



Research Article

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## Synthesis and biological activity study of 1-[4,5,6,7-tetrahydro-1,3-benzothiazol-(2-ylidiazenyl)]-2-naphthol complexes

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### ABSTRACT

A series of new metal complexes  $Cr^{+3}$ ,  $Fe^{+3}$ ,  $Ni^{+2}$ ,  $Co^{+2}$ , and  $Cu^{+2}$ , with dye ligand derived from 2-aminobenzothiazole have been prepared and fully characterized on the basis of microelement analysis, atomic Absorption, <sup>1</sup>HNMR, FT-IR, UV-visible spectra techniques as well as the magnetic moment of solid complexes and molar conductance. The results obtained from (C.H.N.M) analysis and spectral measurements investigated all complexes are octahedral geometries in the formula  $[ML_2(H_2O)_2]X$ , where  $M = Co^{+2}$ , and  $Cu^{+2}$ ,  $X = Cl^{-1}$  for  $Cr^{+3}$  and  $Fe^{+3}$  except  $[NiL_2]Cl_2$  which was square planer. The biological activity of the ligand and their complexes were studied against selected types of bacterial and fungal which included *Staphylococcus*, *Klebsiella*, *Serratia marcescens* and *Pseudomonas aeruginosa*.

**Keywords:** Azo compounds; Metal complexes; Biological activity

### INTRODUCTION

Azo compounds are highly colored that enjoy widespread use as dyes and pigments in a variety of applications that include textile dyeing<sup>(1)</sup> as well as non-linear and photoelectronics<sup>(2)</sup>, especially in optical information storage<sup>(3-6)</sup>. Azo compounds are very important molecules and have attracted much attention in both academic and applied research<sup>(7-9)</sup>. For example, azo derivatives and their metal complexes are very important pigments for synthetic leather and vinyl polymers. On the other hand, azo compounds are known to be involved in a number of biological reactions, such as inhibition of DNA, RNA, and protein synthesis, nitrogen fixation, and carcinogenesis<sup>(10)</sup>. Furthermore, high-density optical data storage has been a subject of extensive research in the past decade. In general, cyanine dyes, phthalocyanine dyes, and metal-azo complex dyes are used in the recording layer of DVD-R (Digital Versatile Disc-Recordable) discs. It has been reported that the new technology, which employs 405 nm blue-violet diode lasers, requires a new optical-recording medium matching the 405 nm wavelength laser. In comparison with the dyes themselves, metal-azo dyes are more light stable, allow for easier control of the wavelength by selection of the appropriate substituent groups, and have good thermal stability<sup>(11-17)</sup>. Because of the good thermal stability of azo compounds and the ease with which the absorption band may be tuned by varying the substituent's, one of the many applications of azo compounds is in optical data storage. In a continuation to the interest in the synthesis of azo-based compounds<sup>(18-20)</sup>. The aim of this work preparation new metal complexes derived from 1-[4, 5, 6, 7-tetrahydro-1, 3-benzothiazol-(2-ylidiazenyl)]-2-naphthol and study the biological activity.

### EXPERIMENTAL SECTION

Melting points were determined in open capillary tubes on a Gallenkamp melting point apparatus and uncorrected. FT-IR spectra were recorded using FT-IR 8300 Shimadzu in the range of (4000-200)  $cm^{-1}$ , samples were measured

as (CsI disc). Electronic spectra were obtained using Hitachi U-2000 and Cary 100 conc. Spectrophotometer at room temperature. The measurements were recorded using a concentration of ( $10^{-3}M$ ) of the complex in ethanol. The metal content was estimated Spectrophotometric ally using Atomic Absorption Shimadzu AA670 Spectrophotometer. Conductivity measurements were obtained using Corning Conductivity meter 220. These measurements were done in ethanol solvent as ( $10^{-3}M$ ) concentration at  $25^{\circ}C$ . Elemental analysis (C.H.N) was carried out in College of Science / University Al - Mustansiriya, Baghdad.  $^1H$ -NMR spectra were recorded on Bruker spectrometer model Ultra-shield at (300MHz) in Al-Albait University, Jordan. Tetramethylsilane (TMS) was used as an internal reference and DMSO- $d_6$  as solvent.

#### Preparation of the ligand (HL)

The ligand (HL) has been prepared according to method previously presented in literature<sup>(21)</sup> as shown in below:

Mixture of concentrated HCl (1mL) and 2-Amino-4,5,6,7-tetrahydrobenzothiazol<sup>(21)</sup> (0.001 mole, 0.15g) was kept at  $0 - 5^{\circ}C$  using an ice-water bath. A solution of sodium nitrite 0.20 g in distilled water 0.5 mL was prepared. The sodium nitrite solution was added to the solution of compound (1) with stirring by using a glass rod. The temperature was controlled below  $10^{\circ}C$  throughout the addition. 2-naphthol (0.001 mol, 0.14 g) was dissolved in 10% NaOH solution (10mL) and then put an ice-water bath to cool to  $5^{\circ}C$ . Then, diazonium salt solution was added occasionally stirring very slowly to the 2-naphthol solution. The color of the solution was changed, then the reaction mixture was left to complete for about 15 min with occasional stirring, then the formed precipitate was filtered and dried in air and then recrystallized from absolute ethanol to give azo compound as pale yellow in 90 % yield, m.p:  $60-62^{\circ}C$ .

