

Synthesis, characterization of new chelate complexes derived from Azo naphthresorcenol ligand

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Abstract

Background: Azo compounds are the oldest and largest class of industrially synthesized organic dyes due to their versatile application in various fields and have attracted much attention in both academic and applied researches. The latter included 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. Therefore, current study was conducted to synthesize new azo-dyes and to study their chemical structures in details. **Methods:** A new azo compounds is prepared by coupling the diazonium salts of (3-amino pyridine) with 1,3- dihydroxynaphthalene to form (E)-4-(pyridin-3-ylidiazonyl) naphthalene-1,3-diol. The azo ligand was identified by: Mass, ¹H-NMR, ¹³C-NMR, 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. **Results:** Analytical data revealed that all the complexes exhibited 1:2 metal–ligand ratios. On the basis of magnetic susceptibility measurements, suitable geometry was proposed for each complex. IR spectra of complexes showed that the ligand is coordinated to the metal ions in bidentate manner with Oxygen and Nitrogen donor sites of hydroxynaphthalene (OH) and azo Nitrogen. These findings suggested octahedral geometry for all complexes. Also, biological evaluation of all synthesized compound showed moderate to good activity against employed strains. All the complexes were stable, non-ionic and exhibited octahedral geometry around the metal center.

Keywords: Azo ligand, Metal complexes, Dihydroxynaphthalene, NMR, Chelate complexes..

1. INTRODUCTION

Azo compounds are the oldest and largest class of industrially synthesized organic dyes due to their versatile application in various fields and have attracted much attention in both academic and applied researches [1–3]. The latter included 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. The N=N group is called an azo group and the name of azo came from azote, the French name of nitrogen that is derived from the Greek (a, which means not, and zoe, which means to live). A large number of (N,N')- donor ligands in azo imine family have been prepared in the last few years [4–6].

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 studied the spectral-structure correlations as well as the effects of 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, photo-physical and photo-chemical 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 is an important and fascinating branch of chemistry, and plays a pivotal role in industry, technology and life processes [14–16].

Therefore, current study was conducted to synthesize new azo-dyes by bringing together two important chemical compounds, 1,3-dihydroxynaphthalene and 3-aminopyridine. In addition, the chemical structures of both azo dyes and azo metal complexes were studied in details.

2. MATERIALS AND METHODS

2.1. Materials

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

2.2. Measurements

Melting points were 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 were 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 Department of Chemistry, College of Sciences/ University of Al – Mustansiriyah. Apparatus and diamagnetic corrections for the ligand were calculated using Pascal's constant. Mass Spectra were recorded on AB Sciex 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

(PANR= H₂L) azo ligand is prepared according to the following general procedure [17] (Figure 1), 3-amino pyridine (4.32 g, 10 mmol) were 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 1,3-dihydroxynaphthalene (2.24 g, 10 mmol) dissolved in 200 ml alkaline ethanol cooled below 0°C. After leaving in the refrigerator for 24 hours, the mixture was acidified with dilute hydrochloric acid until pH = 6. The precipitate was filtered off, recrystallized twice from hot ethanol and dried in oven at (70 °C) for several hours melting point (195-197°C), yield (85%).

2.4. Synthesis of metal complexes

The complexes were 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 were dissolved in a least amount of distilled water to (0.786 g, 2 mmol) of ligand (PANR) dissolved in 50 cm³ 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 CaCl₂.

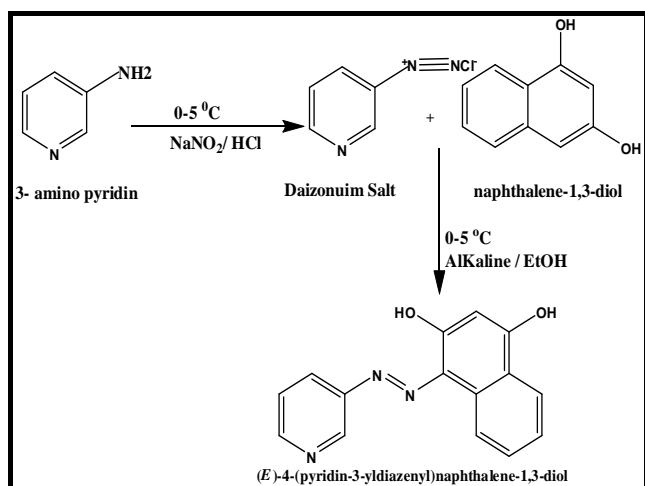


Figure 1. Structure of the ligand (DPDPI)

