

Synthesis, Characterization and Biological activity of Azo-linked Schiff Base Ligand Type (ONO) and its Complexes with Cr^{III}, Mn^{II} and Fe^{II} Ions

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الخلاصة

تضمن العمل تحضير المشتق

[2-(2-(naphthalen-5-yl)diazenyl)-4-amino-3-hydroxynaphthalene-1-sulfonic acid] [W]

من تفاعل 1-amino-2-naphtol-4-sulfonic acid مع diazonium salt حيث استعمل المشتق لتخليق الليكاند [H₂L] ثلاثي السن من نوع (ONO) وذلك بمفاعلة [W] مع 1-hydroxynaphthalene-2-carbaldehyde لينتج اللكند [H₂L]

[2-(2-(naphthalen-5-yl)diazenyl)-4-(2-hydroxynaphthalen-3-yl)methyleneamino)-3-hydroxynaphthalene-1-sulfonic acid]

تم تشخيص الليكاند بواسطة اطياف الاشعة تحت الحمراء وفوق البنفسجية وطيف الرنين النووي المغناطيسي .

كذلك تضمن العمل تحضير المعقدات وذلك من خلال مفاعلة الليكاند مع املاح العناصر التالية: الكروم الثلاثي والمنغنيز الثنائي والحديد الثنائي وباستخدام الايثانول كمذيب والتصعيد الحراري وعند وسط قاعدي باستخدام هيدروكسيد البوتاسيوم.

شخصت هذه المعقدات باستخدام الامتصاص الذري (A.A) واطياف الاشعة تحت الحمراء وفوق البنفسجية- المرئية وقياسات التوصيلية الكهربائية مع درجات الانصهار.

واخيرا استخدمت تقنية التحليل الحراري في اثبات وجود جزيئات الماء المتبلورة H₂O في تركيب المعقدات. الصيغة الجزيئية المقترحة لمعقد الكروم : K [M(L)₂].H₂O بينما لمعقدات المنغنيز والحديد الصيغة K₂[M(L)₂].H₂O. وتم دراسة الفعالية البيولوجية للمركبات المحضرة.

ABSTRACT

In this work the precursor [2-(2-(naphthalen-5-yl)diazenyl)-4-amino-3-hydroxynaphthalene-1-sulfonic acid][W] obtained from reaction of diazonium salt with 1-amino-2-naphtol-4-sulfonic acid. The precursor[W] used for synthesis of the tridentate (ONO) type ligand [H₂L] by reaction of [W] with 1-hydroxynaphthalene-2-carbaldehyde to produce the ligand [H₂L] [2-(2-(naphthalen-5-yl) diazenyl)-4-(2-hydroxynaphthalen-3-yl)methyleneamino)-3-hydroxy naphthalene-1-sulfonic acid]. The ligand was characterized by FT-IR, U.V, ¹HNMR, ¹³CNMR spectroscopy. This work also included the preparation of complexes through reaction of ligand with salts of [Cr^{III}, Mn^{II} and Fe^{II}] ions, under reflux, using ethanol as a solvent, and KOH as a base. These complexes were characterized by IR and U.V-vis spectroscopy, atomic absorption (A.A), chloride content along with conductivity, and melting point measurements. Finally thermal analysis was used to confirm the presence of crystallized H₂O molecule in the complexes structure. The formula proposed for Cr complex: K[M(L)₂].H₂O, while Mn and Fe complexes have the K₂[M(L)₂].H₂O formula. The biological activity of the prepared compounds was studied.

INTRODUCTION

Schiff bases and their metal complexes have been prepared because of their interesting and important properties, e.g., ability to bind toxic and heavy metal atoms, undergo tautomerism, exhibit catalytic reduction and photochromism[1]. Azo compounds have long been used in industry because of their versatile applications in various fields and high

technology areas, including dyes for different materials, lasers, liquid crystalline[2]. One of the many applications of azo compounds is in optical data storage in other words; the thermal properties and suitable absorption band of azo compounds are essential features in relation to their application as high-density optical recording materials [3]. Sulfonated azo dyes are the most numerous of the manufactured synthetic dyes [4]. Azo Schiff bases complexes contain both azo and azomethine groups. Azo Schiff bases are commonly synthesized by coupling a diazonium reagent with an aromatic aldehyde to form an azo aldehyde[5]. In this work we reported the synthesis and characterization of new Azo linked Schiff base and its some metal complexes, the biological activity of the prepared compounds was studied.

MATERIALS AND METHODS

An electrothermal apparatus stuart melting point was used to measure the melting points. Infrared spectra were performed using FT-IR Testscan Shimadzu (FT-IR)- 8300 series spectrophotometer in the range (4000– 400 cm⁻¹). Spectra were recorded as potassium bromide discs at college of education Ibn- Al- Haitham/ Baghdad University. The electronic spectra of the compounds were obtained using (U.V-Vis) spectrophotometer SP-3000 plus type Optima, in the range (1100– 200 nm) using quartz cell of (1.0) cm length with concentration (10⁻³) mole L⁻¹ of samples in DMSO at 25°C. Electrical conductivity measurements of the complexes were recorded at (25 °C) for (10⁻³–10⁻⁵) M solutions of the samples in DMSO using Eutech 150 conductivity meter. ¹HNMR, ¹³CNMR Spectra for the ligand and complex were recorded in DMSO-d₆ using Bruker, model: ultra shield 300 MHz, origin: Switzerland and are reported in ppm (s), at Al – Bayt University, Jordan.

Perkinelmer instruments SII, Diamond TG/DTA, Thermogravimetric/ Differential thermal analyzer in Sulaymaniyah University Sulaymaniyah, Iraq was used to confirm the presence of H₂O molecule in the complex formula

Synthesis of the precursor 2-(2-(naphthalen-5-yl)diazenyl)-4-amino-3-hydroxynaphthalene-1-sulfonic acid

This compound was prepared as described in the literature [6,7]. A mixture of 1-naphthyl amine (1.43g, 10.00 mmol) in water (10 mL) and concentrated hydrochloric acid (2.62 mL, 30.00 mmol) was stirred until a clear solution was obtained.

The mixture was cooled to 0– 5°C and a solution of sodium nitrite (0.76g, 11.00 mmol) in water (5 mL) were then added dropwise, maintaining the temperature below 5°C. The resulting mixture was stirred for an additional 1h in an ice bath and then a little urea was added and was buffered (pH 6–7) with solid sodium acetate (solution 1).

1-Amino-2-naphthol-4-sulfonic acid (2.4g, 10.00 mmol) was dissolved in 10 mL aqueous NaOH (10 mmol) solution, cooled to 0 - 5°C in an ice bath (solution 2). The solution was then gradually added to cooled solution 1, and the resulting mixture was continually stirred at 0- 5°C for 2 hrs., the resulting crude precipitate was filtered by acidification and washed several times with cold water. Yield 71%, m.p(292°C dec.).