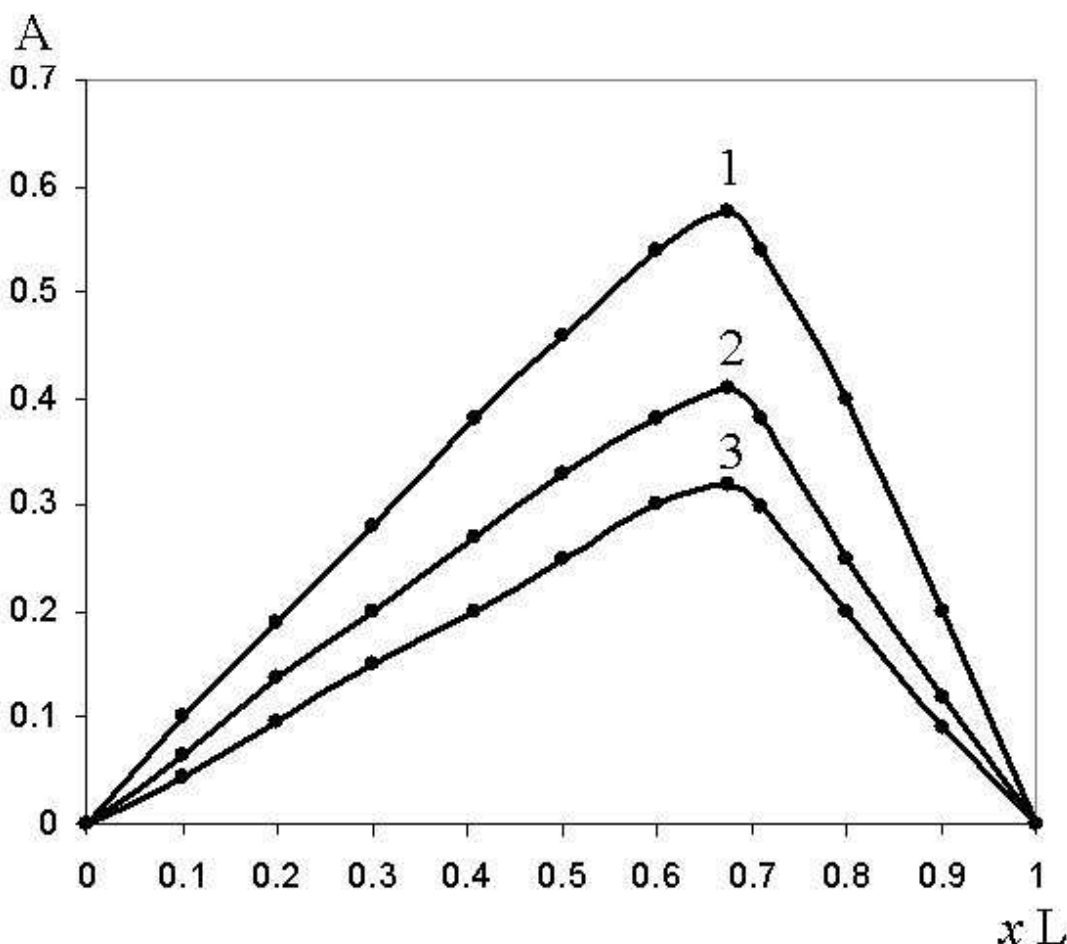


Figure (1): Molar ratios of Cr, Fe(III) and Cu(II) complexes at  $\lambda_{max}$  450,530 and 620nm respective

#### Preparation of the metal complexes

Ethanolic solution of each of the following metal salts (1 mmole of  $CuCl_2 \cdot 2H_2O$  (0.17g),  $Ni(NO_3)_2 \cdot 6H_2O$  (0.29g),  $CoCl_2 \cdot 2H_2O$  (0.17g),  $CrCl_3 \cdot 6H_2O$  (0.13 g) and  $FeCl_3 \cdot 2H_2O$  (0.18g)) was added to ethanolic solution (1 mmole, 0.15g) of ligand (HL) with constant stirring for 15 minutes, then refluxed the mixture on water bath for 90 minutes, during this time a colored precipitate was formed. The product was filtered off, washed with hot ethanol in second period and, then dried under vacuum. The physical properties of complexes were listed in Tables (1), (3) and (4).

**Solution study:****1-Molar ratio method**

Metal complexes of ligand (HL) with metal ions selected, were studied in solution using mix (chloroform-ethanol) as a solvent, in order to determine [M:(L)] ratio in the solid complexes, following molar ratio method. A series of solutions were prepared having a constant concentration ( $10^{-3}$  M) of the metal ion and variable concentrations of free ligand in the same solvent (0.001,0.0002,0.0003,0.0004 and 0.0005M) concentrations. The [M/(L)] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M:(L)], Figure (1). The results of complexes formation in solution were listed in Table (1).