3. RESULTS AND DISCUSSION

Azo ligand was orange semi-crystal, but the chelate 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 ¹HMR spectra. The magnetic susceptibility of the chelate complexes at room temperature was consistent with octahedral geometry. The experimental results of elemental analyses of prepared ligand and its metal chelates were in good agreement with theoretical expectations. The elemental analyses of complexes indicated that the metal-ligand ratios were 1:2 in the [M(PANR)₂(H₂O)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 quite 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 indicating the non-electrolytic nature of these complexes.

3.1. Micro analysis

The elemental analysis data of 1:2 [M:L] ratio complexes showed that the theoretical values were in a good agreement with data reported in current study (Table 1). The purity of azo ligand was tested by TLC technique and C, H, N elemental analyses. Some physical and analytical data are given in Table 1.

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. The infrared spectra of azo compounds under study display a medium and broad band at a range of 3425 to 3400 cm⁻¹, Table 2, corresponding to the νOH of naphthyl moiety (Figure 2). The low frequency and broadening of these bands suggested that these ligands have a strong hydrogen bonding (O-H...N) in the solid state. The low value indicates that this OH group is involved in an intramolecular hydrogen bonding with the N=N group. For azo compounds, a weak band or shoulder appears on the higher wave-number side of this band which corresponds to the νOH of non-hydrogen bonded group.

A medium or weak band within the 2924 cm⁻¹ was assigned to the νCH vibrations of the aromatic rings. The symmetric νN=N stretching mode leads to a medium band at 1502 cm⁻¹, while the νOH mode gives an intense broad band within 1207cm⁻¹[18-20]. Finally, the IR spectra of complexes exhibited new non-ligand bands in the range of 560–520 cm⁻¹ and 499–424 cm⁻¹ assigned as ν (M–O) and ν (M–N) stretching vibrations, respectively. Therefore, it can be concluded that (PANR) ligand binds to the metal ions through phenolic oxygen and nitrogen of azo group and the ligand behaves as mono negative bidentate ligand [21-23].

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

Compound	Color	M.P. °C	Yield%	Formula	Found (Caled) %			
					C	H	N	M
H ₂ L= (PANR)	Orange	195-197	85	C ₁₅ H ₁₁ N ₃ O ₂	67.73 (67.92)	4.06 (4.15)	15.56 (15.85)	-----
[Mn(HL) ₂ (H ₂ O) ₂]	Brown	237-239	81	MnC ₃₀ H ₂₄ N ₆ O ₆	57.92 (58.16)	3.81 (3.88)	13.32 (13.57)	8.58 (8.87)
[Fe(HL) ₂ (H ₂ O) ₂]	bright Brown	189-191	80	FeC ₃₀ H ₂₄ N ₆ O ₆	57.89 (58.06)	3.61 (3.87)	13.29 (13.55)	8.71 (9.00)
[Co(HL) ₂ (H ₂ O) ₂]	Deep Black	253-255	74	CoC ₃₀ H ₂₄ N ₆ O ₆	57.52 (57.78)	3.71 (3.85)	13.22 (13.48)	9.18 (9.46)
[Ni(HL) ₂ (H ₂ O) ₂]	yellowish	285-286	72	NiC ₃₀ H ₂₄ N ₆ O ₆	57.54 (57.78)	3.69 (3.85)	13.23 (13.48)	9.11 (9.47)
[Cu(HL) ₂]. 2H ₂ O	Red	230-231	81	CuC ₃₀ H ₂₂ N ₆ O ₅	58.83 (59.06)	3.49 (3.61)	13.54 (13.78)	10.23 (10.42)
[Zn(HL) ₂]. 2H ₂ O	Brown	208-210	69	ZnC ₃₀ H ₂₂ N ₆ O ₅	58.59 (58.89)	3.51 (3.59)	13.51 (13.74)	10.47 (10.68)
[Cd(HL) ₂]. 2H ₂ O	bright yellow	277-278	80	CdC ₃₀ H ₂₂ N ₆ O ₅	54.47 (54.68)	3.23 (3.34)	12.44 (12.76)	16.78 (17.07)
[Hg(HL) ₂]. 2H ₂ O	Brown	269-271	81	HgC ₃₀ H ₂₂ N ₆ O ₅	48.05 (48.23)	2.87 (2.95)	12.02 (11.25)	-----

