Synthesis, Characterization and Antibacterial Studies of 4-Amino-3-hydroxyn- aphthalene -1-sulphoric acid Derivate Chelates of Cr(III), Mn(II), Co(II) and Cu(II) Complexes

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ABSTRACT: Metal complexes of Cr(III), Mn(II), Co(II) and Cu(II) with the Schiff base derived from 4-(1-(naphthalene-3-yl)ethyleneamino(3-hydroxnaphthalene-1-sulfonic acid have been prepared and characterized on the basis of physical characteristics, micro-analytical data, molar conductivity, magnetic moment measurements, ^{1}H-NMR, IR and UV-Vis spectrum data. The elemental analysis data showed the isolated complexes 1:1 [M:L] ratio. The obtained molar conductance values revealed the complexes of $[Mn(L)(H_2O)_3Cl)]$ $(H_2O)_3$, $[Cu(L)(H_2O)_4](H_2O)_3$ are non-electrolytic nature. The results of magnetic moment measurements exhibited the existence of Cr(III), Mn(II), Co(II) and Cu(II) complexes have unpaired electrons. The infrared spectral data displayed the main coordination sites of 4-(1-(naphthalene-3-yl)ethyleneamino(3-hydroxnaphthalene-1-sulfonic acid towards Cr(III), Co(II), Mn(II) and Cu(II) ions. The electronic spectral results of ligand and its complexes showed $\pi\rightarrow\pi^*$ (phenyl ring), $n\rightarrow\pi^*$ (HC=N), The data suggest that the Cr(III), Mn(II), Co(II) and Cu(II) complexes have octahedral structure. The synthesized Schiff base and its complexes were tested against some pathogenic bacteria [*Staphylococci*, *Proteus, Bacillus subtilis and Pseudomonas aeruginosa*] which showed moderate to good antibacterial activity against all used types of bacteria except *Bacillus subtilis*.

Keywards: Schiff Base Metal Complexes, Spectroscopic Study, Biological Activity

INTRODUCTION

Schiff bases have been studied as a class of ligands contain azometine (Imine) group (-RC=N-) are usually prepared by condensation of primary amines with carbonyl compounds and coordinate with the metal ion through azomethine nitrogen atom[1-4]. The metal complexes show excellent biological activity which makes the mas model compounds for biological processes[5,6]. Schiff bases are one of the most prevalent and important of the mixed donor systems in the field of coordination chemistry. The first

preparation of imines was reported by Schiff by condensing of primary amines with an aldehyde or a ketone under specific conditions[7]. Synthesis and application of Schiff base compounds have been highly considered in recent decades. Schiff base compound especially their complexes have been used in many reactions as important and significant compounds. Schiff base complexes because of their structures that are similar to the porphyrin and phthalocy anine rings have been highly considered in inorganic, organic and biological fields[8,9]. Some new transition metal ion complexes of 2-1-[((*E*)-6-[(*E*)-1-(2-hydroxyphenyl)-ethylidene]aminohexylidene)-amino]ethylphenol were synthesized and characterized by physiochemical studies. The IR spectral result reveal the involvement of azomethine nitrogen atom and hydroxyl groups in coordination to the central metal ion. The Schiff base and its complexes were screened against some pathogenic bacteria[10]. This study aims to prepare and investigation of Schiff base and it's chelates with Cr(III), Mn(II), Co(II) and Cu(II) ions and study their biological activity.

EXPERIMENTAL

Chemicals and Methods

All chemicals and solvents used in this work were of analar Grade (BDH, Aldrich). They include 4-amino-3-hydroxy-naphthalene-1-sulfonic acid and 2-acetonaphthone-methyi-2-naphthylketone and some metal salts, chromium chloride hexa hydrate ($CrCl_3.6H_2O$), manganese chloride tetra hydrate ($MnCl_2.4H_2O$), cobalt chloride hexa hydrate($CoCl_2.6H_2O$), copper chloride pent hydrate ($CuSO_4.5H_2O$), absolute ethanol, glacial acetic acid , ammonia solution, ether and dimethylforamide (DMF). The elemental analysis was carried out using Perkin-Elmer 2400 series-11 CHN/O analyzer (Waltham, MA, USA). Infrared, electronic and nuclear magnetic resonance were recorded on PerkinElmer 1430 (400-4000 cm^{-1}), a Unicam model (UV_2) spectrophotometer at Mansoura University, Egypt, and a Jeol- 90 Fourier Transform (200 MHz) at room temperature using DMSO-d_6 as solvent and TMS as an internal standard, respectively at Mansoura University, Egypt .