**2-Stability constant of Schiff base complexes**

The apparent stability constant of the (1:1) and (1:2) (Metal: Ligand) complex were evaluated as follows:

Two sets of solutions were prepared, the first one were formulated to contain stoichiometric amount (1ml) of ( $10^{-3}$  M) ligand and (1 ml) of ( $10^{-3}$ M) of metal ion by placing in to a three series of (10 ml) volumetric flasks. The solutions of the colored complexes were diluted to the mark with ethanol. The second set were formulated to contain fivefold excess (5ml) of ( $10^{-3}$ M) ligand, by placing in to a three series of (10ml) volumetric flasks followed by addition of (1ml) of ( $10^{-3}$ M) of metal ion solution, the volumes were then completed to the mark with ethanol .The absorbance ( $A_m$ ) of the solutions was measured at ( $\lambda_{max}$ ) of maximum absorption. The stability constant (Kf), and the molar absorptivity ( $\epsilon_{max}$ ) have been calculated, were listed in Table (4).

**Physical measurements and analysis**

Melting points were recorded on Gallen Kamp melting point apparatus and were uncorrected. FT-IR spectra were recorded using FT-IR 8300 Shimadzu in the range of (4000-200)  $\text{cm}^{-1}$ , samples were measured as (CsI disc). Electronic spectra were obtained using Hitachi U-2000 and Cary 100 conc. Spectrophotometer at room temperature. The measurements were recorded using a concentration of ( $10^{-3}$ M) of the complex in DMF. The metal content was estimated Spectrophotometrically using Atomic Absorption Shimadzu AA670 Spectrophotometer. Conductivity measurements were obtained using Corning Conductivity meter 220. These measurements were done in DMF solvent as ( $10^{-3}$ M) concentration at 25C<sup>o</sup>.Elemental analysis (C.H.N) were carried out in College of Science / University of Al - Mustansiriya, Baghdad.

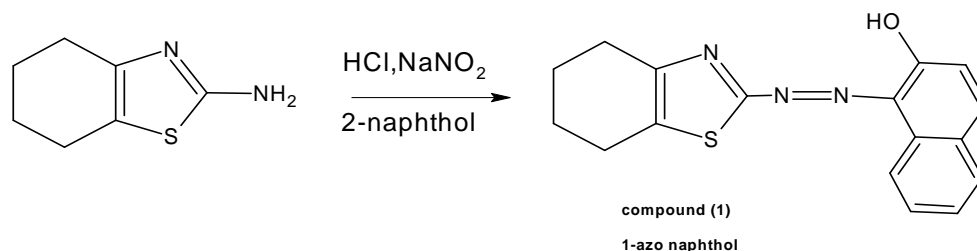
**Biological activity Study of compounds**

The biological activity of the ligand and their complexes were studied against selected types of bacterial and fungal which included *Staphylococcus*, *Klebsiella*, *Serratia marcescens* and *Pseudomonas aeruginosa*.

*In vitro* technique was proceeded for studying antibacterial activity against the strains , DMSO was used as a solvent and as a control , the concentration of the compounds in this solvent were ( $10^{-3}$  M) . The technique was the Disc Sensitivity test <sup>(9)</sup>, this method involves the exposure of the zone of inhibition towards the diffusion of micro-organism on agar plate. The plates were incubated for 24 hr. at 37 °C, the zone of inhibition of bacterial growth around the disc was observed.

**RESULTS AND DISCUSSION**

The ligand (HL) was prepared by diazotized amino compound using sodium nitrate and concentrated hydrochloric acid in aqueous medium. The resulting diazonium salt intermediate was coupled with 2-naphthol to obtain new azo compound, (scheme 1), the physical properties of this compound and complexes were shown in Table (1). The ligand 1-azo naphthol<sup>(21)</sup>was characterized by spectral analysis as UV-Vis., FTIR and <sup>1</sup>HNMR spectra, while complexes were characterized by UV-Vis., and FTIR spectra. The <sup>1</sup>HNMR of ligand shows signal at 1.7 ppm and 2.5 ppm for protons of aliphatic cycle, multiplied at 6.8-8.2 ppm for aromatic protons, and singlet at 10.2 ppm for (OH) group, Figure (2). The data of UV-Vis., and FTIR spectra for ligand and complexes were shown in Table (2).



