Sciem 3200 QTRAP LC/MS/MS, (Mass range - m/z 5-2000-quad mode and 50-1700- linear ion trap mode). Molar conductance of the transition metal complexes were determined in (DMF) using Digital conductivity Series Ino. Lab- 720 at 25°C, the concentration of the solutions was (10\(^{-3}\) mol L\(^{-1}\)).

2.3. Synthesis of azo ligand:

(CANR = HL\(_2\)) azo ligand is prepared according to the following general procedure\(^{[17]}\) Figure (1), 2- Cyano aniline (1.18g, 10 mmol) was dissolved in 30 ml of water and 6 ml of concentrated hydrochloric acid. The filtered solution was diazotized at (5 °C) 12 ml of aqueous (1.0 M) sodium nitrite. The resulting diazonium chloride solution was added drop wise with stirring to the the 1,3-dihydroxynaphthalene (1.60g, 10 mmol) dissolved in 200 ml alkaline ethanol cooled below 0°C. After leaving in the refrigerator for 24 hours. The deep red color mixture was acidified with a dilute a hydrochloric acid until (pH = 8). The precipitate was filtered off, and recrystallized twice from hot ethanol, and dried in oven at (70 °C) for several hours, to obtain L\(_2\) ligand, yield 75% and m.p 215-217°C;yield (75%).
2.4. Synthesis of metal complexes:

The complexes are prepared by adding an appropriate amount of the metal salt (1 mmol), namely Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) hydrated metal chloride and anhydrous Zn(II), Cd(II) and Hg(II) chloride, dissolved in a least amount of distilled water to (0.289 g, 2 mmol) of ligand (CANR) dissolved in 50 cm$^3$ of ethanol. The reaction mixture refluxed for 30 min with stirring. The precipitated solid complexes were filtered, washed with 3 mL of hot 50 vol. % ethanol to remove any traces of unreacted starting materials. Finally, the complexes were washed with 2 mL, diethyl ether, and dried over anhydrous CaCl$_2$.

2.5. Anti- Fungal Activity by Agar- diffusion method

The in vitro antifungal activity of azo ligand (CANR) and its metal complexes were tested against the fungi Candida albicans. Stock solutions were prepared by dissolving ligand and its metal complexes in DMSO solvent at (10, 20 and 50 ppm). The nutrient agar medium was poured into petridish. One ml of the tested microorganism was spread over the solid nutrient agar plates with help of a spreader. An amount of 0.1 ml of test solutions was added carefully in spots on the surface of the inoculated solid media. After evaporating the solvent, the petri dishes were placed at low temperature for two hours to allow the diffusion of the chemical materials and then incubated at 37°C for 48 hours. The diameter of the inhibition Zones measured in millimeters$^{17-20}$.

3. Results and discussion

Azo ligand was orange semi-crystal, but the chelates complexes of this ligand vary in color depending on metal ion. The metal complexes were characterized by elemental analysis, molar conductivities, IR, UV-Vis and $^1$HMNR spectra. The magnetic susceptibility of the chelate complexes at room temperature were consistent with octahedral geometry. The experimental results of the elemental analyses of the prepared ligand and its metal chelates are in good agreement with theoretical expectations. The elemental analyses of the complexes indicate that the metal-ligand ratios were 1:2 in the [M(CANR)$_2$(H$_2$O)$_2$], [M = Mn (II), Fe (II), Co (II), Ni (II), Cu (II) Zn (II), Cd (II), or Hg (II)], metal complexes. The ligand and its complexes were quiet air stable, insoluble in water but soluble in common organic solvents such as methanol, ethanol, acetone, chloroform, and pyridine giving stable solutions at room temperature. complexes prepared in this work showed lower conductivity values of the complexes. This proves that complexes have non- electrolytic nature.
3.1. Micro analysis:

The elemental analysis data of 1:2 [M:L] ratio complexes showed that the theoretical values are in a good agreement with the found data, as listed in Table 1. The purity of azo ligand were tested by TLC technique and C, H, N elemental analysis, some physical and analytical data are given in Table 1.