Table 2: Characteristic IR absorption bands of the ligand and its complexes in cm⁻¹ units

No.	Chemical formula	ν (O-H)	ν (C=N)	N=N)(ν	ν (M-N)	ν (M-O)
1	L=C ₁₅ H ₁₁ N ₃ O ₂	3425	1581	1502	-	-
2	MnC ₃₀ H ₂₄ N ₆ O ₆	3423	1585	1498	499	551
3	FeC ₃₀ H ₂₄ N ₆ O ₆	3257	1587	1498	462	534
4	CoC ₃₀ H ₂₄ N ₆ O ₆	3383	1585	1494	497	530
5	NiC ₃₀ H ₂₄ N ₆ O ₆	3332	1587	1508	466	520
6	CuC ₃₀ H ₂₂ N ₆ O ₅	3421	1585	1506	424	547
7	ZnC ₃₀ H ₂₂ N ₆ O ₅	3423	1583	1494	499	532
8	CdC ₃₀ H ₂₂ N ₆ O ₅	3390	1662	1581	484	521
9	HgC ₃₀ H ₂₂ N ₆ O ₅	3458	1585	1498	492	560

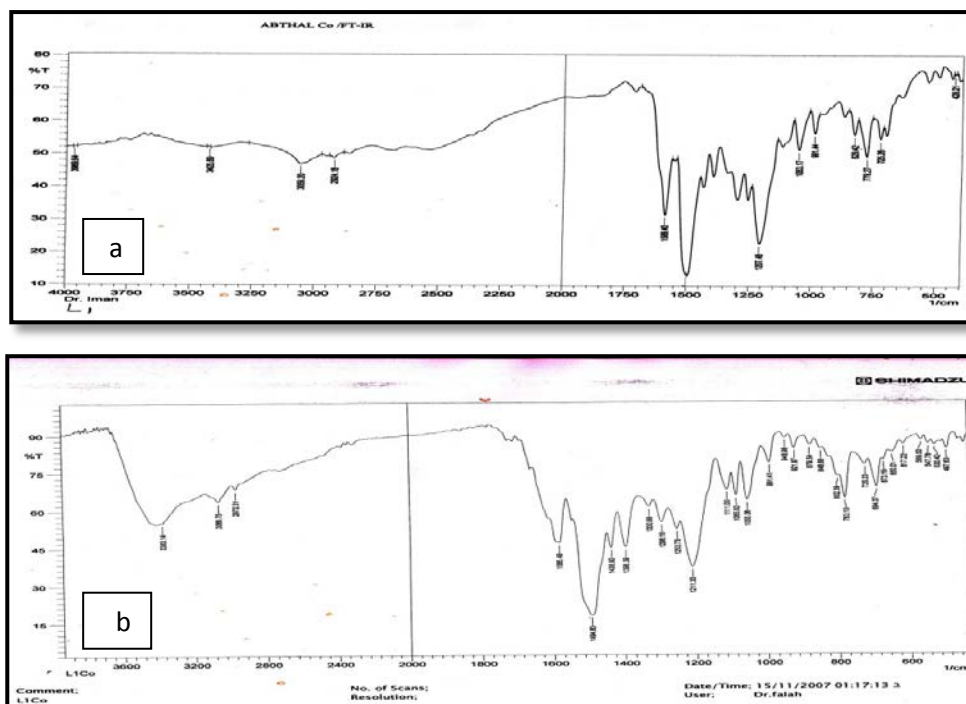


Figure 2: IR spectrum of (a) the azo ligand and (b) Co (II) complex.