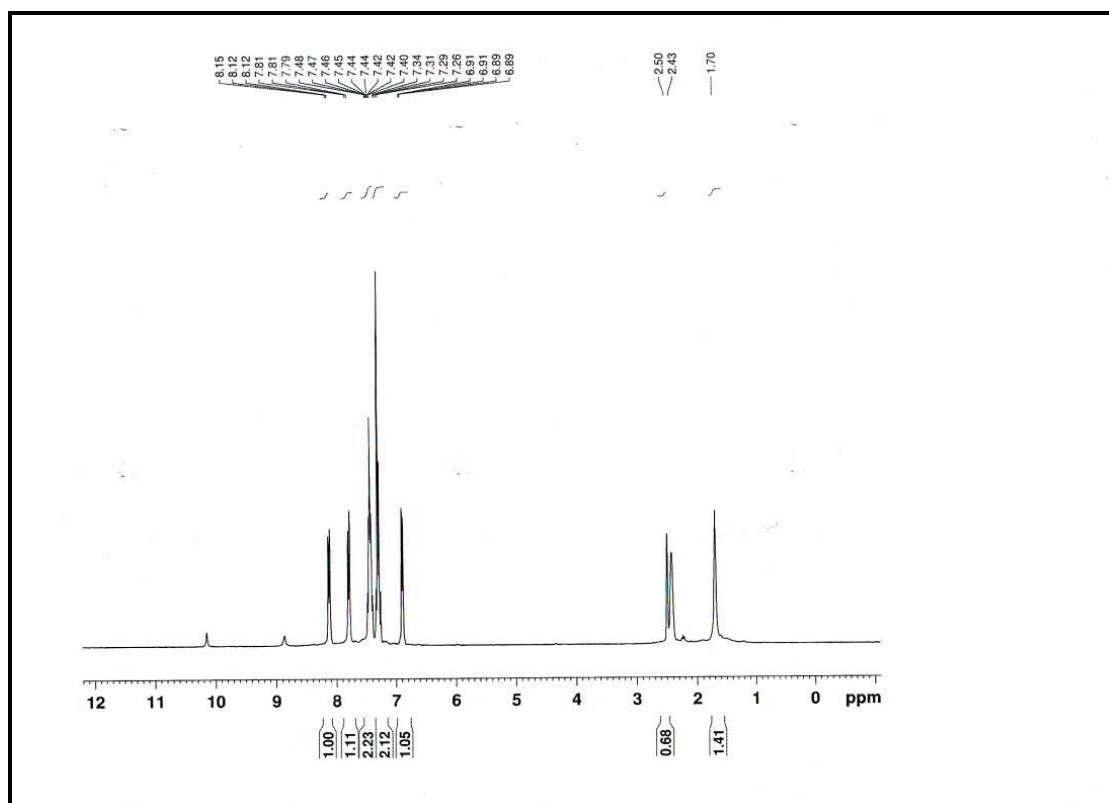
**Scheme (1): preparation of ligand (HL)**

**Table (1): Physical properties of ligand and their complexes**

Symp.	Colour	M.P. C°	Yield %	M :L	Suggested formula
L	Palle yellow	60-62	90	-	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> OS
LCr	Green	>350	50	1:2	[Cr(C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> OS) <sub>2</sub> Cl <sub>2</sub> ]Cl
LNi	Red	>350	91	1:2	[Ni(C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> OS) <sub>2</sub> ]Cl <sub>2</sub>
LCo	Dark brown	>350	85	1:2	[Co(C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> OS) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>
LFe	Brown	>350	90	1:2	[Fe(C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> OS) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>3</sub>
LCu	Dark green	>350	92	1:2	[Cu(C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> OS) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>

**Table ( 2 ) : The spectra data of prepared compounds**

Compounds	FT-IR (cm <sup>-1</sup> )	UN-Vis (nm)
ligand	3248 (OH) , 1629 (C=N), 1384 (N=N), 1512 (N=C), 1172 (C-S), 1276 (C-O)	233 $\pi \rightarrow \pi^*$ and 325 $n \rightarrow \pi^*$
LCr	3564-3524 (OH) (br.), 1631 (C=N), 1465 (N=N), 1120-1172 (C-S), 500-600 (M-N) (weak),	342 $A_g^3 \rightarrow T_2g^4$ , 296 (C.T), 242 $\pi \rightarrow \pi$ , 330 $n \rightarrow \pi$
LNi	3454 (OH), 1635(C=N), 1452(N=N), 1068 (C-S), 426, 449, 605 (M-O and M-N),	500, 424, 326 $A_1g^1 \rightarrow B_1g^1$ , $A_1g^1 \rightarrow B_2g^1$
LCo	3406 (OH), 1613-1560 (C=N), 1450 (N=N), 480, 414 (M-N),	496, 402, 388 (d-d), 240 $\pi \rightarrow \pi$ , 304 $n \rightarrow \pi$
LFe	3460 (OH), 1689-1629 (C=N) (br.), 1462 (N=N), 478,435 (M-O and M-N),	506, 330 (d-d), 238 $\pi \rightarrow \pi$ , 304 $n \rightarrow \pi$
LCu	3248 (OH), 1690-1500 (C=N), 1477 (N=N), 1149 (C-S), 565 (M-N),	428, $B_1g^2 \rightarrow B_2g^2$ , 400 $B_1g^2 \rightarrow A_1g^2$ , 354 (C.T) , 282 $n \rightarrow \pi$ , 246 $\pi \rightarrow \pi$

**Figure (2) : The <sup>1</sup>HNMR spectrum of 1-azo naphtholin DMSO-d<sup>6</sup>**

The molar conductivity values of 10<sup>-3</sup> M DMF solutions of the different complexes synthesized are found to be in the range 149-170 ohm<sup>-1</sup>. cm<sup>2</sup>.mol<sup>-1</sup> for Co<sup>+2</sup>, Cu<sup>+2</sup>, and Ni<sup>+2</sup>, which indicate a none-electrolytic nature of these complexes. However, the molar conductivity for Cr<sup>+3</sup> and Fe<sup>+3</sup> falls in the range 80-185 ohm<sup>-1</sup>. cm<sup>2</sup>.mol<sup>-1</sup>, which investigate its electrolytic behavior in 1 : 1 ratio<sup>(22)</sup>. It should be noted that the relatively high molar conductivity values of Cr<sup>+3</sup> and Fe<sup>+3</sup> complexes in DMF is due to the probable solvolysis and dissociation of the complexes by DMF<sup>(22)</sup>.