Synthesis of the ligand [H₂L]

To (2.74 g, 6.96 mmol) of the precursor [W] dissolved in 25 mL of methanol, it was added (1.20 g, 6.97 mmol) of 2-hydroxy-1-naphthaldehyde in 10 mL of methanol with a few drops of glacial acetic acid as a catalyst, refluxed for 2 hrs., then left at room temperature extended to 15 minutes, filtered off, the precipitate was collected with 10 mL of cold dry methanol. Yield 52%, m.p(262°C dec.).

Synthesis of the complex K[Cr(L)₂].H₂O (1)

To a solution of (0.40 g, 0.73 mmol) from the ligand (H₂L) dissolved in (40 mL) of ethanol, it was added (0.082 g, 1.461 mmol) of potassium hydroxide dissolved in 10 mL ethanol with stirring and heating then (0.097 g, 0.364 mmol) of chromium (III) chloride hexahydrate dissolved in 10 mL ethanol was added to ligand solution. The resulting mixture were refluxed for 2 hrs., the product was filtered off, washed with absolute ethanol and recrystallized in ethanol. Yield 50%, m.p(over 320 °C dec).

Synthesis of the complex K₂[Mn(L)₂].H₂O (2), K₂[Fe(L)₂].H₂O (3)

A similar method to that mentioned in preparation of Cr^{III} complex was used to prepare the complexes of [H₂L] with [Mn^{II} and Fe^{II}], ions. Table (1) shows the physical properties of the complexes.

Biological activity

Antibacterial activity of the synthesized ligand [H₂L] and its complexes were tested utilizing the agar diffusion technique. The organism tested were *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Candida albicans*. The agar media were inoculated with test organisms and a solution of the tested compound (100 µg/ml) was placed separately in cups (6 mm diameter) in the agar medium. The inhibition zones were measured after 24 hours incubation. Separate studies were carried out with the solution alone of DMSO and showed no activity against any organism.

RESULTS AND DISCUSSION

Potentially tridentate new acyclic ligand type ONO donor atoms have been synthesized. The ligand contains two labile protons [H₂L] and by removing these protons an anionic (-2) tridentate system is formed. The ligand [H₂L] was synthesized by the condensation reaction of precursor [W] with 1-hydroxynaphthalene-2-carbaldehyde in 1:1

molar ratio using methanol as a solvent according to the general route shown in Scheme (1).

The ¹H-NMR spectrum of [H₂L] is shown in Fig. (1), the spectrum showed the broad signal at (δ=4.6 ppm) may be due to OH proton of sulfonic acid group[8]. The multiplet signal at (δ=7.3– 8.8 ppm) range could be assignable to protons of aromatic rings[1]. The singlet signal at chemical shift (δ=9.9 ppm) can be attributed to the proton of the azomethine group (N=C–H)[9]. The signal at (δ=10.7 ppm) may be considered to the OH proton in the carbaldehyde ring because of intramolecular hydrogen bonding with the nitrogen atom on the naphthalene ring[1]. The naphtholic OH proton chemical shift was observed weakly at (δ=16.2 ppm) because of the tautomerization of the azo- linked Schiff base compounds[10]. These data support the formulation of the isolated azo-linked Schiff base. The data of ¹H-NMR of ligand(H₂L) are summarized in Table (2).

The ¹³C-NMR spectrum of [H₂L], Fig. (2) in DMSO–d⁶ solvent shows the multiplet chemical shifts at (δ= 118.8–129.7 ppm) range could be assignable to C–C aromatic. The chemical shifts at the range (δ=136.6– 145.2 ppm) can be attributed to C–S, C–O, C–N and C–C groups.

The chemical shift at (δ=162.1 ppm) can be attributed to C=C of aromatic rings. The chemical shift at (δ=169.5 ppm) can be attributed to the azomethine group C=N. The naphtholic carbonyl group C=O resulted from the tautomerization in the azo- linked Schiff base compounds observed around (δ=193 ppm)[11]. The data of C¹³NMR of ligand (H₂L) are summarized in Table (3).

I.R. spectrum of ligand and complexes

I.R. spectrum for ligand [H₂L], Fig. (3), displayed a broad band at (3442.9) cm⁻¹ may due to interference of the two OH phenolic groups[12,13,14]. On the other hand the spectrum displayed band of weak intensity at (2926) cm⁻¹, this band was ascribed of intramolecular hydrogen bonding (OH...N) group[15]. The bands at [1624, 1211] cm⁻¹ can be attributed to stretching of (C=N) imine and (C–N) groups respectively. The appearance of imine (C=N) band and the disappearance of amine (NH₂) band in the spectrum, confirms the formation of Schiff base legend[16,17,18]. The spectrum showed band at (1466) cm⁻¹ can be attributed to (N=N) azo group[8], while the two bands at (1396 and 1348) cm⁻¹ may be referred to (C–O)_{car.} and (C–O)_{naphth.} Stretching[19].

Finally the spectrum showed bands at (1188 and 1051) cm^{-1} can be attributed to the $\nu_{\text{asy}}(\text{SO}_3\text{-H})$, $\nu_{\text{sym}}(\text{SO}_3\text{-H})$ respectively[20]. The characteristic bands are summarized in Table (4).

The I.R. spectra for complexes Cr, Mn and Fe are shown in Figs. (4), (5) and (6) respectively. The band at (1624) cm^{-1} which referred to $\nu(\text{C}=\text{N})$ of imine group in the free ligand were shifted to lower frequency and appeared at (1618), (1612) and (1614) cm^{-1} for complexes Cr, Mn and Fe respectively.

The shift to lower frequency can be attributed to the coordination of the iminic nitrogen to the metal atom[21,22,23]. This feature can be explained by the transfer of electrons from the nitrogen to the metal ion due to coordination. The shift to lower frequency may be due to delocalization of metal electron density into the ligand π -system[24,25] (HOMO \rightarrow LUMO), (where HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital). The band at (1466) cm^{-1} which referred to $\nu(\text{N}=\text{N})$ azo compound in the free ligand notes, in the infrared spectra of the complexes did not present any frequency shift and appeared at (1458), (1456) and (1460) cm^{-1} for complexes Cr, Mn and Fe respectively, which may be explained by non-participation of azo nitrogen atoms in complex formation[15], because the azo and azomethine groups on azo Schiff base ligands are oriented in such a way that coordination of both groups to a metal ion is not possible thus, preferential coordination of the azomethine group while the azo group is left free and uncoordination has been observed[21,26-28].