Table 1: Physical properties and elemental analysis of azo ligand and their metal complexes.

| Compound          | General formula | M. wt. g.mol<sup>−1</sup> | m.p. C° | Color      | Element analysis (%) | Found (calc.) |
|-------------------|----------------|--------------------------|--------|-----------|----------------------|---------------|
|                   |                |                          |        |           | C        | H        | N        | M        |
| HL<sub>2</sub>=(CANR) | C<sub>17</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> | 289                      | 215-217 | Brown     | 70.45    | 3.59     | 14.46    |          |
| [Mn(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | MnC<sub>3</sub>H<sub>24</sub>N<sub>6</sub>O<sub>6</sub> | 666.93                  | 258    | Orange    | 61.05    | 3.47     | 12.38    | 8.15     |
| [Fe(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | FeC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub> | 667.84                  | 208    | Dark-yellow | 61.11   | 3.46     | 12.48    | 8.19     |
| [Co(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | CoC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub> | 670.93                  | 225    | Reddish-brown | 60.60  | 3.35     | 12.29    | 8.65     |
| [Ni(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | NiC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub> | 670.98                  | 263    | Pale-brown | 60.51   | 3.75     | 12.36    | 8.68     |
| [Cu(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | CuC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub> | 675.55                  | 278    | Yellow    | 60.01   | 3.47     | 11.68    | 8.74     |
| [Zn(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | ZnC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub> | 677.38                  | 290    | Yellowish-brown | 60.15  | 3.47     | 11.68    | 9.17     |
| [Cd(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | CdC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub> | 724.41                  | 289    | Pale-yellow | 56.27   | 3.16     | 13.68    | 15.38    |
| [Hg(HL<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>] | HgC<sub>3</sub>H<sub>26</sub>N<sub>6</sub>O<sub>6</sub> | 812.59                  | 310    | Dark-brown | 50.06   | 2.88     | 10.15    |          |

Ligand=HL<sub>2</sub>=(CANR)

3.2. Infrared [IR] spectra of azo dyes:

The IR spectra provided valuable information regarding the nature of functional group attached to the metal atom. There are similarities in IR spectra of the ligands and their corresponding metal complexes to each other, except for some slight variations in the shifts and intensities caused by different metal (II) ions. There is an absorption weak band at 3063 cm<sup>−1</sup> that is assigned to υ(C-H) vibrations mode of aromatic rings[21,22]. A medium or weak band in (2847-2972) cm<sup>−1</sup> is assigned to the aliphatic υCH vibrations. A weak band in range (2218-2212) cm<sup>−1</sup> is related to cyano group[23]. The absorption band at 1502 cm<sup>−1</sup> is related to the symmetric υN=N stretching[24,25]. Also the υ(N=N) vibration exhibits a band at 1506 cm<sup>−1</sup> in the free ligand spectrum, sometimes is shifted to lower frequencies and is appeared as a multiple band in some complexes spectra with differences in their shape and intensity. This shift and change may be due to the involvement of (N) atom of azo group and the delocalization of electron density between metal ion and ligand.[26,27] Finally, the IR spectra of complexes exhibited new bands in the range of (599 – 534) cm<sup>−1</sup>, (499 – 441) cm<sup>−1</sup> and (700-900) cm<sup>−1</sup> assigned as υ(M—O), υ(M—N) and υ(M—OH<sub>2</sub>) stretching vibrations, respectively, as shown in Figure 2.3. Therefore, it can be concluded that (CANR) ligand binds to the metal ions through phenolic oxygen and nitrogen of azo group and the ligand behaves as a mono negative bidentate ligand[28]. The Characteristic vibrations and assignments of the complexes are shown in Table 2. The FT-IR spectra of the ligands and other complexes show bands in the range (3500-3300) cm<sup>−1</sup> corresponding to υ(OH) of H<sub>2</sub>O[28].
Table 2: Characteristic IR absorption bands of the ligand and its complexes in cm⁻¹ units.