Table (3): The Elemental analysis of ligand and their complexes

Symp.	Elemental analysis				
	Calc. / (Found)				
	C%	H%	N%	S%	M%
L	66.01 (66.59)	4.58 (4.92)	13.59 (13.61)	10.35 (10.41)	-
LCr	52.55 (52.51)	3.89 (3.69)	10.81 (10.91)	8.25 (9.05)	6.69 (6.92)
LNi	56.67 (56.10)	4.17 (4.55)	11.67 (11.21)	8.89 (9.22)	8.19 (8.31)
LCo	52.04 (51.71)	4.37 (3.53)	10.71 (9.65)	8.15 (8.31)	7.51 (8.00)
LFe	54.73 (53.95)	4.59 (3.71)	11.26 (10.50)	8.57 (8.41)	7.48 (7.30)
LCu	51.74 (50.91)	4.34 (3.61)	10.65 (11.21)	8.10 (8.20)	8.05 (8.21)

Table (4): Physical properties of complexes

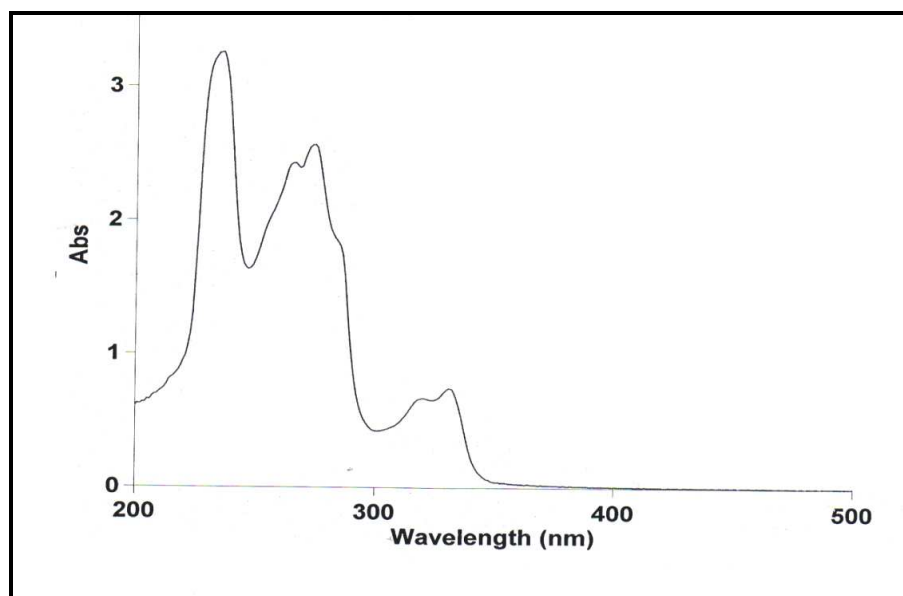
Symp.	Molar conductivity $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Stability constant $K_f (\text{L}^{-1} \cdot \text{mol})$	$M_{\text{eff}}$ (Bm)
LCr	80	$5.9 \times 10^3$	3.25
LNi	170	$2.3 \times 10^4$	zero
LCo	155	$1.3 \times 10^4$	2.51
LFe	185	$9.8 \times 10^4$	5.21
LCu	149	$13.5 \times 10^4$	1.45

The chemical analysis data clearly indicate that prepared complexes agree well with the proposed formula are  $[\text{ML}_2(\text{H}_2\text{O})_2]\text{X}$  where  $\text{M} = \text{Co}^{+2}$ , and  $\text{Cu}^{+2}$ ,  $\text{X} = \text{Cl}^{-1}$  for  $\text{Cr}^{+3}$  and  $\text{Fe}^{+3}$ , and  $[\text{NiL}_2]$  are square planer. The data from continuous variation method were applied for the determination of the apparent formation constant values ( $K_f$ ) of the different complexes formed in solution. The ( $K_f$ ) values obtained are listed in Table (4).

Examination of these results reveals that the stability of 1: 2 and 1: 1 [ $\text{M}^{+2}$  : Ligand] complexes increases in the order  $\text{Cr}^{+3} < \text{Co}^{+2} < \text{Ni}^{+2} < \text{Fe}^{+3} < \text{Cu}^{+2}$ , this is agreement with the general order of stability of complexes of these ions which was established by Ginberg and by Irving-Williamson<sup>(23)</sup>

#### Electronic spectra of ligand and complexes

The UV-Visible spectra of the azo ligand and its metal complexes were measured in ethanol ( $10^{-4}$  M) and DMF for complexes in ( $10^{-5}$  M) at room temperature. The free azo (HL) ligand and complexes solution exhibited dye character since the molar extinction coefficient ( $\epsilon$ ) were over  $40,000 \text{ cm}^{-1} \text{ M}^{-1}$  (maximum absorbance 0.45)<sup>(24)</sup>. The bands between 390-450 nm were assigned to the azo  $\pi \rightarrow \pi^*$  transition in the azo ligand (Figure 3), most likely involving extended conjugation.

