Synthesis, Characterization of New Tridentate Schiff base Type (NOO) Derived From 4-aminoantipyrine and Glyoxylic Acid and it's Complexes with Some Metal Ions and Evaluation of their Antibacterial Activity

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Abstract

The new tridentate schiff base type (NOO) namely ((1,5-Diemthyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino) (HL) was prepared from condensation of 4-AAP and glyoxylic acid in ethanol as a solvent in presence of a few drops of 48% HBr as catalyst. The new schiff base ligand (HL) was reacted with some metal ions in ethanol to give a series of new metal complexes of two molecular formula: $[VO(HL)_2(SO_4)].3H_2O$ and $[M(L)_2].XH_2O$, (Where: M^{II}=(Mn, X=3); (Co, X=2); (Ni, X=3); (Cu, X=2); (Zn, X=2); (Cd, X=2); (Hg, X=3); HL=$C_{13}H_{13}N_3O_3$, L= $C_{13}H_{12}N_3O_3$. All prepared compounds were characterized by spectroscopic methods (FT-IR, U.V-Vis, ^{1}H-, ^{13}C-NMR atomic absorption), elemental microanalysis C.H.N., magnetic susceptibility, molar conductivity along with melting point. From the data of all technique, the suggested geometrical structure for all prepared complexes were octahedral geometry. The new schiff base ligand (HL) and it's metal complexes were screened for their antibacterial activity against *bacteria*, *staphylococcus aureus*, *Bacillus*, *Escherichia coli* and *pseudomonas aureus*.

Keywords: 4-aminoantipyrine, glyoxylic acid, schiff base.

تحضير، تشخيص قاعدة شف جديدة ثلاثية السن نوع (NOO) مشتقة من 4-امينوانتي بايرين وحامض كلايوكسيلك ومعقداتها مع بعض الايونات الفلزية وتقدير فعاليتها المضادة للبكتيريا

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الخلاصة

تضمنت هذه الدراسة تحضير وتشخيص ليكاند قاعدة شف جديدة نوع (NOO) بصفتها ذرات مانحة:
(1,5-Diemthyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-%48 HBr.
بمفاعلة 4-امينوانتي بايرين وحامض كلايوكسيلك في الايثانول. الدراسة شملت أيضاً تحضير وتشخيص معقدات قاعدة شف (HL) مع بعض الايونات الفلزية ثنائية التكافؤ ذو الصيغ العامة:

$[VO(HL)_2SO_4].3H_2O$, $[M(L)_2].mH_2O$

حيث:

(M^{II}=Mn, Ni, Zn, Hg; m=3), (M^{II}= Co, Cu, Cd; m=2), HL=$C_{13}H_{13}N_3O_3$, L=$C_{13}H_{12}N_3O_3$
بمفاعلة ملح كلوريد الفلز (II) باستثناء كبريتات الفناديل (II) مع قاعدة شف (HL) في الايثانول.
شخصت قاعدة شف وجميع المعقدات المحضرة بوساطة الطرائق الطيفية (طيف الاشعة تحت الحمراء، طيف الاشعة فوق البنفسجية-المرئية، الامتصاص الذري، طيف الرنين النووي المغناطيسي بنوعيه (^{13}C, ^{1}H)، التحليل الدقيق للعناصر (C.H.N)، الحساسية المغناطيسية، التوصيلية المولارية، محتوى الكلور فضلاً عن قياس درجة الانصهار.
أظهرت الدراسة ان الشكل الهندسي المقترح للمعقدات المحضرة هو ثماني السطوح. كذلك فان الدراسة شملت دراسة الفعالية المضادة للبكتريا لليكاند قاعدة شف (HL) ولجميع معقداته المحضرة حيث اختبرت فعاليتها المضادة للبكتريا باتجاه اربعة انواع من البكتيريا هي:

Staphylococcus aurens, *Bacillus*, *Escherichia coli* and *Pesudomonas*.