Preparation of ligand : 4-(1-(naphthalene-3-yl)ethyleneamino(3-hydroxnaphthalene-1-sulfonic acid (L) was synthesized by adding (2.393g, 0.01 mole) of 4-amino-3-hydroxy-naphthalene-1-sulfonic acid drop wise to 2-Acetonaphthone-methyl-2-naphthylketon (1.70g, 0.01 mole) in 50 cm^3 of absolute ethanol. The reaction mixture was refluxed for three hours. The obtained product was allowed to cool at ambient temperature, filtered and recrystallized from ethanol, and then dried under vacuum to get Brown precipitate obtained was stored at room temperature (yield 87%).

Synthesis of the complexes

These complexes were prepared by adding the Schiff base L (3.91g) in50 cm^3 absolute ethanol to 0.01 mole of the metal salts of $CrCl_2.6H_2O$, $MnCl_2.4H_2O$,$CoCl_3.6H_2O$ and $CuSO_4.5H_2O$, (2.310g), (1.9791g), (2.379 g) and (2.496 g) respectively in the same amount of the absolute

ethanol. The reaction mixtures were refluxed for three hours, and the isolated solid complexes were filtered off, recrystallized from ethanol ,and finally kept in a desiccator over silica gel.

Bacteria assay

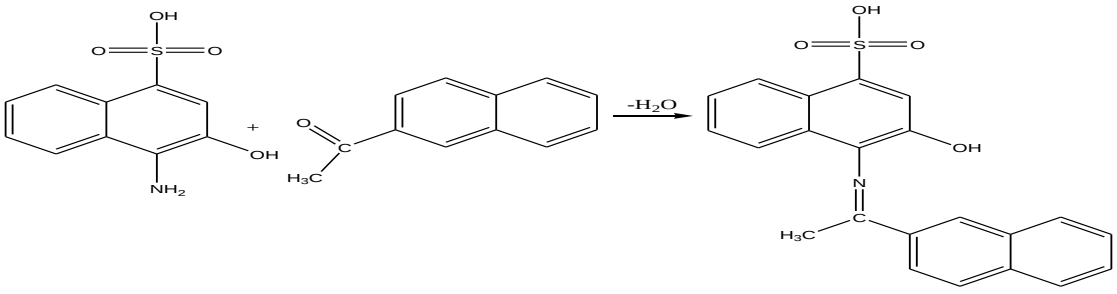
The Schiff base complexes with Cr(III), Mn(II), Co(II) and Cu(II) ions were added separately to the mixture of DMF and H_2O solvents (1:1). The obtained mixtures were further purified and filtrated by using Whatman filter paper No 1. Then stock solutions of extracts were sterilized by filtration using a Millipore membrane filter of 0.2 µm pore-size. The sterile mixture resulted from each compound was stored at 40 ^oC for further uses and the stock mixtures of the compounds were tested against four pathogenic bacteria species (*Escherichia coli , Proteus Sp, Pseudomonas aeruginosa and Staphylococcus aureus*). Antibacterial activity was determined by the well (6 mm diameter) diffusion method. Petridishes containing Mueller Hinton agar medium were seeded with a 24 hrs. culture of the bacterial species were growth on nutrient agar. Each well was filed with 50µl of the compound. Solvents were used as a negative control. Inoculated plates were incubated at 37 ^oC for 24 hrs. The assessment of antibacterial activity was based on measurement of the diameter of inhibition formed around the well.

RESLUTS AND DISCUSSION

The reaction between 4-amino-3-hydroxy-naphthalene-1-sulfonic acid and 2-Acetonaphthone-methyl-2-naphthylketon yields only one product as shown in scheme.

Studies on the Schiff base :- Microanalysis of the Schiff base

The Schiff base was synthesized by the reaction of 4-amino-3-hydroxynaphtha- lene-1-sulfonic acid and 2-Acetonaphthone-methyl-2-naphthaylketon.The synthesized Schiff base was subjected to: CHNS elemental analyses, infrared, ultraviolet and proton nuclear magnetic resonance. The CHNS microanalysis results of the Schiff bases under investigation, the obtained molar conductance values of the complexes in DMF solvent lie in the range of 22 - 105 ohm^{-1} cm^2 mol^{-1} indicating their Mn^{2+} and Co^{2+} complexes are non-electrolytic and complexes of Cr^{3+} and Cu^{2+} are electrolytic behavior and some physical properties are listed in table 1. The obtained data are in good agreement with the calculated values.



(Scheme): Synthesis of Schiff base.