On the other hand the two bands at (1396 and 1348) cm^{-1} referred to $\nu(\text{C}-\text{O})$ of 2-hydroxy-1-naphthaldehyde and 1-amino-2-naphthol-4-sulfonic acid in the free ligand is shifted to lower frequency and appeared at (1389, 1339); (1339, 1320) and (1373, 1327) cm^{-1} for complexes Cr, Mn and Fe respectively. The shift in $\nu(\text{C}-\text{O})$ confirming the coordination of the ligand through oxygen atoms of the two phenolic groups to the metal[29,30]. The spectra of complexes revealed a broad band at (3419, 3441 and 3447) cm^{-1} can be attributed to $\nu(\text{OH})$ which indicates OH group of the adsorbed water molecules [1]. Finally the spectra showed new bands at [521, 457 and 422]; [519, (488 and 444)] and [534, 492 and 473] cm^{-1} can be refer to $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{O})_{\text{car}}$. and $\nu(\text{M}-\text{O})_{\text{naphth}}$. for complexes Cr, Mn and Fe respectively.

The new bands supported the coordination of the ligand to the metal centre through imin group nitrogen and phenolic oxygen atoms. These results are supported by several reports [31,32]. The characteristic bands are summarized in Table (4).

Electronic spectra of ligand and complexes

The (U.V-vis) spectrum for [H₂L], Fig. (7), shows bands of shortest wave length presenting at (245 nm) (40816 cm⁻¹) (ϵ_{\max} =608 molar⁻¹ cm⁻¹) and (265 nm) (37736 cm⁻¹) (ϵ_{\max} =2351 molar⁻¹ cm⁻¹) may assigned to π - π^* transition of the aromatic rings of azo-linked Schiff base ligand[1]. The band at (305 nm) (32787 cm⁻¹) (ϵ_{\max} =1288 molar⁻¹ cm⁻¹) may assigned to the imine π - π^* or n- π^* transition and this absorption assigned in the keto amine quinoid tautomer forms of the azo-linked Schiff base ligand[33,34].

Finally the band at the range (423 nm) (23641 cm⁻¹) (ϵ_{\max} =1204 molar⁻¹ cm⁻¹) in the ligand spectrum may be attributed to the azo group (N=N)(35). The absorption data of the ligand are given in Table(4).

Figs. (8), (9) and (10) show the (U.V-Vis) spectra of the complexes Cr, Mn and Fe respectively. Table (5) summarized the absorption peaks of the complexes. In each case the spectrum showed intense peaks in the (U.V) region at (240 nm) (41667 cm⁻¹) (ϵ_{\max} =861 molar⁻¹ cm⁻¹), (270 nm) (37037 cm⁻¹) (ϵ_{\max} =2520 molar⁻¹ cm⁻¹); (245 nm) (40816 cm⁻¹) (ϵ_{\max} =2111 molar⁻¹ cm⁻¹), (265 nm) (37736 cm⁻¹) (ϵ_{\max} =744 molar⁻¹ cm⁻¹) and (240nm) (41667 cm⁻¹) (ϵ_{\max} =821 molar⁻¹ cm⁻¹), (260 nm) (38462 cm⁻¹) (ϵ_{\max} =2820 molar⁻¹ cm⁻¹) for complexes Cr, Mn and Fe respectively, can be assigned to π - π^* transition of the aromatic rings[1]. While the band at (305 nm) in the free ligand shifted to longer wave lengths in the complexes and appeared at (315 nm) (31746 cm⁻¹) (ϵ_{\max} =1307 molar⁻¹ cm⁻¹), (310 nm) (32258 cm⁻¹) (ϵ_{\max} =2047 molar⁻¹ cm⁻¹) and (325nm) (30769 cm⁻¹) (ϵ_{\max} =1354 molar⁻¹ cm⁻¹) for complexes Cr, Mn and Fe respectively as a consequence of coordination when binding with a metal, confirming the imine nitrogen was coordinated to the metal atom[36].

The bands at (347 nm) (28818 cm⁻¹) (ϵ_{\max} =1170 molar⁻¹ cm⁻¹), (370 nm) (27027 cm⁻¹) (ϵ_{\max} =1189 molar⁻¹ cm⁻¹) and (350 nm) (28571 cm⁻¹) (ϵ_{\max} =1250 molar⁻¹ cm⁻¹) for complexes Cr, Mn and Fe

respectively may assigned to M→L charge transfer transition for the complexes[1].

The N=N band of the free ligand at (423 nm) (23641 cm⁻¹) (ϵ_{\max} =1204 molar⁻¹ cm⁻¹) did not shift in the corresponding metal complexes and appeared at (421 nm) (23753 cm⁻¹) (ϵ_{\max} =680 molar⁻¹ cm⁻¹), (422 nm) (23697 cm⁻¹) (ϵ_{\max} =800 molar⁻¹ cm⁻¹) and (425 nm) (23529 cm⁻¹) (ϵ_{\max} =995 molar⁻¹ cm⁻¹) for complexes Cr, Mn and Fe respectively, which reveals that the diazo group didn't participate in complex formation, therefore it was concluded from the electronic spectra that the azo-linked Schiff base ligand coordinated to the metal

atom through the carbaldehydic and naphtholic oxygen beside the imine nitrogen[1].

Finally the bands in the visible region can be associated with d-d transitions.

The Cr^{III} complex shows a band at (626 nm) (15974 cm^{-1}) ($\epsilon_{\text{max}}=630\text{ molar}^{-1}\text{ cm}^{-1}$) and (825 nm) (12121 cm^{-1}) ($\epsilon_{\text{max}}=10\text{ molar}^{-1}\text{ cm}^{-1}$) assignable to ${}^4\text{A}_{2g(\text{F})}\rightarrow{}^4\text{T}_{2g(\text{F})}$ and ${}^4\text{A}_{2g}\rightarrow{}^2\text{T}_{1g(\text{G})}$, ${}^4\text{E}_{2g(\text{G})}$ suggesting distorted octahedral geometry around Cr^{III} ion[37-39].

The Mn^{II} complex shows a band at (525 nm) (19048 cm^{-1}) ($\epsilon_{\text{max}}=520\text{ molar}^{-1}\text{ cm}^{-1}$) and (555 nm) (18018 cm^{-1}) ($\epsilon_{\text{max}}=430\text{ molar}^{-1}\text{ cm}^{-1}$) assignable to ${}^6\text{A}_{1g(\text{S})}\rightarrow{}^4\text{T}_{1g(\text{G})}$, ${}^4\text{T}_{2g(\text{G})}$ and suggesting distorted octahedral geometry around Mn^{II} ion[37,93,40].

The Fe^{II} complex shows a band at (510 nm) (19608 cm^{-1}) ($\epsilon_{\text{max}}=500\text{ molar}^{-1}\text{ cm}^{-1}$) assignable to ${}^5\text{T}_{2g}\rightarrow{}^5\text{E}_g$ suggesting distorted octahedral geometry around Fe^{II} ion[41].