الكلمات المفتاحية :
4- امينو انتي بايرين ، وحامض كلايوكسيلك ، قاعدة شف

Introduction

Azomethine group (-C=N-) is the effective group of the compounds that know schiff bases, which are usually synthesized by the condensation of primary amines and active carbonyl groups. Schiff bases represent important class of compounds in medical, pharmaceutical, biological, corrosion inhibitors and catalysts[1-3]. Schiff base complexes containing nitrogen and oxygen as donor atoms play an important role in biological systems and represent models for matalloproteins and metaloenzymes[4]. Several research papers have been published on transition metal complexes of schiff base derived from 4-aminoantipyrine[5-7]. In recent years, shciff base of 4-aminoantipyrine and its complexes have a variety of applications in biological, clinincal, analytical and pharmacological areas[8].Glyoxylic acid and its derivatives play important roles in natural processes, participating in glyoxylate cycle which functions in plant and in some microorganism[9]. The presence of aldehyde group in glyoxylic acid allows numerous a cyclic derivatives containing a zomethine group and hydrazones[10]. The present study deals with the synthesis, characterization and antibacterial activity study of schiff base derived from 4-aminoantipyrine and glyoxylic acid and it's VO(II), MN(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes.

Experimental

Materials and instrumentation

All chemicals are form fluka and B.D.H. companies. Elemental microanalysis were carried out by (C.H.N.S.) perkin Elemar (2)nm 400 at collage of Education for pure sciences, Ibn Al-Haitham, Baghdad University.Metal contents of the complexes were determined by atomic absorption (A.A) technique using a shimadzu (A.A 620) atomic absorption spectrophotometer.

FT-IR spectra were recorded as KBr discs by using shimadsu (4800s) FT-IR spectrophotometer in the range (4000- 400) cm^{-1} of Education for pure sciences, Ibn Al-Haitham, Baghdad University. Electronic spectra of the prepared compounds were measured in the range (200- 1000)nm for 10^{-3}M solution in DMSO at room temperature by using double- beam (U.V-Vis) spectrophotometer type with quartz cell of (1.0 cm) length and the concentration of (10^{-3} mole. l^{-1}). In Ibn- Sina Company Baghdad, Iraq. Electrical molar conductivity measurements of the complexes were recorded at room temperature for 10^{-3}M solution of samples in DMSO by using (conductivity meter, Jewnwary, model 4070) and the determination of cell constant was made using the following relation at College of Education for pure sciences/ Ibn- AL-Haitham, Baghdad University. Magnetic moments for complexes were measured with magnetic susceptibility balance (Janson malty catalytic systems division), in Al-Nahrain University Baghdad, Iraq. ^{1}H and ^{13}C-NMR spectra were acquired in DMSO-d^6 solution using a Bruker 400 MHz instrument with a tetramethylsaline (TMS)as an internal standard and are reported in PPm(δ) at Al-Bayt University, Jordan. Melting points were recorded by using. (Stuart melting point apparatus).

Synthesis of ligand (HL)

A solution of (4-AAP) (0.203 g, 1mmole) in ethanol (20 ml), and a few drop of 48% of HBr, was added to a solution of (Glyoxylic acid) (0.074 g, 1 mmole) in ethanol (10 ml). The mixture was refluxed for (6 hrs) with stirring. The resulting was an orange solution allowed to cool and dried at room temperature, then washed with ethanol and re-crystallization to the precipitate with methanol/ H_2O to give orange crystals during (24 hr), m.p. (128 -132) ºC.

Synthesis of complexes

1. Synthesis of $[Co(L)_2].2H_2O$ complex:

A solution of (HL) (0.518 g, 2 mmole) in ethanol (10 ml), was added to a stirred solution of Co(II) chloride hexahydrate (0.238 g, 1 mmole) in ethanol (5 ml). The resulting mixture was heated under reflux for (1 hr). Then the mixture was filtered and the precipitation was dried and washed with an excess of ethanol and dried at room temperature during (24 hr). A dark green crystals were obtained, m.p. (115-118)ºC.