Figure ( 3 ) : The UV-Vis. spectrum of 1-azo naphtholin  $10^{-3}$  M ethanol

The UV-Vis. Spectra of the metal complexes,(Figure 4), provide additional evidence for the transformation that arise from complexation when compared to those of the unbound azo ligand and clear difference can be observed between the electronic absorption spectra of the azo ligand and its metal complexes. The high intensity peaks in all UV-Visible spectra of complexes lying in the range [296-342 nm] are assigned to ML CT<sup>(25)</sup>.

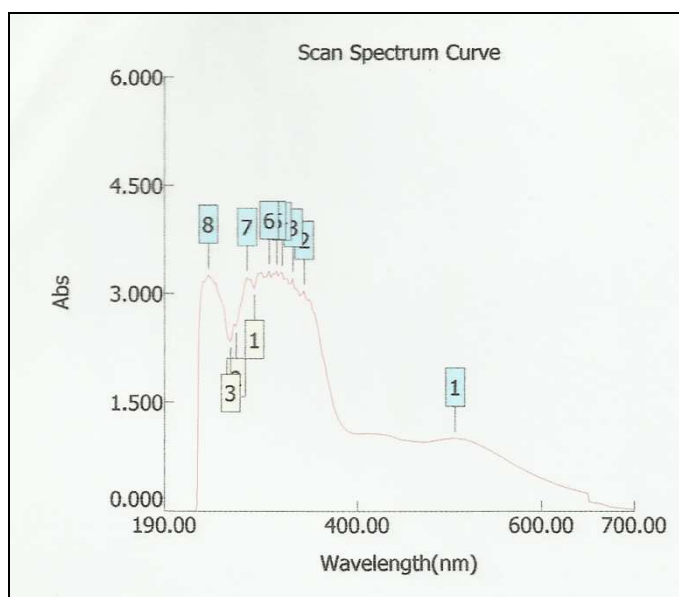
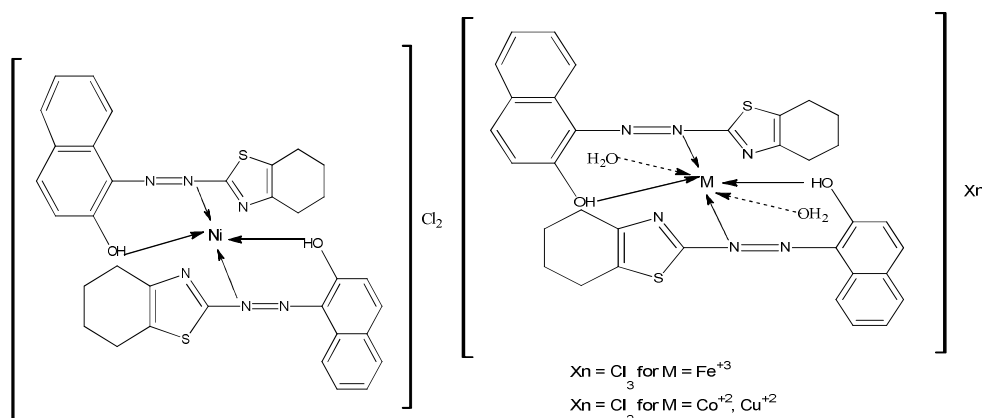


Figure (4):The UV-Vis. spectrum of Fe- complex in  $10^{-3}$  M ethanol

The green solution of  $\text{Cr}^{+3}$  in DMF exhibits this weak absorption in the range, which assignable to  $A_g^4 \rightarrow T_{2g}^4, T_{1g}^4$  (F) and to  $T_{1g}^4$  (P)<sup>(26)</sup> which suggests the octahedral environment around  $\text{Cr}^{+3}$  ion. As well as the d-d transition (broad band) for  $\text{Cu}^{+2}$  complex in DMF at 550 nm may be due to  $E_g^2 \rightarrow T_{1g}^2$  transitions, confirms the distorted octahedral symmetry.

As well as the electronic transition for brown solution of  $\text{Fe}^{+3}$  provide additional profs for octahedral symmetry, in control  $\text{Ni}^{+2}$  complex solution in DMF showed high energy electronic transition, assigned square planer symmetry of diamagnetic properties.

The magnetic moment of the synthesized metal complexes are given in Table ( 4 ). The general structural formula of the complexes is shown in Figure (5). It was determined that  $\text{Cr}^{+3}$  and  $\text{Fe}^{+3}$  complexes were paramagnetic with magnetic moments in the 3.25 B.M and 5.21 B.M range respectively which agree with high spin octahedral of  $d^3$  and  $d^5$  configuration respectively. As well as the magnetic moment of  $\text{Cu}^{+2}$  complex was 1.45 B. Mas expected for distorted octahedral, while the diamagnetic  $\text{Ni}^{+2}$  complex investigate the square planner geometry around  $\text{Ni}^{+2}$  ion<sup>(23)</sup>.