Table (1): CHNS Elemental analyses and some physical properties of the Schiff base L and its complexes

Compound	Color	M.wt.	M.P.^{0}C	%(Calc.) (Found)				Λ (µs)	BM
				C%	H%	N%	S%		
L ($C_{22}H_{17}NO_4S$)	Pale pink	391.44	>250	67.50(67.97)	4.38(4.13)	3.58(3.86)	8.19(7.61)	-	-
[Cr L $Cl(H_2O)_3$]Cl	Gray	567.38	>250	46.57(46.96)	3.91(3.65)	2.47(2.84)	5.65(5.55)	98	3.80
[Mn L $Cl(H_2O)_3$].$(H_2O)_3$	Purple	588.05	>250	44.87(44.97)	4.79(3.26)	2.38(2.99)	5.44(5.79)	31	5.90
[Co L $Cl(H_2O)_3$].$(H_2O)_3$	Brown	592.91	>250	44.57(47.56)	4.76(4.99)	2.36(2.64)	5.41(5.46)	22	4.64
[Cu L $(H_2O)_4$]SO_4	Pale Pink	623.11	>250	42.41(42.59)	4.04(3.86)	2.25(2.84)	10.29(9.93)	105	1.87

Proton nuclear magnetic resonance spectra of the Schiff bases:

The ^{1}H-NMR spectrum recorded in d^6 DMSO solvent on a Jeol- 90 Fourier Transform (200 MHz). The L shows peaks (figure 1) at 0.923, 5.459, 6.916 – 7.857 and 10.985 ppm, downfield of TMS, assignable to the protons of CH_3, OH(suf.), phenyl ring and OH(pheny.), respectively [11,12].

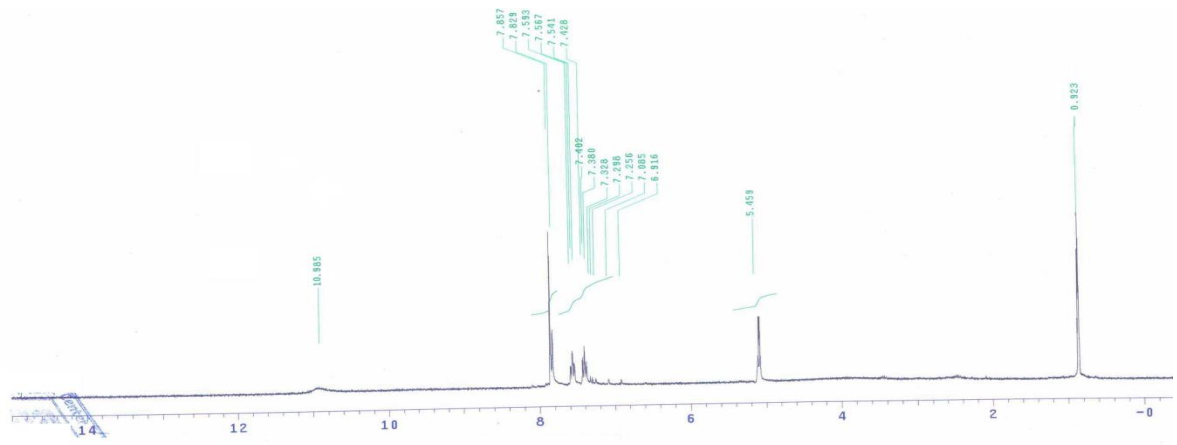


Fig.(1): ^{1}HNMR spectrum of L.

Electronic spectra: The Electronic spectral data of the ligand (L) and their complexes with Cr(III), Mn(II), Co(II) and Cu(II) ions are summarized in table (2) and figures (2 – 6). The UV-spectral data of the Schiff base under investigation (L) display two bands at 37735 cm^{-1} and 34246 cm^{-1} corresponding to π→π* and n→π* respectively[13,14]. The spectral data of the complexes Cr(III)L show two bands at 44000 cm^{-1} and 37037 cm^{-1} which are due to π→π* and n→π* and also two bands in the visible region laying at 22222 cm^{-1} and 24813 cm^{-1}corresponding to $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_2$