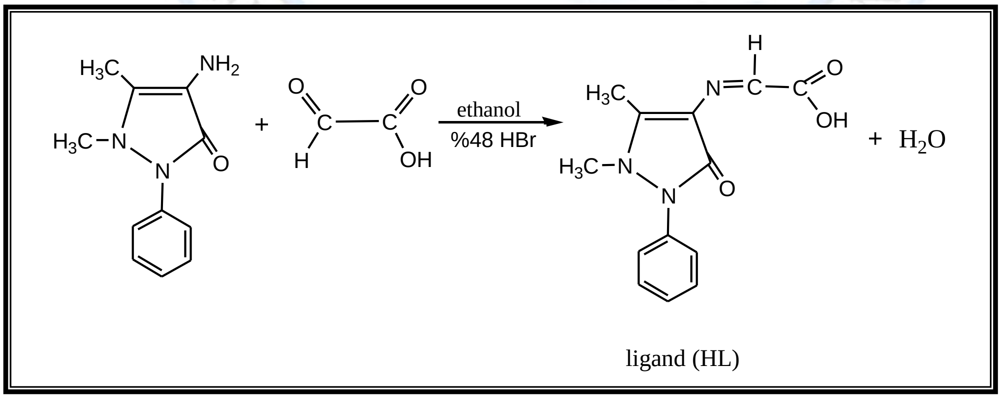
2. Synthesis of other complexes

A similer method to that mentioned in (1) to prepare of $[Co(L)_2].2H_2O$ complex was used to prepare the complexes: $[VO(HL)_2SO_4].3H_2O$, $[Mn(L)_2].3H_2O$, $[Ni(L)_2].3H_2O$, $[Cu(L)_2].2H_2O$, $[Zn(L)_2].3H_2O$, $[Cd(L)_2].2H_2O$ and $[Hg(L)_2].3H_2O$. Table (1) shows the physical properties of the complexes and their reactant quantities.

Results and Discussion

Ligand (HL)

The pro-ligand (HL) was prepared by reaction of 4-aminoantipyrine and glyoxylic acid in ethanol solvent in presence of a few drops of 48% HBr according to the general method shown in scheme. (1). The ligand dissolves in methanol, ehanol, aceton, DMSO and DMF. Some physical properties and elemental microanalysis C.H.N. of the ligand (HL) were listed in
table (2).



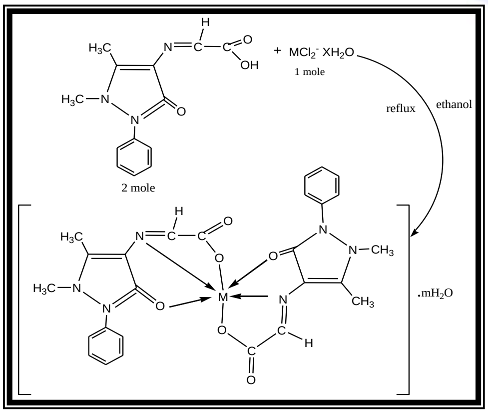
Scheme (1): Synthesis route of ligand (HL)

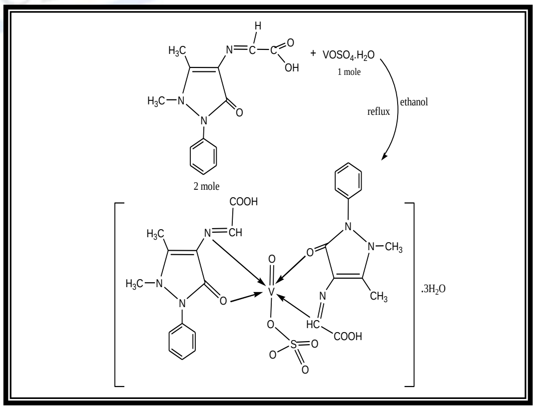
The FT-IR spectrum of the ligand (HL) (fig. 1) shows strong band at (3421)cm^{-1} due to stretching frequency υ(O–H) for carboxylic group[11].The band at (1645)cm^{-1} refers to υC=O of 4-aminoantipyrine ring and the band at (1724)cm^{-1} which appeared as shoulder, was assigned to υC=O of carboxylic group.