Thermal analysis

To understand thermal decomposition process, azo-linked Schiff base ligand and their metal complexes were examined by thermogravimetric analysis in the temperature range of (50.0–500.0) C°. The obtained thermoanalytical results from TG curves for all these compounds are given in Table (6).

All the complexes lost adsorbed water at the range (92.31–96.43) C°. The thermographs of the tested complexes show in Fig.(11). Comparison of ligands and the complexes shows that the complexes were more thermally stable[1,42].

Conductance

The molar conductance of the complexes in (DMSO) is summarized in Table (7). The molar conductance of complexes Mn and Fe were in the range (70.6– 75.3) S.cm².mole⁻¹, indicating the 1:2 electrolyte nature. While the conductance of the complex Cr was (30.4) S.cm².mole⁻¹, indicating the 1:1 electrolyte nature.

Biological activity for the ligand and some of its complexes

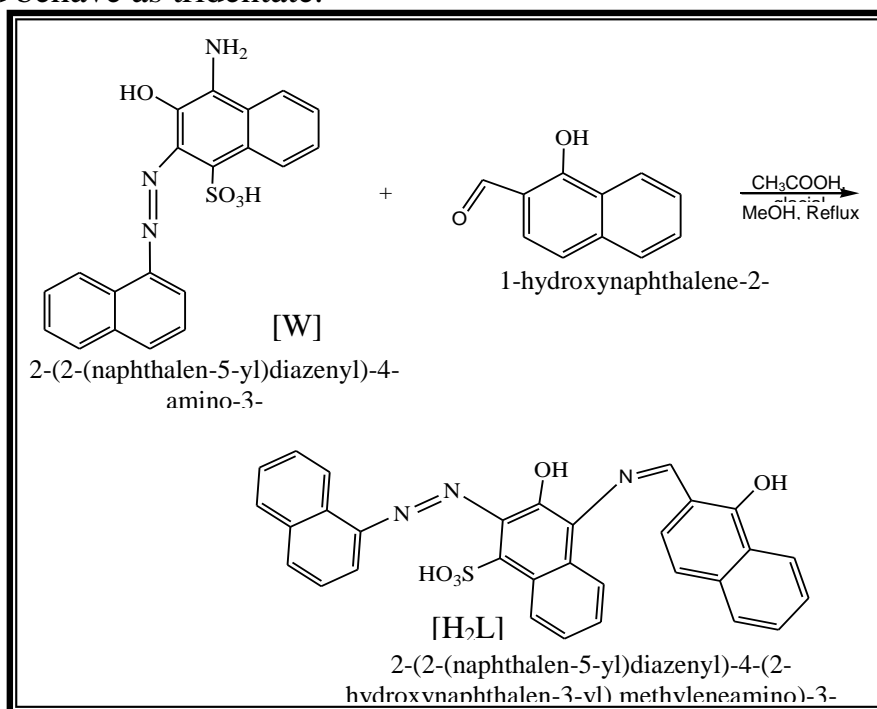
The biological activity of the ligand H₂L and some of its complexes were studied by using inhibition method[43-46] for four types of pathogenic bacteria and Candida albicans fungi. Two type of bacteria was gram positive which is *staphylococcus aureu* and *Bacillus subtilis*, the Second two was gram negative which is *escherichia coli* and *psedomonas Aeruginosa*.The results shows the ligand show inhibition diameter against Escherichia Coli, Cr-complex show inhibition diameter against *Pseudomonas aeruginosa*, Mn-complex show inhibition

diameter against *Staphylococcus aureus*, Fe-complex show inhibition diameter against *Bacillus subtilis*, Table (8), this may be due to that the chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelate ring such, chelation could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane[47]. The ligand and complexes didn't show any antifungal activity against *Candida albicans*.