$\rightarrow {}^4T_{1g}$ respectively, while three absorption bands were observed for Co(II)L in uv region 37037 cm^{-1}, 38464 and 41666 cm^{-1} which are assigned for $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ and $\sigma\rightarrow\pi^*$ respectively, and two bands in the visible region for Co(II)L were observed at 17857 cm^{-1} and 21276 cm^{-1} corresponding for ${}^4A_{2g(f)} \rightarrow {}^4A_{1g(p)}$ and ${}^4A_{2g(f)} \rightarrow {}^4A_{1g(f)}$ respectively[15,16]. The Mn(II)L complex show one band in the uv-region at 38464 cm^{-1} which are due to $\pi\rightarrow\pi^*$ where in the visible region the Mn(II)L show two bands one at 19607 $cm^{-1}$and 25211 cm-1 due to ${}^2A_2 \rightarrow {}^2T_1$ and ${}^2T_2 \rightarrow {}^2T_1$ d-d transition the vis spectrum of Co(II)L show two bands at 14285 and 20833 cm^{-1} which are assigned for d – d transation ${}^4A_{2g} \rightarrow {}^4T_1$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ respectively[17] and two bands in uv region at 35000 cm-1 and 33333 cm^{-1} corresponding to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$. The electronic spectrum of Cu(II)L show two bands at 37037 cm^{-1} and 41000 cm^{-1} which are due $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ in the uv region and show only one absorption band at 23253 cm^{-1} which assigned for ${}^3A_{2g} \rightarrow {}^3T_{2g}$ [18].

Table (2) Infrared and electronic spectral data of ligand and synthesized complexes.

Ligand / Complexes	IR (cm^{-1})				UV - Vis λ max (cm^{-1})
	OH	v C=N	vM-N	vM-O	
L ($C_{22}H_{17}NO_4S$)	3240	1533	-	-	37735 , 34246
$[Cr(L)(H_2O)_3Cl]Cl$	3401	1619	570	527	44000, 37o37, 24813, 2222
$[Mn(L)(H_2O)_3Cl)](H_2O)_3$	3404	1620	563	455	35000, 33333, 25111, 19607
$[Co(L)(H_2O)_3Cl)](H_2O)$	3424	1602	609	460	41666, 38464, 21276, 17857
$[Cu(L)(H_2O)_4]SO_4$	3250	1540	535	485	41000, 3737, 23253

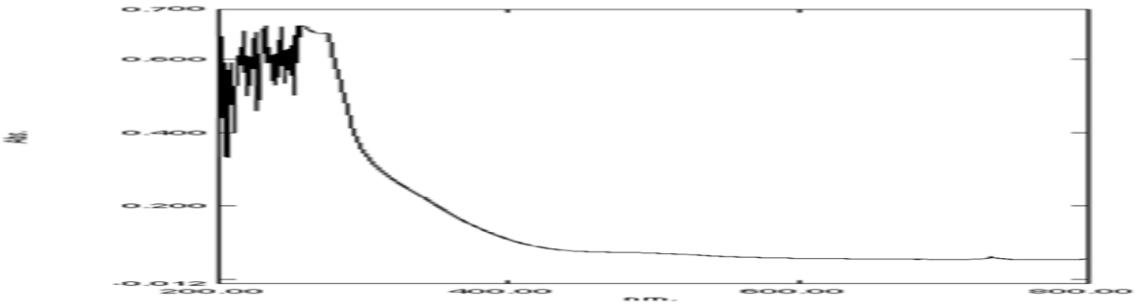


Fig.(2): UV spectrum of L ($C_{22}H_{17}NO_4S$).

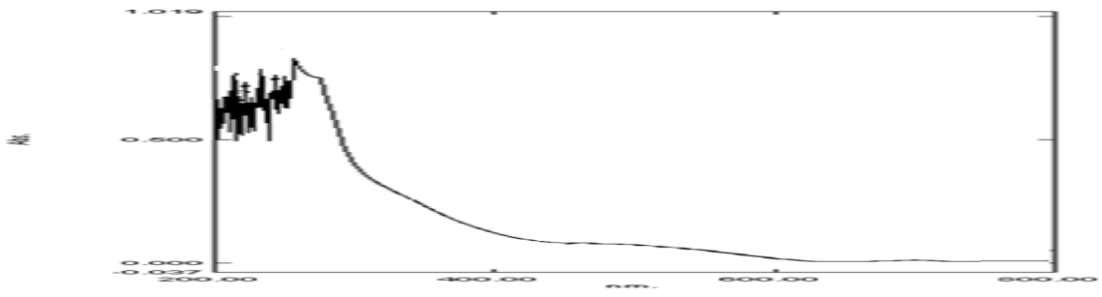


Fig.(3): Electronic spectrum of $[Cr(L)(H_2O)_3Cl].Cl$ complex.