The two bands at (1419)cm^{-1} and (1369)cm^{-1} were assigned to stretching frequency υ_{asy}.COO^{-} and υ_{sy}.COO^{-} respectively[12,13].The new band at (1608)cm^{-1} was due to υN=CH group of the azomethine stretching frequency of the ligand, this referes to formation of schiff base compound[1,15].The important characteristic bands for the FT-IR spectrum of the ligand (HL) are listed in table (3).The U.V-Vis spectrum of ligand (HL) (fig. 2) displayed three absorption peaks, the first peak at (276)nm (36231)cm^{-1} (ε_{max}=1885)mol^{-1}. L.cm^{-1} may be assigned to $\pi\rightarrow\pi^*$ electronic transition. The second peak at (346)nm (28901)cm^{-1} (ε_{max}=614)mol^{-1}.L.cm^{-1} and the third peak at (362)nm (27624)cm^{-1} ε_{max}=500)mol^{-1}.L.cm^{-1} were attributied to $n\rightarrow\pi^*$ electronic transition[16,17]. The U.V-Vis spectral data of the ligand were given in table (4).In the ^{1}H-NMR spectrum of ligand (fig. 3) single peaks attributed to two methyl groups appeared at range (δ1.06- δ2.91) ppm. The strong signal obtained at (δ3.35)ppm. due to DMSO-d$_6$. The weak peak at (δ8.14)ppm. was attributed to proton of azomethine group. Single weak peak attributed to proton of (-COOH) appeared at (δ9.30) ppm. The multiple chemical shifts around (6.98- 7.47)ppm. may assigned to aromatic protons. The two weak signals at (δ3.04) ppm. and (δ3.14) ppm. refere to water molecules[14,18]. ^{13}C-NMR spectrum of ligand (fig. 4) shows chemical shifts at (15.54) ppm. and (18.35)ppm. refere to C$_5$ and C$_6$ for two CH$_3$ group respectively. The chemical shifts at (61.79)ppm. and (88.32)ppm. were attributed to
C$_3$ and C$_4$ of C=C of 4-aminoantipyrine ring respectively. Signals related to aromatic carbon (C$_7$-C$_{12}$) were detected at range (δ126.04- δ130.89)ppm. The chemical shift of C$_1$ for carboxylic group appeared at expected downfield at (170.25)ppm. The two chemical shifts at (165.51)ppm. and (135.47)ppm. were attributed to C$_2$ for azomethine group (-N=CH-) and C$_{13}$ of (C=O) for
4-aminoantipyrine respectively. Finally the chemical shift at (40.86) ppm. due to DMSO-d$_6$[15].

Complexes

The reaction of ligand (HL) with VOSO$_4$.H$_2$O or with metal chloride salt of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) were carried out in ethanol solvent under reflux Scheme (2). All complexes are stable in solution table (9) and they dissolve in methanol, ethanol, acetone, DMSO and DMF solvents.