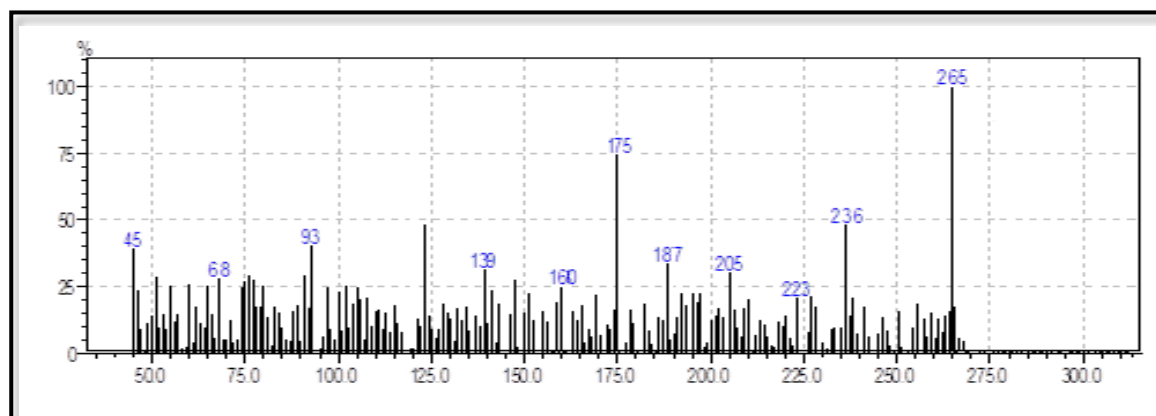


Figure 3: Mass spectrum of azo ligand

3.3. Mass spectrum of azo ligand (PANR)

The mass spectra of synthesized azo ligand were recorded at room temperature. This spectrum confirms the proposed formula by showing a molecular ion peak (m/z) at 265 (M^+) with a relative intensity 100% corresponding to the ligand molecule [$C_{15}H_{11}N_3O_2$] and the main mass fragment of organic ligand is given in Figure 3. The latter presents series of peaks at 78, 93, 105, 159, 160, 175, 187 and 236 u which were assigned to various fragments.

3.4. 1H -NMR spectrum of azo dye

The 1H -NMR spectrum of azo-compound (PANR) under study displayed a group of signals corresponding to the protons of each molecule. The spectrum of this compound was produced using d_6 -DMSO as a solvent and (TMS) as a reference. The phenyl multiples at 6.0-8.8 ppm were assigned to the aromatic protons. In general, the compounds exhibited the following characteristics chemical shifts as shown in Table 3. As previously reported, the compounds shown in Figure 4 were present in solution as a proton transfer

equilibrium. In all cases, their 1H -NMR spectrum showed a signal with a chemical shift in the range of 17-11 ppm, corresponding to the $O-H \cdots N$ proton involved in the relevant intramolecular hydrogen bond. The signal at higher field, at 13.03 ppm for azo-compound, was due to the free OH group. In 1H -NMR spectra of ligand, it was seen that the signal of OH group (2-H) which made hydrogen bond is broader than the signal of free OH group [24-26].

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

The ^{13}C NMR spectrum of azo ligand was measured at room temperature in D_6 -DMSO. A spectrum of the ligand is shown in Figure 5. The ^{13}C NMR spectrum of the ligand displayed characteristic signals at 148.6 ppm and at 168.6 and 178 ppm due to $>(C-py$ pyridine ring) and $>(C-OH$ naphthol ring) azo ligand, respectively [27]. Moreover, the ligand spectrum showed another peaks in the regions of 99, 107.3, 129.6 and 140.8 ppm due to aromatic carbon atoms.