| Compounds          | ν(O-H)phe + ν(O-H) H₂O | ν(O-H) | v (C-H)₅⁺ | v (C≡N) | v (N=N) | v (M-N) | v (M-O) |
|--------------------|------------------------|--------|------------|----------|---------|---------|---------|
| L₂(CANR)          | 3421 wbr               | 3421 m | 3063 w     | 2874 w   | 2221 s  | 1506 s  | ---     |
| [Mn(L₂)₂(H₂O)₂]   | 3421 wbr               | 3421 m | 3040 w     | 2850 w   | 2218 w  | 1456 m  | 445 w   | 561 w   |
| [Fe(L₂)₂(H₂O)₂]   | 3381 wbr               | 3381 m | 3070 w     | 2847 w   | 2220 w  | 1490 s  | 462 w   | 534 w   |
| [Co(L₂)₂(H₂O)₂]   | 3421 wbr               | 3421 m | 3007 w     | 2873 w   | 2220 w  | 1496 s  | 482 w   | 569 w   |
| [Ni(L₂)₂(H₂O)₂]   | 3419 wbr               | 3419 m | 3004 w     | 2920 w   | 2222 m  | 1492 s  | 484 w   | 587 w   |
| [Cu(L₂)₂(H₂O)₂]   | 3394 wbr               | 3394 m | 3005 w     | 2922 w   | 2220 w  | 1454 s  | 441 w   | 547 w   |
| [Zn(L₂)₂(H₂O)₂]   | 3421 wbr               | 3421 m | 3009 w     | 2924 w   | 2222 m  | 1490 m  | 443 w   | 587 w   |
| [Cd(L₂)₂(H₂O)₂]   | 3423 wbr               | 3423 m | 3173 w     | 2935 w   | 2220 w  | 1487 s  | 484 w   | 599 w   |
| [Hg(L₂)₂(H₂O)₂]   | 3444 wbr               | 3444 m | 3068 w     | 2972 w   | 2220 w  | 1492 s  | 499 w   | 589 w   |

Figure 2: IR spectrum of: (a) the azo ligand & (b) Co (II) complex.
3.3. Mass spectrum of azo ligand (CANR):

The mass spectra of synthesized azo ligand was recorded at room temperature. This spectrum confirms the proposed formula by showing a molecular ion peak (m/z) at 289 (M⁺) with a relative intensity 100% corresponding to the ligand molecule [C₁₇H₁₁N₃O₂] and the main mass fragment of organic ligand is given in Figure (3). It shows assigned to various fragments.

**Figure 3:** Mass spectrum of azo ligand

**Scheme 1:** Proposed fragmentation pathways of L₂(CANR)
3.4. $^1$H-NMR spectrum of azo dye:

The $^1$H-NMR spectrum of azo-compound L(CANR) under study display a group of signals corresponding to the protons of each molecule, the spectrum of this compound is produced using d6-DMSO as solvent and (TMS) as reference. The phenyl multiples at (8.38-6.06)ppm were assigned to the aromatic protons. In general, the compounds exhibit the following characteristics chemical shifts as shown in Table 3. As previously reported, the compounds shown in Figure(4) are present in solution as a proton transfer equilibrium. In all cases, their $^1$H-NMR spectrum showed a signal with a chemical shift in the range of (17-11) ppm, corresponding to the O–H· · · N proton involved in the relevant intramolecular hydrogen bond. The signal at higher field within at (12.34) ppm for azo-compound is due to the free OH group. In 1H-NMR spectra of ligand, it is seen that the signal of OH group (2-H) which do hydrogen bond is broader than the signal of free OH group. \[30-32\]

![Figure 4: $^1$H-NMR spectrum of azo ligand](image)