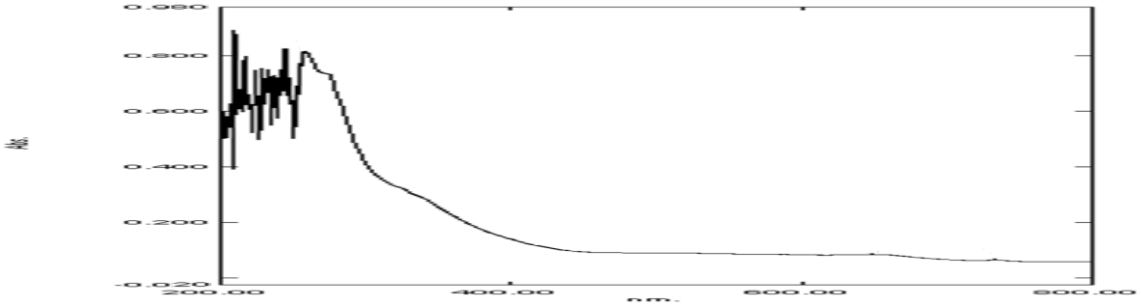


Fig.(4): Electronic spectrum of [Mn(L)(H_2O)$_3$Cl)]. (H_2O)$_3$ complex.

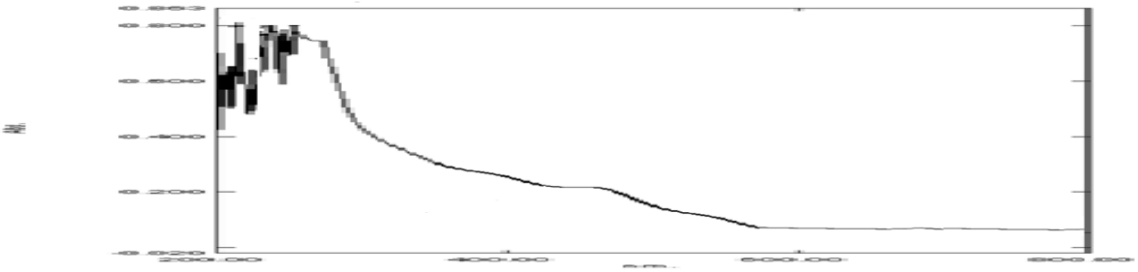


Fig.(5): Electronic spectrum of [Co(L)(H_2O)$_3$Cl)].(H_2O)$_3$ complex.

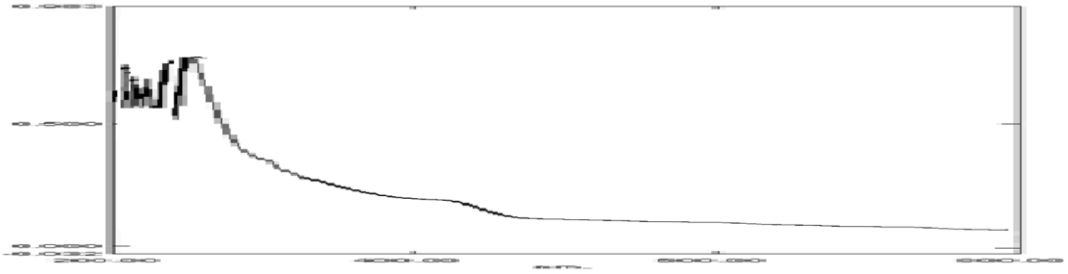
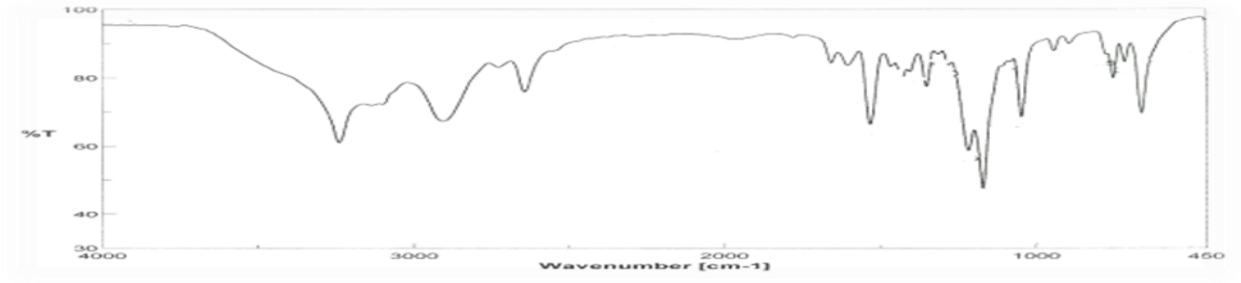


Fig.(6): Electronic spectrum of [Cu(L)(H_2O)$_4$)].SO_4 complex.