Where: M^{II}=Mn, X=4, m=3
Co, X=6, m=2
Ni, X=6, m=3
Cu, X=2, m=2
Zn, X=0, m=3
Cd, X=1, m=2
Hg, X=0, m=3

Scheme (2): Synthesis route of $[VO(HL)_2SO_4].3H_2O$ complex and of ligand (HL) complexes

On the bases of elemental microanalysis data table (5), the molecular formula for prepared complexes was assigned to $[VO(HL)_2(SO_4)].3H_2O$, $[M(L)].XH_2O$, (Where: M(II)=(Mn, X=3); (Co, X=2); (Ni, X=3); (Cu, X=2); (Zn, X=3); (Cd, X=2); (Hg, X=3); HL=$C_{13}H_{13}N_3O_3$, L= $C_{13}H_{12}N_3O_3$. The suggested molecular formula was also supported by spectral measurements as well as molar conductivity and magnetic moment. Some physical properties of prepared complexes were listed in table (6).

Molar conductance

The molar condnctance values table (6) of the soluble complexes in DMSO solvent in 10^{-3} M solution at room temperature refer to non- electrolytic nature[19].

Magnetic susceptibility

The magnetic susceptibility for all complexes were measured at room temperature and the effective magnetic moment (μ_{eff}) values were listed in table (7).The values of (μ_{eff}) for $[Mn(L)_2].3H_2O$ (5.52) B.M, $[Co(L)_2].2H_2O$ (4.81) B.M and $[Ni(L)_2].3H_2O$ (2.81) B.M, corresponded to high spin octahedral geometry around each of Mn(II), Co(II), and Ni(II)[20,21]. Also the value of $[Cu(L)_2].2H_2O$ (1.74) B.M, showed one unpaired electron with parametric nature and suggested distorted octahedral geometry around Cu(II) in terms of Jahn- Teller effect[20].

FT- IR spectral data

The FT- IR spectra for all prepared complexes: $[VO(HL)_2SO_4].3H_2O$, $[Mn(L)_2].3H_2O$, $[Ni(L)_2].3H_2O$, $[Cu(L)_2].2H_2O$, $[Zn(L)_2].3H_2O$, $[Cd(L)_2].2H_2O$ and $[Hg(L)_2].3H_2O$, $[Co(L)_2].2H_2O$ is shown in (fig. 5). The assignment of the characteristic bands are summarized in table (9). The IR spectra of all prepared complexes were compared with that of free ligand (HL) in order to determine the coordination sites involved in chelation, that is means the position of some guide bands in the spectrum of free ligand were expected to change upon chelation. The IR spectra of all prepared complexes exhibited broad band at range (3446-3342) cm^{-1}, that may be attributed to υO-H of hydrated water molecules in molecular formula of complexes[22]. The detected band at (1608) cm^{-1} which was assigned to the stretching frequency of azomethine group (υ-N=CH-) of the free ligand, this band was shifted to lower frequency at range (1593-1558) cm^{-1} in spectra of all prepared complexes, this shift to lower frequency may be due to involved nitrogen atom of azomethine group in coordination with metal ions and delocalization of metal electronic density to the ligand (π–system)[20,23], (HOMO→LUMO), where:

HOMO= Highest Occupied Molecular Orbital, LUMO= Lowest unoccupied Molecular Orbital.