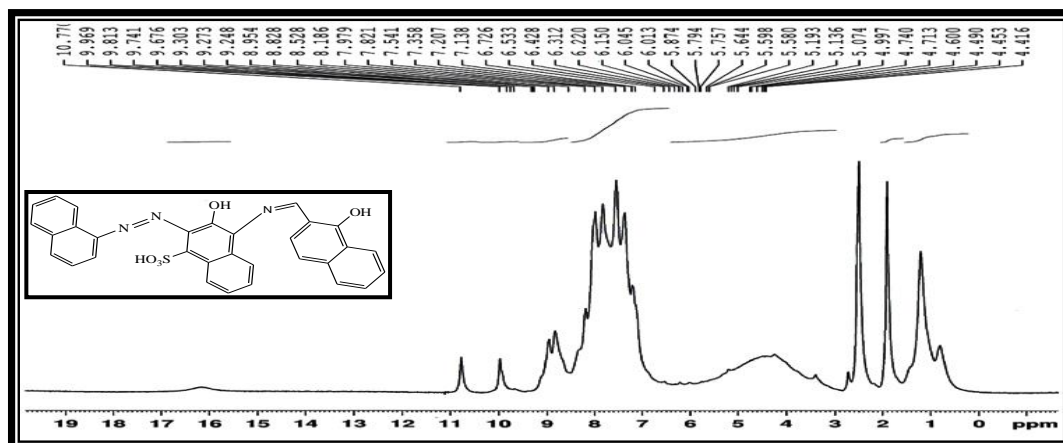
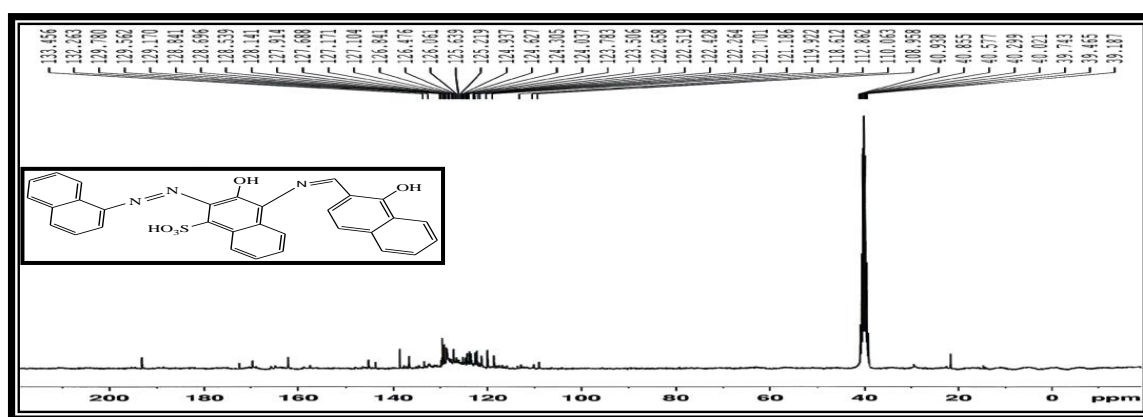
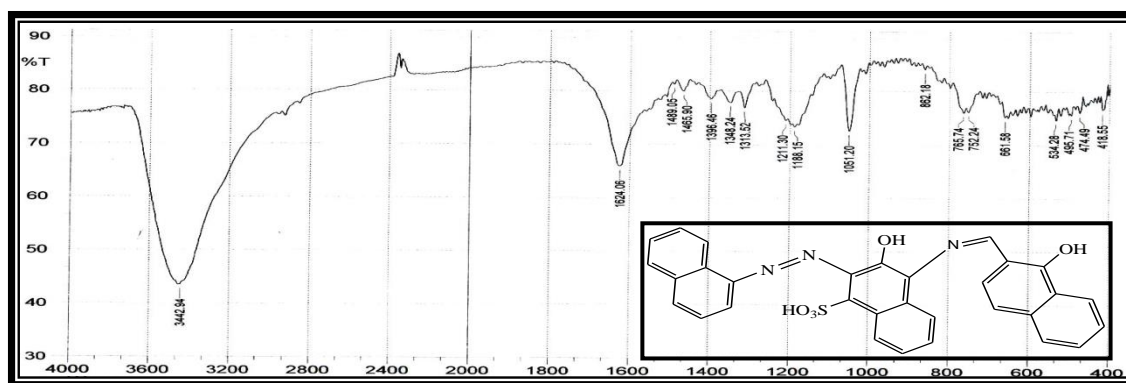
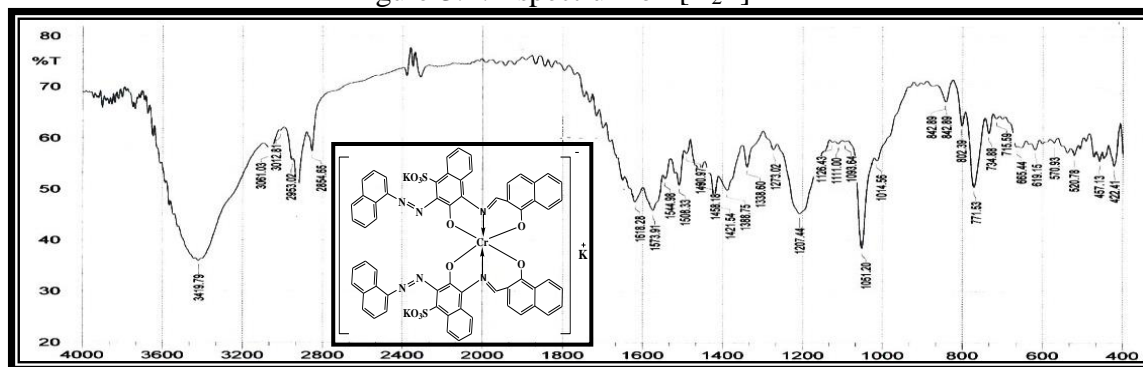
Figs. (12) show the inhibition zone against the bacteria for the ligand and complexes and Fig. (13) show the inhibition zone against fungi for the ligand and complex.

CONCLUSIONS

We have prepared new Schiff base ligand containing azo groups via condensation reactions between diazo compounds and 2-hydroxy-1-naphthaldehyde. The satisfactory analytical data and the instrumental studies suggest the complexes are of the general formula $K_m[M(L)_2].H_2O$ where M is chromium(III), manganese(II), or iron(II). According to the UV-Vis and infrared data, the azo-linked Schiff base ligand coordinated to the metal atom through the 2-hydroxy-1-naphthaldehyde ring oxygen, the naphtholic oxygen, and the imino nitrogen. The infrared, UV-Vis, studies suggest that the azo-methine nitrogen and deprotonated oxygen atoms of the ligand are coordinated and covalently bonded, respectively, to metal atoms. The ligand behave as tridentate.



Scheme (1) Synthesis route of the ligand(H₂L)

Figure-1: $^1\text{H-NMR}$ spectrum for the ligand $[\text{H}_2\text{L}]$ in DMSO-d_6 Figure-2: $^{13}\text{C-NMR}$ spectrum for the ligand $[\text{H}_2\text{L}]$ in DMSO-d_6 Figure-3: I.R spectrum of $[\text{H}_2\text{L}]$ Figure-4: I.R spectrum of $\text{K}[\text{Cr}(\text{L})_2]\cdot\text{H}_2\text{O}$