3.5. $^{13}$C NMR spectrum of azo dye:

The $^{13}$C NMR spectrum of azo ligand was measured at room temperature in D6-DMSO. A spectrum of the ligand is shown in Figure 5. The $^{13}$C NMR spectrum of the ligand displayed characteristic as show in table 3.

| Assignment | Chemical shifts δ(ppm) |
|------------|------------------------|
| C$_5$-O, C$_4$-O, | 180.81, 164.51, |
| C$_{11}$-NH, C$_{12}$-CN, | 145.94, 98.88, |
| C$_5$-C-O, C$_{16}$=C, C$_{17}$≡N, | 104.70, 115.88, |
| C$_{14}$≡C, | 116.82, 122.95, 135.30, 133.81, 133.45, 131.03, |
| C$_{15}$, C$_{13}$, C$_{10}$, C$_5$, C$_7$, C$_1$, | 127.91, 127.28, 125.43, 124.51, 124.14 |
3.6. Electronic Spectra:

Electronic spectra provide the most detailed information about the electronic structure. The UV-Vis spectrum of azo ligand (HL) exhibits two charge transfer (CT) bands at (246 nm) and (419 nm) attributed to $\pi-\pi^*$ and n- $\pi^*$ transition within the azo ligand. UV-Vis spectra of complexes showed broad absorption bands in the ultraviolet region, which are related to (Charge Transfer) bands. Behind these, many other packages disappear and the apparent bands and their electronic transitions will be limited. The band observed at (426 nm) in the spectrum of the free ligand (HL) is red-shifted to (458-493 nm) in complexes due to ligand to metal charge transfer (LMCT) transition\cite{34,35}, suggesting an octahedral geometry around metal (II) ion in complexes. The electronic spectra of the ligand and Co (II) complex are shown in Figure 6,7. Magnetic properties and conductivity values of the ligand and its complexes are listed in table 3.

Figure 5: $^{13}$C NMR spectrum of azo ligand

Figure 6: Electronic spectrum of Ligand.

Figure 7: Electronic spectrum of Co(II) complex.
3.7. Magnetic measurements:

The high spin magnetic moment value of Mn (II) complex has been found 5.79 B.M. The Fe(III) complex showed magnetic value at 4.92 B.M. which are consistent with an octahedral geometry [31]. The Co (II) complex has a magnetic moment of 3.98 B.M. in the high spin state, which is in agreement with the reported value for octahedral Co(II) complexes[32]. The present Ni(II) complex shows a magnetic moment value of 3.12 B.M. a high-spin Ni(II) complex depended on the magnitude of the orbital contribution [33] suggesting an octahedral environment. The Cu(II) complex shows a magnetic moment value of 1.72 B.M., monomeric and consistent with a distorted octahedral geometry. The Zn(II), Cd(II), Hg(II) are diamagnetic and according to the empirical formulae of complexes, an octahedral geometry is proposed[36-39]. Based on the above results, we can deduce the probable structures of the complexes as in Figure 8.

Table 4: Electronic spectra, conductivity and magnetic moment of complexes

| Compound       | Absorption Bonds(nm) | Transition | µeff(B.M) | Conductivity S.mol⁻¹.cm² | Geometry       | Hybridization |
|----------------|----------------------|------------|-----------|--------------------------|----------------|---------------|
| PANR           | π→π*                 |            |           |                          |                |               |
| [Mn(CANR)₂(H₂O)₂] | 481 M→L,CT       | 5.79       | 12.05     | Octahedral               | sp³d⁵          |               |
| [Fe(CANR)₂(H₂O)₂] | 487 M→L,CT       | 4.92       | 20.31     | Octahedral               | sp³d⁵          |               |
| [Co(CANR)₂(H₂O)₂] | 464 M→L,CT       | 3.98       | 7.16      | Octahedral Distorted     | sp³d⁵          |               |
| [Ni(CANR)₂(H₂O)₂] | 463 M→L,CT       | 3.12       | 4.76      | Octahedral (regular)     | sp³d⁵          |               |
| [Cu(CANR)₂(H₂O)₂] | 473 M→L,CT       | 1.72       | 13.52     | Octahedral Distorted     | sp³d⁵          |               |
| [Zn(CANR)₂(H₂O)₂] | 459 M→L,CT       | 9.22       | 11.35     | Octahedral (regular)     | sp³d⁵          |               |
| [Cd(CANR)₂(H₂O)₂] | 458 M→L,CT       | 11.35      | 15.21     | Octahedral (regular)     | sp³d⁵          |               |
| [Hg(CANR)₂(H₂O)₂] | 493 M→L,CT       | 11.35      | 15.21     | Octahedral (regular)     | sp³d⁵          |               |