The band at (1645) cm^{-1} stretching vibration which refers to υC=O for 4-AAP ring of free ligand, was shifted to lower frequency at range (1635-1608) cm^{-1} in the spectra of all complexes, showing that the coordination between oxygen atom of this group (C=O) and metal ions was happened[24,25]. The two bands at (1419) cm^{-1} and (1369) cm^{-1} in the spectrum of free ligand which were assigned to stretching frequency of $\upsilon_{asy.}COO^-$ and $\upsilon_{sy.}COO^-$, respectively, on complexation these to bands have been shifted to lower or higher frequency in the spectra of all complexes, except VO(II) complex, which appeared at range (1456-1408) cm^{-1} for $\upsilon_{asy.}COO^-$ and at range (1386-1317) cm^{-1} for $\upsilon_{sy.}COO^-$. The shift in the stretching frequency of $\upsilon_{asy.}COO^-$ and $\upsilon_{sy.}COO^-$ in the IR spectra for all complexes, except VO(II) complex, shows that the coordination with metal ion occurred through oxygen atom of Carboxylate group[26]. The weak band at range (1739-1722) cm^{-1} in the IR spectra for all complexes refers to stretching frequency υC=O for carboxylate group, which it was overlap with (C=O) aldehydic group in IR spectrum of starting material (glyoxylic acid)[14].Further, the two bands which are assigned to υ_{asy}.COO- and υ_{sy}.COO- vibrations in the IR spectrum of free ligand, partically no or slightly change on it's frequencies in IR spectrum of VO(II) complex was observed, indicating noninvolvement of carboxylate group in coordination with vanadyl ion VO(II). The new band in the IR spectrum of VO(II) complex at (985) cm^{-1} was attributed to υV=O group[27]. Also new other bands in the spectrum of VO(II) complex, at (470, 653) cm^{-1} and at (1045, 1118) cm^{-1} which refer to ($\delta_{SO_4^{-2}}$) and ($\upsilon_{SO_4^{-2}}$) respectively indicates that the SO_4^{-2} involved in the coordination with VO(II) ion as monodentate ligand[28,29]. At the lower frequency region, the IR spectra of all prepared complexes showed new bands which are not present in the spectrum of the free ligand, these bands are located at (589– 538) cm^{-1} and at (503– 439) cm^{-1}which are attributed to υM-N and υM-O respectively[16,30]. Other bands in the IR spectra of all complexes were listed in table (8).

These observation in the IR spectra of the ligand (HL) and it's complexes indicate that the ligand coordinates with metal ions: Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) via oxygen atom of (C=O) group of 4-AAP ring, nitrogen atom of azomethine group and oxygen atom of carboxylate group, behaving tridentate ligand toward these metal ions, but the ligand behaves as bidentate ligand toward VO(II) via nitrogen atom of azomethine group and oxygen atom of (C=O) group of 4-AAP ring only.

Electronic spectral data

The electronic spectral data for all prepared complexes are summarized in table (9) together with electronic transitions and suggested geometries. The electronic spectra for all prepared complexes displayed three absorption peaks in the ultraviolet region. The first peak at range (274– 281) nm (36496– 35587) cm^{-1} (ε_{max}=1853– ε_{max}=2236) mol^{-1}.L.cm^{-1}, the second peak at range (344-355) nm (29070-28169) cm^{-1} (ε_{max}=766– ε_{max}=1902) mol^{-1}.L.cm^{-1}, and the third peak at range (354-363) nm (28249– 27548) cm^{-1} (ε_{max}=576– ε_{max}=1127) mol^{-1}.L.cm^{-1} except Cu(II) complex-were attributed to the intra-ligand $\pi\rightarrow\pi^*$, and $n\rightarrow\pi^*$, respectively[17], which exhibited bathochromic shift or hypsochromic shift when it comparison with that of free ligand, except the third peak at (377) nm (26525) cm^{-1} (ε_{max}=992) mol^{-1}.L.cm^{-1} for Cu(II) complex related to charge transfer electronic transition[31].

$[VO(HL)(SO_4)].3H_2O$

The electronic spectrum of VO(II) complex, displayed three additional peaks, the first peak at (454) nm (22026) cm^{-1} (ε_{max}=190) $mol^{-1}.L.cm^{-1}$, the second peak at (654) nm (15291) cm^{-1} (ε_{max}=209) mol^{-1}. $L.cm^{-1}$, and the third peak at (746) nm (13409) cm^{-1} (ε_{max}=14) $mol^{-1}.L.cm^{-1}$, were attributed to (d-d) spin-allowed electronic transitions type $^2B_2g \rightarrow ^2A_1g$, $^2B_2g \rightarrow ^2B_1g$, and $^2B_2g \rightarrow ^2Eg$, respectively, suggesting octahedral geometry about VO(II) ion[20,32].