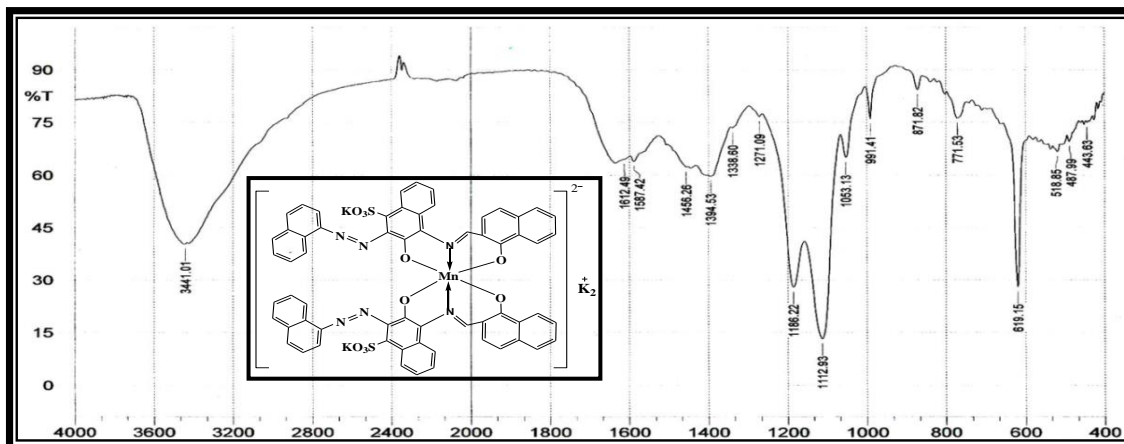


Figure-5: I.R spectrum of K₂[Mn (L)₂].H₂O

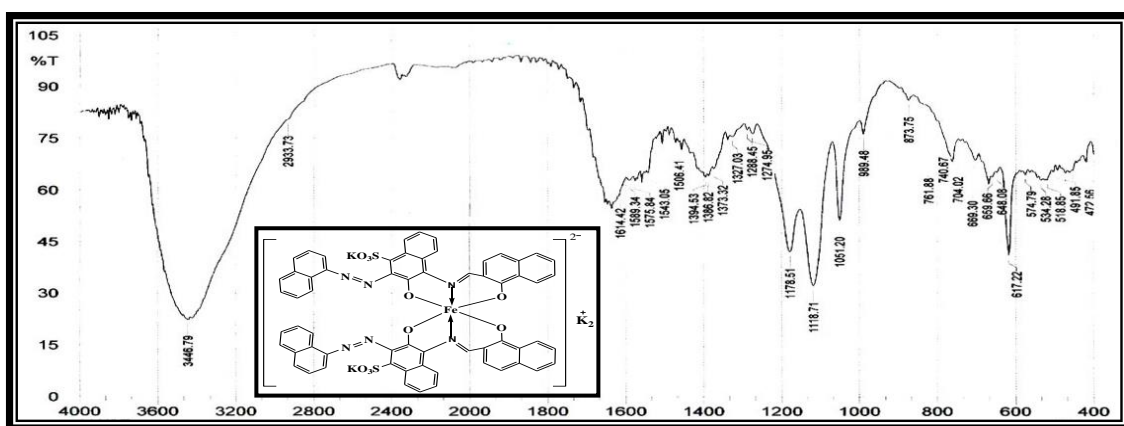


Figure-6: I.R spectrum of K₂[Fe (L)₂].H₂O



Figure-7: I.R spectrum of K₂[Fe (L)₂].H₂O

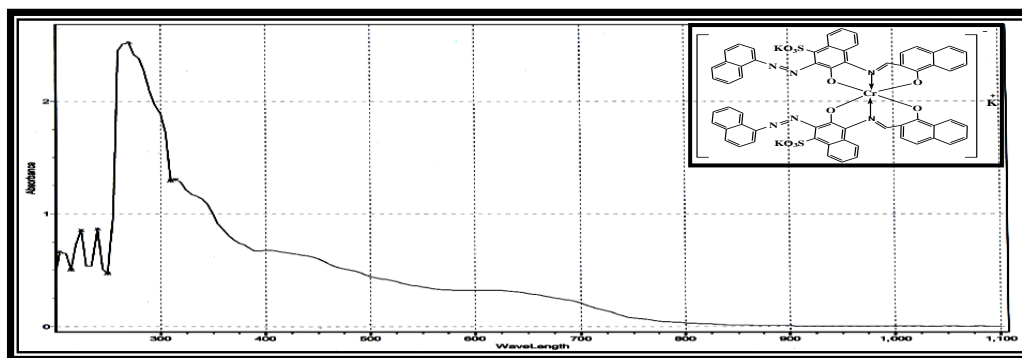


Figure-8: Electronic spectrum of ligand [H₂L]

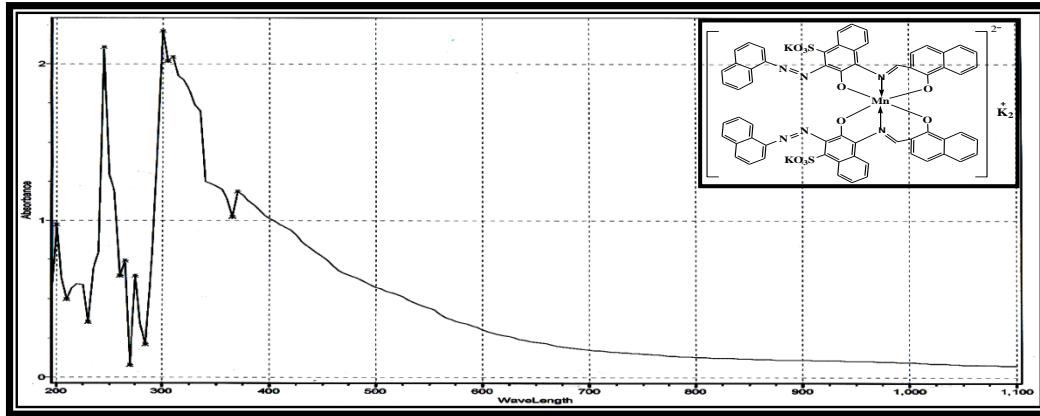


Figure-9: Electronic spectrum of $K[Cr(L)_2].H_2O$

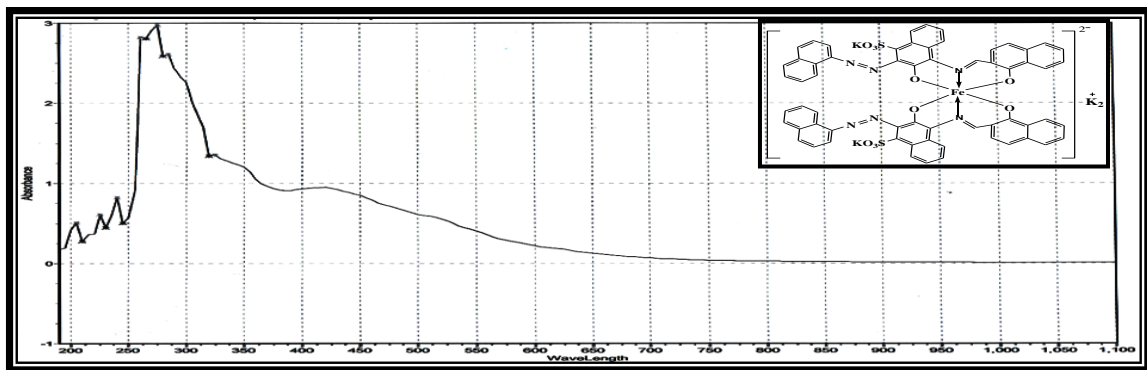


Figure-10: Electronic spectrum of $K_2[Mn(L)_2].H_2O$

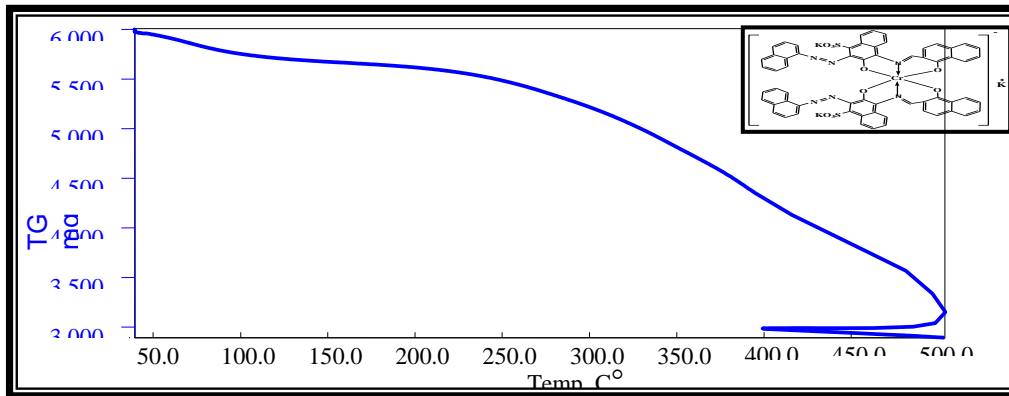


Figure-11: Thermogram of $K[Cr(L)_2].H_2O$



Fig.-12: The effect of synthesized compounds $[H_2L]$, $K[Cr(L)_2].H_2O$, $K_2[Mn(L)_2].H_2O$, $K_2[Fe(L)_2].H_2O$ on *Staphylococcus aurea*