Infrared spectra

The IR spectra of the ligand and their complexes with Cr(III), Mn(II), Ni(II) and Cu(II) were recorded in the solid state, in the rang 400 – 4000 cm^{-1} using KBr disc on a Perkin – Elmer 1430 ratio recording infrared spectrophotometer. The IR spectra of the complexes exhibit broad bands in the range of 3401 – 3424 cm^{-1} which are attributed to νOH vibration of water molecules associated with complex formation[19,20]. The change of phenolic OH group positions in the spectra of the complexes supports the participation of OH groups in coordination with metal ion, this confirmed by the existence of new bands in the range of 570 – 609 cm^{-1} in the spectra of the complexes, these new bands can be referred to νM-O vibration which is absent in the IR spectrum of free Schiff base[21,22]. The νC=N band of the Schiff base which observed at 1533 cm^{-1} is shifted to lower frequency in the IR spectra of all complexes confirming the complexation of the nitrogen atom of azomethine group to the metal ions. This can be supported by the existence of new bands in the range of 460–527 cm^{-1} assigned to νM-N bands[23]. The infrared results are summarized in table 2 and figures 7 – 11.



Fi g.(7): IR spectrum of the free ligand (L) in KBr.

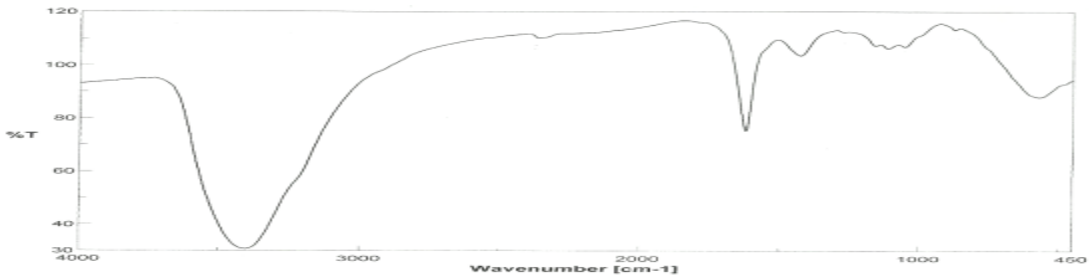


Fig.(8): IR spectrum of [Cr(L)(H_2O)$_3$Cl]Cl complex.

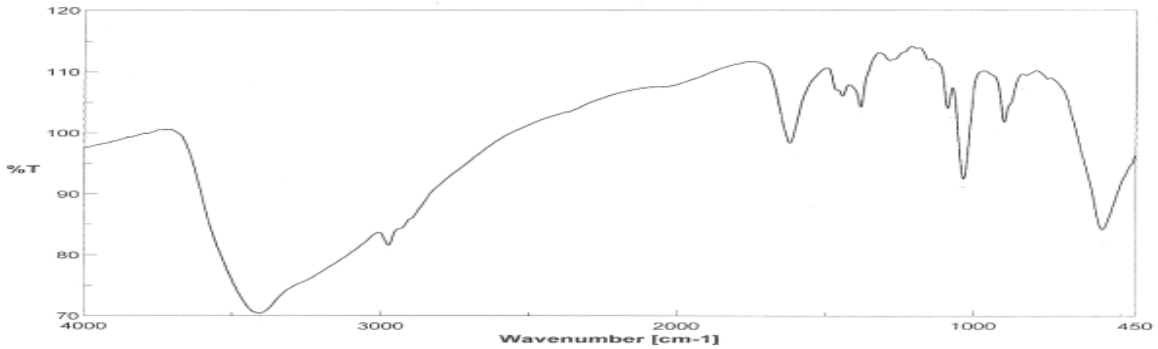


Fig.(9) : IR spectrum of [Mn(L)Cl.(H_2O)$_3$].(H_2O)$_3$ complex.

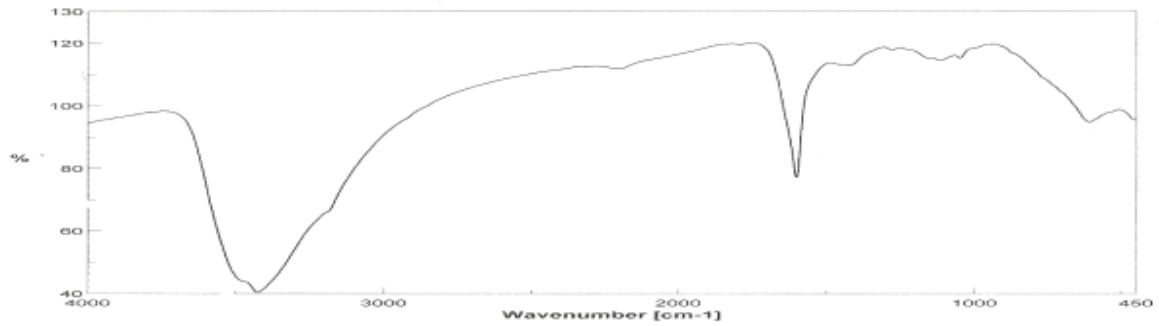


Fig.(10) : IR spectrum of [Co(L)Cl(H_2O)$_3$].(H_2O)$_3$ complex.