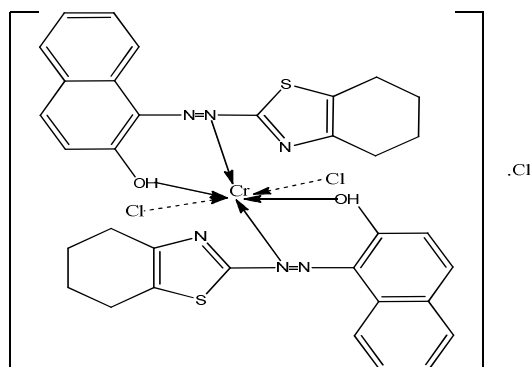


Figure (5): The general structural formula of the complexes Infrared spectra

FT-IR spectral data of the azo ligand (HL) and its metal complexes are provided in table (2). The IR spectra of the azo ligand, (Figure 6), displayed a shoulder in a broad band of weak intensity around  $2730\text{-}2990\text{ cm}^{-1}$ . This band was attributed to the O-H stretching, which is known to shift to lower frequencies as intrahydrogen bonding<sup>(27)</sup>. This band is disappeared and obscured by O-H strong bands in the region  $3400\text{-}3600\text{ cm}^{-1}$  of coordinated water molecule in  $\text{Cr}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$  and  $\text{Cu}^{+2}$  complexes<sup>(27)</sup>.

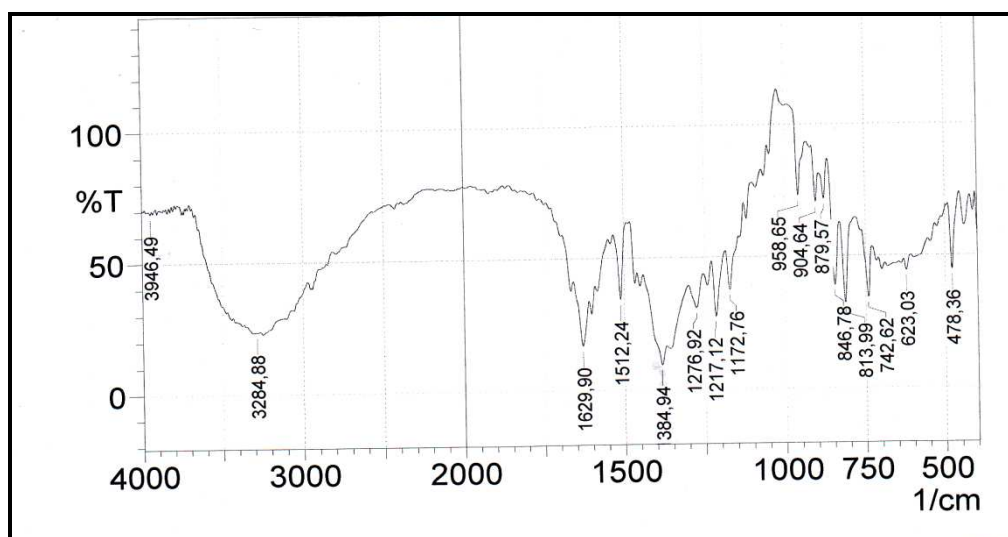


Figure (6): The FT-IR spectrum of 1-azo naphthol

The strong bands at  $1500, 1600\text{ cm}^{-1}$  are due to C=C of naphthalene aromatic ring, while the weak bands at  $940\text{-}970\text{ cm}^{-1}$  correspond to C-H deformations. The bands in the  $1440\text{-}1470\text{ cm}^{-1}$  range are assigned to  $\text{-N=N-}$  group in both the azo ligand and complexes. The azo peak in the spectra of metal complexes displayed red shifts of complex  $10\text{-}20\text{ cm}^{-1}$  compared to the free azo ligand (HL), confirming coordination of the azo nitrogen to the metal ion<sup>(28)</sup>.

The IR spectra of the all complexes showed down shift of C-O stretching of naphthalene ring, which due to the formation of M-O bond in the range  $490\text{-}530\text{ cm}^{-1(28)}$ , Figure (7).

The far infrared spectra of all metal complexes show bands in the regions  $420\text{-}450$  and  $505\text{-}580\text{ cm}^{-1}$  corresponding to (M-N) and (M-O) respectively. The presence of bands in all complexes in these regions, originating from (M-N), and (M-O) of  $\text{N=N}$  and  $\text{O}^-$  vibrational modes, identify coordination of azo group  $\text{N=N}\rightarrow\text{M}$  and oxygen of hydroxyl (O-H) via deprotonation.