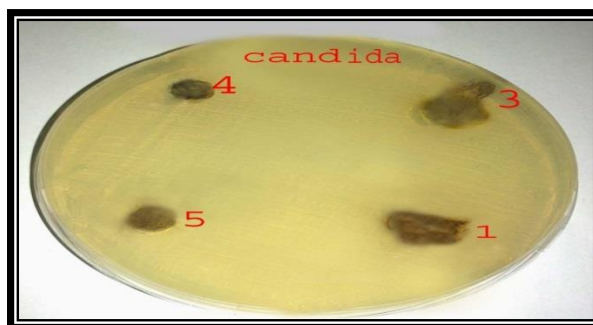


Fig.-13: The effect of synthesized compounds [H₂L], K [Cr(L)₂].H₂O, K₂[Mn(L)₂].H₂O, K₂[Fe(L)₂].H₂O on *Candida albicans*

Table-1: Some physical properties of the prepared [H₂L] complexes and their reactant quantity

Empirical formula	Color	m.p. °C	Wt of metal salt (g)	Wt of product (g)	Yield %
K[Cr(L) ₂].H ₂ O	Dark olivy	> 320 Dec.	0.097	0.47	50
K ₂ [Mn(L) ₂].H ₂ O	Brown	> 320 Dec.	0.036	0.23	47
K ₂ [Fe(L) ₂].H ₂ O	Dark green	> 320 Dec.	0.036	0.23	47

Dec. = Decomposition

Table-1: ¹H-NMR data for [H₂L] measured in DMSO-d₆ and chemical shift in ppm (δ)

Compound	Funct. Group	δ (ppm)
H ₂ L	O-H [sulfonic group]	4.6 (1H, br)
	Ar - H	(7.3– 9.0) (17H, m)
	N=C - H	(8.8) (1H, S)
	O - H	(10.7) (1H, S)

S= singlet, m= multiplet, br= broad

Table-2: ¹³C NMR data for [H₂L] measured in DMSO-d₆ and chemical shift in ppm (δ)

Compound	Funct. Group	δ (ppm)
H ₂ L	C-C aromatic	118.8 – 129.7
	C-S, C-O, C- N and C-C	136.6 – 145.2
	C=C aromatic	162.1
	C=N	169.5
	C=O [naphtholic]	193

Table-3: Infrared spectral data (wave number ν⁻) cm⁻¹ of the ligand and its metal complexes

Cmpound	ν(OH) broad	ν(C=N)	ν(N=N)	ν(C-O) _{car.} ν(C-O) _{naph.}	ν(M-N)	ν(M-O)
H ₂ L	3443 (br)	1624(s)	1466 (m)	1396 (m) 1348 (m)	-	-
K[Cr(L) ₂].H ₂ O	3419 (br)	1618 (s)	1458 (m)	1389 (m) 1339 (m)	521 (m)	457 (m) 422 (m)
K ₂ [Mn(L) ₂].H ₂ O	3441(br)	1612 (m)	1456 (w)	1339 (w) 1320(w)	519 (w)	488 (w) 444 (w)
K ₂ [Fe(L) ₂].H ₂ O	3447 (br)	1614 (m)	1460(w)	1373 (m) 1327(w)	534 (w)	492 (w) 473 (w)

m=medium, W=weak, S=strong, br=broad

Table-4: Electronic spectral data of the ligand [H₂L]

Compound	λ (nm)	ν^{-1} cm ⁻¹	ϵ_{\max} molar ⁻¹ cm ⁻¹	Assignments
[H ₂ L]	245	40816	608	$\pi \rightarrow \pi^*$
	265	37736	2351	
	305	32787	1289	$n \rightarrow \pi^*$
			1288	$\pi \rightarrow \pi^*$
	423	23641	1204	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$

Table-5: Electronic spectral data of metal complexes

Compound	Wave number		ϵ_{\max} molar ⁻¹ cm ⁻¹	Assignment	Suggested structure
	Nm	Cm ⁻¹			
K[Cr(L) ₂].H ₂ O	240	41667	861	$\pi - \pi^*$	Octahedral
	270	37037	2520		
	315	31746	1307	$n - \pi^*$ $\pi - \pi^*$	
	347	28818	1170	Charge transfer	
	421	23753	680	$n - \pi^*$	
	626	15974	630	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$	
	825	12121	10	${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$	
K ₂ [Mn(L) ₂].H ₂ O	245	40816	2111	$\pi - \pi^*$	Octahedral
	265	37736	744		
	310	32258	2047	$n - \pi^*$ $\pi - \pi^*$	
	370	27027	1189	Charge transfer	
	422	23697	800	$n - \pi^*$	
	525	19048	520	${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G), {}^4T_{2g}(G)$	
K ₂ [Fe(L) ₂].H ₂ O	240	41667	821	$\pi - \pi^*$	Octahedral
	260	38462	2820		
	325	30769	1354	$n - \pi^*$ $\pi - \pi^*$	
	350	28571	1250	Charge transfer	
	425	23529	995	$n - \pi^*$	
	510	19608	500	${}^5T_{2g} \rightarrow {}^5E_g$	

Table-6: Thermal decomposition data of the azo linked Schiff base and the metal complexes

Compounds	Mass loss temp./°C	Mass loss Theoretically	Mass loss Practically
K[Cr(L) ₂].H ₂ O	92.31	0.085	0.21
K ₂ [Mn(L) ₂].H ₂ O	96.15	0.108	0.21
K ₂ [Fe(L) ₂].H ₂ O	95.83	0.100	0.057

Table-7: The molar conductivity of the complexes

No. Compound	Compound	Λ_m S.cm ² molar ⁻¹	Ratio
1	K[Cr(L) ₂].H ₂ O	30.4	1:1
2	K ₂ [Mn(L) ₂].H ₂ O	75.3	1:2
3	K ₂ [Fe(L) ₂].H ₂ O	70.6	1:2

Table -8: Inhibition circle diameter in millimeter for the ligand and some complexes

No.	Compounds	<i>Staphylococcus aureu</i>	<i>Pseudomonas aeruginosa</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Candida albicans</i>
1	L	–	–	–	+++	–
2	K ₂ [Cr(L) ₂].H ₂ O	–	++++	–	–	–
3	K ₂ [Mn(L) ₂].H ₂ O	+	–	–	–	–
4	K ₂ [Fe(L) ₂].H ₂ O	–	–	++	–	–