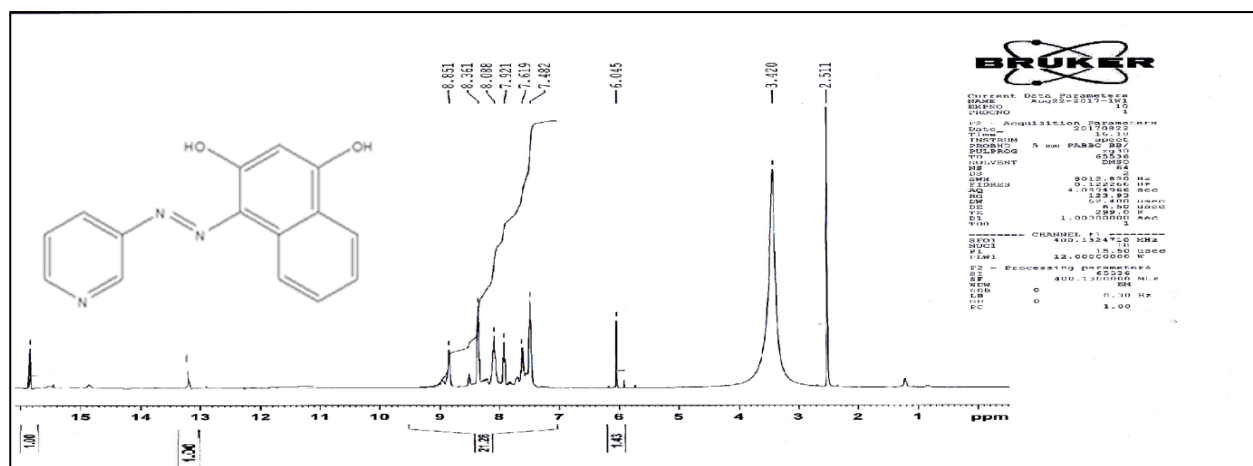
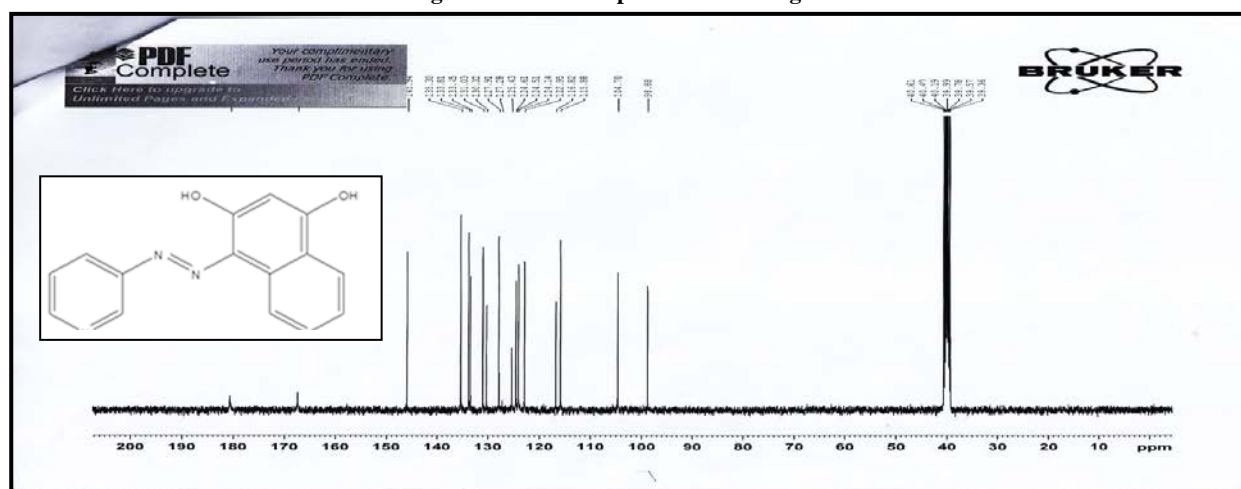
Figure 4: ¹H-NMR spectrum of azo ligand.Figure 5: ¹³CNMR spectrum of azo ligand.

Table 3: Electronic spectra, conductivity and magnetic moment of complexes

Compound	Absorption Bonds(nm)	Absorption Bonds(cm ⁻¹)	Transition	$\mu_{eff}(B.M)$	Conductivity S.mol ⁻¹ . cm ²	Geometry	Hybridization
PANR	304 426	32894 23474	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-----	-----	-----	-----
[Mn(PANR) ₂ (H ₂ O) ₂]	481	20790	M→L,CT	5.2	7.23	Octahedral (regular)	sp ³ d ²
[Fe(PANR) ₂ (H ₂ O) ₂]	487	20533	M→L,CT	5.40	3.52	Octahedral (regular)	sp ³ d ²
[Co(PANR) ₂ (H ₂ O) ₂]	464	21551	M→L,CT	4.90	12.56	Octahedral distorted	sp ³ d ²
[Ni(PANR) ₂ (H ₂ O) ₂]	463	21598	M→L,CT	3.06	17.43	Octahedral (regular)	sp ³ d ²
[Cu(PANR) ₂ (H ₂ O) ₂]	473	21141	M→L,CT	1.79	11.97	Octahedral distorted	sp ³ d ²
[Zn(PANR) ₂ (H ₂ O) ₂]	459	21786	M→L,CT	Dia	10.22	Octahedral (regular)	sp ³ d ²
[Cd(PANR) ₂ (H ₂ O) ₂]	458	21834	M→L,CT	Dia	9.65	Octahedral (regular)	sp ³ d ²
[Hg(PANR) ₂ (H ₂ O) ₂]	493	20283	M→L,CT	Dia	11	Octahedral (regular)	sp ³ d ²