$[Mn(L)_2].3H_2O$ complex

The UV-Vis spectrum of Mn(II) complex, showed three new peaks. The first peak at (415) nm (24096) cm^{-1} (ε_{max}=462) $mol^{-1}.L.cm^{-1}$, the second peak at (500) nm (20000) cm^{-1} (ε_{max}=114) $mol^{-1}.L.cm^{-1}$, and the third peak at (711) nm (14665) cm^{-1} (ε_{max}=7) $mol^{-1}.L.cm^{-1}$, were attributed to (d-d) spin-forbidden electronic transitions type $^6A_1g \rightarrow ^4A_1g$, $^4Eg_{(G)}$, $^6A_1g \rightarrow ^4T_2g_{(G)}$, and $^6A_1g \rightarrow ^4Eg_{(G)}$, respectively, indicating octahedral geometry around Mn(II) ion[14,32].

$[Co(L)_2].2H_2O$

The electronic spectrum of Co(II) complex showed three additional absorption peaks. The first peak at (523) nm (19120) cm^{-1} (ε_{max}=76) $mol^{-1}.L.cm^{-1}$, the second peak at (661) nm (15129) cm^{-1} (ε_{max}=24) mol^{-1}. $L.cm^{-1}$, and the third peak at (745) nm (13423) cm^{-1} (ε_{max}=14) $mol^{-1}.L.cm^{-1}$, were attributed to (d-d) spin-allowed electronic transitions type $^4T_1g \rightarrow ^4T_2g(P)$, $^4T_1g \rightarrow ^4A_2g$, and $^4T_1g \rightarrow ^4T_2g$, respectively, characteristic octahedral geometry around Co(II) ion[20,32].

$[Ni(L)_2].3H_2O$

The electronic spectrum of Ni(II) complex, (fig. 6) displayed three new absorption peaks. The first peak at (588) nm (17007) cm^{-1} (ε_{max}=25) $mol^{-1}.L.cm^{-1}$, the second peak at (783) nm (12771) cm^{-1} (ε_{max}=19) $mol^{-1}.L.cm^{-1}$, and the third peak at (962) nm (10395) cm^{-1} (ε_{max}=16) $mol^{-1}.L.cm^{-1}$, due to (d-d) spin-allowed electronic transitions type $^3A_2g \rightarrow ^3T_1g_{(P)}$, $^3A_2g \rightarrow ^3T_1g$ and $^3A_2g \rightarrow ^3T_2g$, which are a good evidence for octahedral geometry of Ni(II) complexes[14,32].

$[Cu(L)_2].2H_2O$

The UV-Vis spectrum of Cu(II) complex, showed additional absorption peak at (815) nm (12270) cm^{-1} (ε_{max}=33) $mol^{-1}.L.cm^{-1}$ was attributed to (d-d) spin-allowed electronic transitions type $^2Eg \rightarrow ^2T_2g$, confirming distorted octahedral geometry about Cu(II) ion[14,32].

$[Zn(L)_2].3H_2O$, $[Cd(L)_2].2H_2O$, and $[Hg(L)_2].3H_2O$

The electronic spectra of Zn(II), Cd(II), and Hg(II) complexes, exhibit no peak in the visible region because of (d^{10}-system) of metal (II) ion, this is mean no (d-d) electronic transition happened[14].