Where:(-):no effect, (+):1-5 ,(++):6-10 ,(+++):11-15,(++++):16-20 mm

REFERENCES

1. E. Erdem, E.Y. Sari, R. Kiliñarslan and N. Kabay, Trans. Met. Chem., 34, 167-174, (2009).
2. S. Yazici, C. Albayrak, I. E. Gümrükçüoğlu, I. Şenel and O. Büyükgüngör, Turk J. Chem., 35, 341-347, (2011).
3. K. Nejati, Z. Rezvani and M. Seyedahmadian, J. Dyes and Pigments, 83, 304-311, (2009).
4. M.B. Pasti-Grigsby, A. Paszczynski, S. Goszczynski, D.L. Crawford and R.L. Crawford, J. Appl. Environ. Microbiology, 58, 11, 3605-3613, (1992).
5. R.A. Ahmadi and S. Amani, J. Molecules, 17, 6434-6448, (2012).
6. H. Kocaokutgen and E. Erdem, Synth. React. Inorg. Met-Org. Chem., 34-1843, (2004).
7. KY. Law, IW. Tarnawskyj and PT. Lubberts, Dyes Pigment, 23-243, (1993).
8. Swati, P. Singh, R. Karnawat, I.K. Sharma and P.S. Verma, Int. J. Chem. Tech. Res., 3, 3, 1164-1171, (2011).
9. N. Sarikavakli and G. Irez, Turk. J. Chem., 29, 107-115, (2005).
10. M. Tunçel and S. Serin, Synth. React. Inorg. Met-Org. Nano-Met. Chem., 35-203, (2005).
11. H.A.H. Al-Salehy "Ph.D. Thesis", University of Baghdad College of Education (Ibn-Al-Haitham), (2006).
12. F. Karipcin and E. Kabalcilar, Acta. Chim. Slov., 54, 242-247, (2007).
13. V.M. Parikh, "Absorption spectroscopy of Organic Molecules", Translated By Abdul Hussain Khuthier, Jasim, M.A., Al-Rawi, and Mahammed A. Al-Iraqi, (1985).
14. M. Tunçel and S. Serin, Trans. Met. Chem., 31, 805-812, (2006).
15. R.M. Silverschtien, Bassler and Morrill, "Spectrophotometers Identification of Organic Compound", Translated by Ali Hussain and Suphi Al-Azawi, (1981).
16. J. Sanmartim, M.R. Bermejo, A.M. Garcia Deibe and I.M. Rivas, J. Chem. Soc. Dalton Trans., 4174-4181, (2000).
17. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley, New York, 232, (1978).

- 18.S. Aime, M. Bottaand and U. Casellato, *Inorg. Chem.*, 34, 5825, (1995).
19. A.A. Khandar, Z. Rezvani, K. Nejati, A.I. Yanovsky and J.M. Martinez, *Acta. Chim. Slov.*, 49, 733-741, (2002).
- 20.L.A.R. Al-Rubaie and R. J. Mhessn, *E-J. Chem.*, 9, 1, 465-470, (2012).
- 21.K. Nejati and Z. Rezvani, *New J. Chem.*, 27, 1665-1669, (2003).
- 22.M. Mikuraya, T. Sasaki, A. Anjiki, S. Ikenoue and T. Tokh, *Bull Chem. Soc. Jpn.*, 65-334, (1992).
- 23.M. Lee, YS. Yoo and MG. Chol, *Macromolecules*, 32-2777, (1999).
- 24.R.K. Agrawal, S. Prasad and N. Gahlot, *Twk.J.Chem.*28 (2004
- 25.A.E. Al-Janabi, "M.Sc. Thesis", University of Baghdad, (2005).
- 26.A. Khandar, K. Nejati, *Polyhedron*, 19, 607–613, (2000).
- 27.A.A. Khandar, Z. Rezvani, K. Nejati and I. Yanovsky, J.M. Martines, *Acta. Chim. Slov.*, 49, 733–741, (2002).
- 28.A.A. Khandar, K. Nejati and Z. Rezvani, *Molecules*, 10, 302–311, (2005).
- 29.M. Tumer, C. Celik, H. Koksall and S. Serin, *Trans. Met. Chem.*, 24, 525, (1999).
- 30.M. Tumer, H. Koksall, S. Serin and M. Digrak, *Trans. Met. Chem.*, 24, 13, (1999).
- 31.A.W. Addison, T.N. Rao and E. Sinn, *Inorg. Chem.*, 23, 1957-1967, (1984).
- 32.C. Preti and G. Tosi, *Can J. Chem.*, 55, 1409, (1977).
- 33.H. Colchoubian, WL. Waltz and JW. Quail, *Can .J .Chem.*, 37-77, (1999).
- 34.JW. Ledbetter, *J. Phys. Chem.*, 70-2245 , (1966).
- 35.R.M. Silverschtien, Bassler and Morrill, "Spectrophotometers Identification of Organic Compound", Translated by Ali Hussain and Suphi Al-Azawi, (1981).
- 36.W. Guangbin, *Spectrosc Lett* , 32-1061, (1999).
- 37.A.B.P. Lever, *Inorganic Electronic Spectroscopy*, second ed., Elsevier Publishing, New York, (1984).
- 38.D. Sutton, *Electronic Spectra of Trans. Met. Complex*, first ed., McGraw-Hill Public Co. Ltd., New York, (1969).
- 39.E.J.Waheed , "M.Sc. Thesis", University of Baghdad College of Education (Ibn-Al-Haitham), (2008).
- 40.A. Shrivastav, N.K. Singh and S.M. Singh, *Biometals*, 16, 2, 311-320, (2003).
- 41.G. Pandey and K.K. Narang, *Synth. React. Inorg. Met-Org. Chem.*, 34, 291-311, (2004).

42. Q. Chemn, M-H. Zeng, L-Q. Wei, M. Kurmoo, *Chem. Mater.*, 22, 4328-4334, (2010).
43. J.R. Anaconda, *J. Coord. Chem.*, 54, 355– 365 (2006).
44. D. Petra, Z. Tatjano and P. Boriset. *J. inorg. Bio. chemistry*, 99, 2, 432– 442, (2005).
45. S. C. Tauber and R. Nau, “Immunomodulatory properties of antibiotics”, *Current molecular pharmacology*, 1, 68–79, (2008).
46. N. Sultana and M. S. Arayne, *Pakistan J. pharma. Sci.*, 20, 4, 305– 310, (2007).
47. H.N. Aliyu, U. Sani and A. Galadima, *European J. Sci. Res.*, 59, 2, 276-283, (2011).