3.6. Electronic spectra

Electronic spectra provide the most detailed information about electronic structure. The UV-Vis spectrum of azo ligand (HL) exhibited three charge transfer (CT) bands at (245 nm; 39370 cm⁻¹), (304 nm; 32894 cm⁻¹) and (426 nm; 23474 cm⁻¹) attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition within the azo ligand. In the spectra of complexes, CT band at (326 nm) remains in agreement with the $\pi \rightarrow \pi^*$ transition of azo ligand. The band observed at (426 nm) in the

spectrum of the free ligand (HL), was red-shifted to (458-493 nm) in complexes due to ligand metal charge transfer (LMCT) transition [28,29] suggesting an octahedral geometry around metal (II) ion in complexes. The electronic spectra of the ligand and Co (II) complex are shown in Figures 6 and 7, whereas magnetic properties and conductivity values of the ligand and its complexes are listed in Table 3.

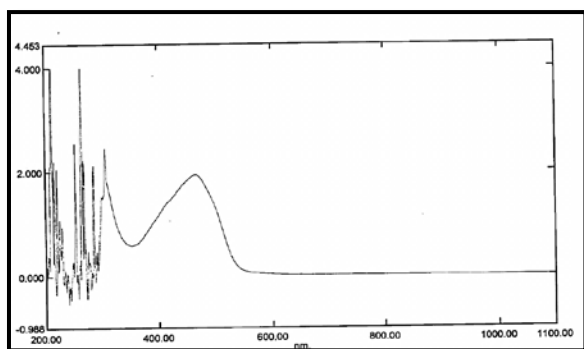


Figure 6: Electronic spectrum of ligand (PANR).

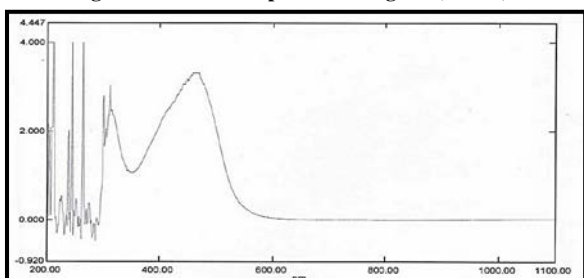


Figure 7: Electronic spectrum of Co (II) complex.

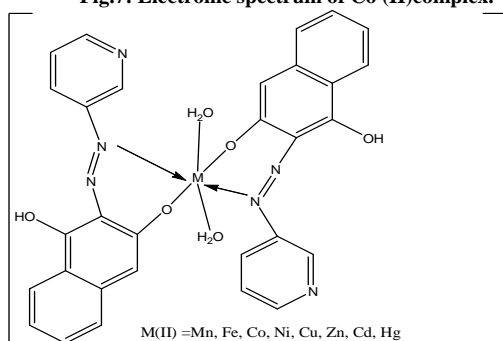


Figure 8: The proposed structural formula of the complexes.

3.7. Magnetic measurements

The high spin magnetic moment value of Mn (II) complex has been found 5.93 B.M. The Fe (III) complex showed magnetic value at 5.1 B.M which were consistent with an octahedral geometry^[31]. The Co (II) complex has a magnetic moment of 4.90 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 showed a magnetic moment value of 3.06 B.M within the range 2.9–3.3 B.M for a high-spin Ni (II) complex depended on the magnitude of the orbital contribution^[33] suggested an octahedral environment. The Cu (II) complex shows a magnetic moment value of 1.79 B.M monomeric and consistent with a distorted octahedral geometry. The Zn (II), Cd (II) and Hg(II) are diamagnetic and according to the empirical formulae of complexes, an octahedral geometry was proposed^[34]. Based on the above results, we can deduce the probable structures of the complexes as shown in Figure 8.

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 were ranged from 9.65 to 17.43 S.mol⁻¹.cm² that were non-electrolyte and no conductive species^[35]. According to these results, the structural formulas of this ligand and chelate complexes can be proposed as in Figure 8

CONCLUSIONS

In the current study we had explored the synthesis and coordination chemistry of some monomeric complexes obtained from the reaction of the didentate azo ligand PANR with some metal ions. The mode of bonding and overall structures of the complexes were determined through physico-chemical and spectroscopic methods. All the complexes were stable, non-ionic and exhibited octahedral geometry around the metal center.

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Conflict of Interest: None to declare.

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