3.8. Molar Conductivity measurement:

Molar conductance of the metal complexes was measured in DMSO as a solvent at room temperature. All chelate complexes prepared in this work showed conductivity values ranged between (4.76-15.21) S.mol⁻¹.cm² that non-electrolyte and no conductive species [40]. According to these results the structural formulas of this ligand and chelate complexes may be proposed in Figure (8).

![Figure 8](image.png)

Figure 8. The proposed structural formula of the complexes
3.9. Antifungal Activity:

Some azo compounds are screened against fungus *C. albicans*.

**Table 5**: Inhibition zone (mm) for Antifungal Activity of L (CANR) and complexes ion.

| Comp.       | Conc.10 | Conc.20 | Conc.5 |
|-------------|---------|---------|--------|
| L (CANR)    | 0       | 10      | 15     |
| [Cd(L)₂]    | 0       | 10      | 18     |
| [Zn(L)₂]    | 0       | 13      | 20     |
| [Mn(L)₂]    | 12      | 13      | 21     |
| [Co(L)₂]    | 12      | 15      | 21     |
| [Fe(L)₂]    | 0       | 12      | 22     |
| [Ni(L)₂]    | 15      | 17      | 23     |
| [Cu(L)₂]    | 10      | 17      | 23     |
| [Hg(L)₂]    | 0       | 17      | 29*    |
| DMSO        | 0       | 0       | 0      |

*Figure 9.* Antifungal Activity of L (CANR) and complexes.

Some images for the petri dishes of the effect of the L₂ and its complexes are supplied in Appendix II. From the data listed in the table, it is noted that ligand and complexes have various antifungal activities against the fungal *C. albicans*, but [Cd(L)₂], [Zn(L)₂] and [Hg(L)₂] have no activity against of fungi at 10 ppm, but [Hg(L)₂] has the highest activity against of fungi, as shown Figure 9.

Electron transfer is another possible mode of action. A wide variety of synthesized drug molecules have electron transfer capabilities which allow them to generate reactive oxygen species (ROS). In particular, many antibiotics that kill or inhibit bacteria, yeasts and cancer cells readily transfer electrons to oxygen making superoxide and hydrogen peroxide in the process. When suitable, redox active forms of copper are available to generate the highly damaging hydroxyl radical. This type of chemistry is very similar to that which evolved within phagocytic cells as part of their microbial killing [41,42]. Redox processes could be involved in the observed biological activity, especially for the copper complexes. In the present study, the observed cyclic voltammetry and behavior, the redox properties of copper ion may also contribute to their inherent toxicity. Our synthesized complexes can catalyze the production of highly reactive hydroxyl radicals, which can subsequently damage lipids, proteins, DNA and other biomolecules [43].
3.10. Conclusions:

In this paper we have explored the synthesis and coordination chemistry of some monomeric complexes obtained from the reaction of the bidentate azo ligand $L$(CANR) with some metal ions as shown in Figureure [8 ]. According to above results, a significant biological activity against Candida albicans was observed for the synthesized metal complexes compared to free ligand. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. All the complexes exhibited octahedral geometry around the metal center. The complexes were stable and not ionic.

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