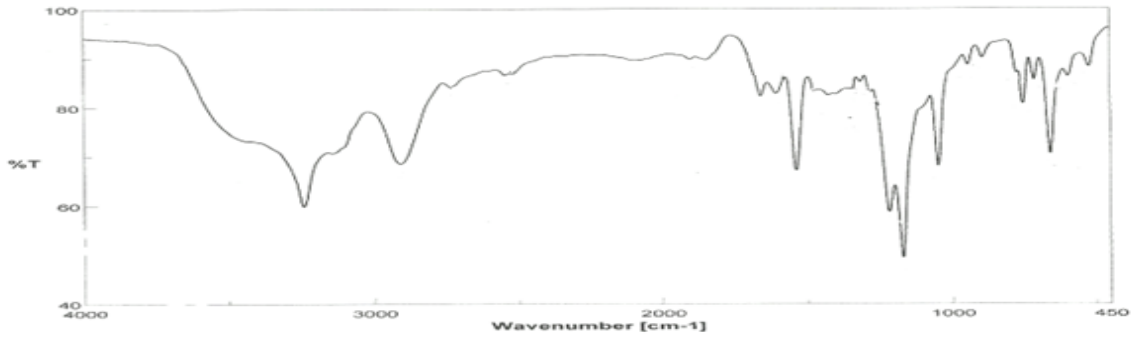


Fig.(11): IR spectrum of $[Cu(L)(H_2O)_4]SO_4$ complex.

Antibacterial activity

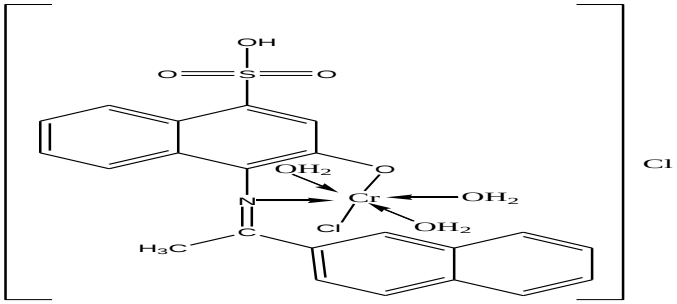
The ligand 4-(1-(naphthalene-3-yl)ethyleneamino(3-hydroxnaphthalene-1-sulfonic acid and the synthesized complexes were Screened for their possible antibacterial activities against *Pseudomonas aeruginosa*, *Proteus*, *Bacillus subtilis* and *Staphylococci*. The ligand and complexes showed moderate to good antibacterial activity against all used types of bacteria except *Bacillus subtilis*. The results of antibacterial study are tabulated in table (3).

Table (3): Antibacterial activity results (mm) of Schiff base and its complexes

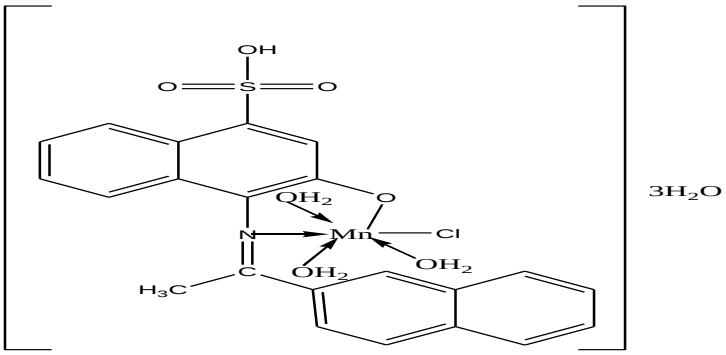
L and its complexes	bacteria			
	Pseudomonas aeruginosa	Proteus	Bacillus subtilis	Staphylococci
L ($C_{22}H_{17}NO_4S$)	14	18	-	17
$[Cr(L)(H_2O)_3Cl]Cl$	11	-	-	-
$[Mn(L)(H_2O)_3Cl)](H_2O)_3$	16	-	-	12
$[Co(L)(H_2O)_3Cl)](H_2O)_3$	12	-	-	-
$[Cu(L)(H_2O)_4]SO_4$	13	15	-	12