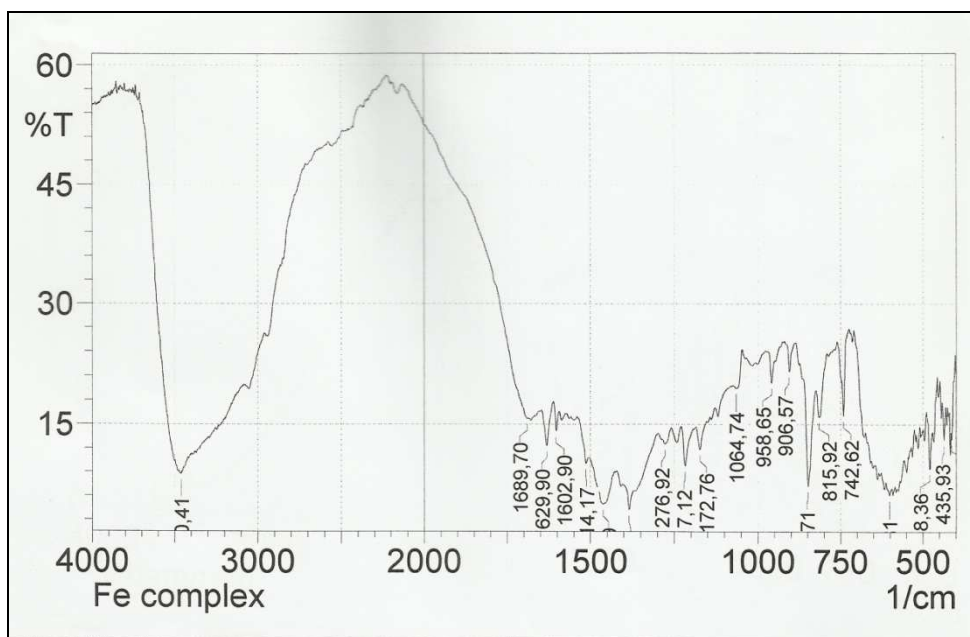


Figure (7): The FT-IR spectrum of Fe- complex

#### Study of complex formation in solution

The molar ratio method were followed to determine the [M:( L)] ratio. The results of complexes in ethanol (solvents), suggest that the metal to ligand ratio was (1:1) and (1:2) which were comparable to those obtained from solid state study, Table (1).

#### Stability constant of the Schiff base complexes

The apparent stability constant of the (1:1) [Metal : Ligand] (eq.1) or (1:2) [Metal : Ligand] (eq.2) complex, were evaluated using the following equations<sup>(29)</sup>:

$$(1) K = \frac{(1 - \alpha)}{\alpha^2 C} \text{ for Cr}^{+3} \text{ and Fe}^{+3}$$

$$(2) K = \frac{(1 - \alpha)}{4\alpha^3 C^2} \text{ for Cu}^{+2}, \text{ Ni}^{+2} \text{ and Co}^{+2}$$

( $A_m$ ) of the solutions, was measured at ( $\lambda_{max}$ ) of maximum absorption, furthermore the molar absorptivity ( $\epsilon_{max}$ ) for three complexes were calculated from the (eq.3) :

$$(3) A_m = \epsilon_{max} .bc$$

K : stability constant, C : concentration,  $\alpha$  : degree of dissociation,

$A_m$  : average of measurements of the absorption of solution containing a stoichiometric amount of ligand and metal ion.

$A_S$  : average of measurements of the absorption of solution containing the same amount of metal and fivefold excess of ligand.

#### Biological activity

##### Biological Screening: Antimicrobial Activity Tests.

The biological activity of some of the prepared compounds was tested against *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Klebsiella*, and *Serratia marcescens*.

Disc sensitivity test<sup>(30)</sup> was employed for the *in vitro* study for anti-bacterial and anti-fungal studies. This method involves the exposure of the zone of inhibition toward the diffusion of microorganism on agar plate. The plates were incubated for 24 hrs. at 37 °C, the zone of inhibition of bacterial growth around the disc was measured.



In order to complete this study, some of these new compounds were tested for their *in vitro* growth inhibitory activity against a strain of *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Klebsiella*, and *Serratia marcescens*, then incubated at 30 °C for 72 hrs. The results are presented in table (3), complexes (Cr and Co) were nearly as active as the antibiotics against all selected types of bacteria, also complexes (Cr and Ni) have more activity than another complexes against the *Pseudomonas aeruginosa*. Moreover complexes (Fe and Cu) have more activity than another complexes against the *Klebsiella*, and complex of Cu has more activity than another complexes against the *Serratia marcescens*.

**Table (5): Results of antimicrobial activities of the compounds ( $10^{-3}$  mg, mL $^{-1}$ )**

Compound	<i>Klebsiella</i>	<i>Staphylococcus</i>	<i>Pseudomonas aeruginosa</i>	<i>Serratia marcescens</i>
Control (DMSO)	-	-	-	-
Ligand	++	+++	++	+
LCr	+	+	++	+
LNi	+	-	++	+
LCo	+	+	+	+
LFe	+++	-	+	+
LCu	++	-	+	++

Where:(-): no effect, (+): 4-5 mm, (++) : 8-10 mm, (+++): 11-15 mm

### CONCLUSION

As a result from the study of antimicrobial for complexes, we are concluded:

1- It was of interest to investigate the effect of introducing the pharmacologically important azo moiety in the structure of the some of prepared complex and their antibacterial. For this purpose five complexes were prepared and the results in Table (5) show large increase in the activity for some complexes, which indicate the importance of the azo moiety (N=N groups) in enhancement of biological activity of the studied complexes.

2- Results of the antimicrobial activity of the new compounds, Table (5) showed that the metal ion chelates were more toxic toward the same micro-organism and under the identical experimental conditions. The increase in the antifungal activity of metal chelates may be due to the effect of metal ion on the normal cell process. These activities may be explained by Tweedy's Chelation Theory<sup>(31)</sup>, according to which chelation reduces the polarity of the metal atom mainly, because of the partial sharing of its positive charge with the donor groups of the ligand which favors permeation of the complexes through the lipid layer of cell membrane<sup>(32)</sup>.

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