CONCLUSION

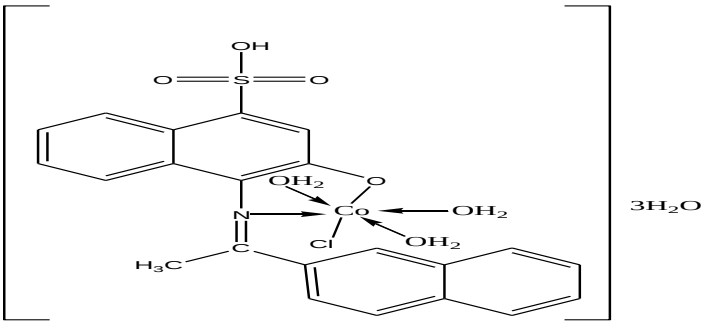
On the basis of CHNS elemental analysis data, molar conductivity, and spectros- copic studies (Infrared and electronic) of the Schiff base and its complexes under investigation, octahedral structures are suggested for all complexes.



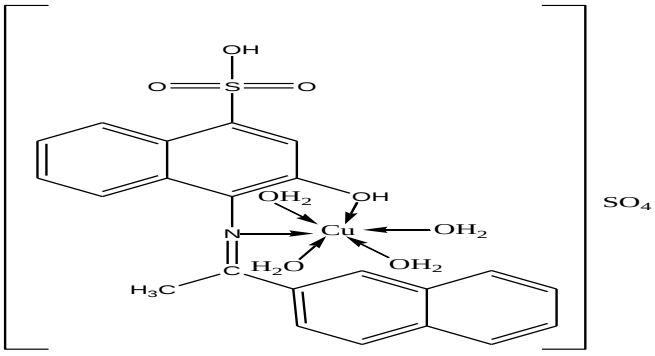
$[Cr(L)Cl(H_2O)_3]Cl$



$[Mn(L)Cl(H_2O)_3].(H_2O)_3$



$[Co(L)Cl(H_2O)_3].(H_2O)_3$



$[Cu(L)(H_2O)_4].SO_4$

تحضير وتشخيص متراكبات Cu(II) , Co(II), Mn(II), Cr(III) مع مرتبط 4-(1- نفثالين)-3- يل) اثلين امين (3-هيدروكسي نفثالين -1- حمض الكبريتيك.

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الملخص: معقدات عناصر الكروم الثلاثي ,المنجنيز الثنائي ,الكوبلت الثنائي و النحاس الثنائي مع قاعدة شيف المشتقة من 4-(1-(naphthalene-3-yl)ethyleneamino(3-hydroxnaphthalene-1-sulfonic acid تم تحضيرها وتشخيصها استنادا على الخواص الفزيائية, التحليل العنصري, قياس الموصلية المولارية, القياسات المغناطيسية, الرنين النووي المغناطيسي, الاشعة تحت الحمراء وكذلك طيف الامتصاص الالكتروني. أثبتث نتائج دراسة الموصلية بإن المتراكبات $[MnL(H_2O)_3Cl].(H_2O)_3$, $[CoL(H_2O)_3Cl].(H_2O)_3$ مركبات ذات طبيعه غير الكتروليتية , كما أثبتث نتائج القياسات المغناطيسية إن المتراكبات $[CrL(H_2O)_3Cl].Cl$, $[CuL(H_2O)_4].SO_4$ تحتوى على الكترونات مفردة. وتبين من دراسة طيف الاشعة تحت الحمراء ارتباط 4-(1-(naphthalene-3-yl)ethyleneamino(3-hydroxnaphthalene-1-sulfonic acid مع ايونات Cu(II) and Co(II), Mn(II) Cr(III) واوضحت نتائج طيف الامتصاص الالكتروني إن المرتبط به انتقالات $\pi \rightarrow \pi^*$ Cu(II) and Co(II), Mn(II) Cr(III) , وأثبتت التحاليل إن متراكبات (phenyl ring), $n \rightarrow \pi^*$ (HC=N), لها تركيب ثماني الاوجه. كما أن المرتبط ومتراكباته تم اختبارها على بعض انواع من البكتيريا وهي *Pseudomonas aeruginosa*, *Proteus*, *Bacillus subtilis* and *Staphylococci*. والتي أظهرت نتائج ايجابية من معتدلة الى جيدة ماعدا *Bacillus subtilis*.

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