Antibacterial activity

The new synthesized ligand (HL) and its metal complexes were screened for their antibacterial activity against bacteria, *staphylococcus aureus*, *Bacillus*, *Escherichia coli*, and *Pseudomonad aureus*.The zone of inhibitions of the ligand (HL) and its complexes against the growth of bacteria were given in table (10) and (fig. 7). The organism tested were the agar media was inoculated with test organisms and a solution of the tested compound (100 mg/ml) was placed separately in cups (10 mm diameter) in the agar medium. The plates were incubated for 24 hrs. at (37°C) and the well was filled with the test solution using micropipette. During this period, the test solution was diffused and affected the growth of the incubated microorganisms. Activity was determined by measuring the diameter of the zone showing complete inhibition (mm). Growth of inhibition was compared with the control DMSO.The antibacterial activity results revealed that the ligand and its complexes shown weak to good activity when compared to the control DMSO[33]. In general the antibacterial activity was found to be in order: ligand (HL) > control for all bacteria type used in this study. The activity of ligand may be due to carboxyl group, imine group and five member ring[34,35]. The antibacterial effect of all prepared complexes was studied of four types of bacteria as shown in table (10). The rate of inhibition diameter was varied according to the variation in complex type and bacterial type. The complexes: $[Mn(L)_2].H_2O$, $[Zn(L)_2].H_2O$, $[Cu(L)_2].H_2O$ were found to be inactive against *Eshcerichia coli*, also against *Pseudonomas*, $[Mn(L)_2].H_2O$, $[Co(L)_2].H_2O$ $[VO(HL)_2(SO_4)].H_2O$ against *Bacillus*. In general the values indicate that most complexes have higher antibacterial activity than the free ligand (HL). $[Cd(L)_2].H_2O$ and $[Hg(L)_2].H_2O$ complexes are more active against *Eshcerechia coli*, also $[Ni(L)_2].H_2O$ against *Pseudomonas* and *Staphylococcus* and $[Hg (L)_2].H_2O$ against *Bacillus.*

Conclusions and the proposed molecular structure for all prepared complexes

According to the characterization data for new schiff base (HL) derived from 4-aminoantipyrine with glyoxylic acid, and it's complexes based schiff base liagnd HL by FT-IR, U.V-Vis, atomic absorption, ^{1}H-NMR, ^{13}C-NMR, magnetic susceptibility, molar conductivity, elemental microanalysis, chloride content alonge with melting point, we found that:

1. The schiff base (HL) behaves as tridentate ligand through it's azomethine nitrogen, oxygen atom of carboxylato group and oxygen atom of C=O group of five member ring with the central metal ions: (Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) forming complexes with general molecular formula: $[M(L)_2].mH_2O$, where: (M^{II}=Mn, Ni, Zn, Hg; m=3), (M^{II}= Co, Cu, Cd; m=2) as shown in (fig. 9), except in VO(II) complex, as shown in (fig. 8). schiff base (HL) behaves bidentate ligand via azomethine nitrogen and oxygen atom of C=O group of five member ring forming complex with molecular formula $[VO(HL)_2(SO_4)].3H_2O$.
2. The octahedral geometrical structure was suggested for all prepaved complexes based on the characterization data for all technique.

Table (1): Some physical properties of the prepared ligand (HL) complexes and their reactant quantities

Compound	Weight of metal salt (g) (1 mmole)	Weight of HL (g) (2 mmole)	Colour	m.p. ºC
$[VO(HL)_2SO_4].3H_2O$	0.180	0.518	Reddish orange	106-113
$[Mn(L)_2].3H_2O$	0.198	0.518	Reddish orange	128-135
$[Co(L)_2].2H_2O$	0.238	0.518	Dark green	115-118
$[Ni(L)_2].3H_2O$	0.118	0.518	Dark orange	116-120
$[Cu(L)_2].2H_2O$	0.170	0.518	Bluish violet	96-100
$[Zn(L)_2].3H_2O$	0.136	0.518	Brownish orange	221-229
$[Cd(L)_2].2H_2O$	0.259	0.518	Reddish orange	135-140
$[Hg(L)_2].3H_2O$	0.271	0.518	Reddish orange	155-162

Table (2) : Elemental microanalysis C.H.N. and some physical properties of ligand (HL)

Ligand	Empirical formula	M.wt g/mol	Yield %	M.P.°C	Colour	Found, (Calc.) %		
						C	H	Metal
(HL)	$C_{13}H_{13}N_3O_3$	259	92	130	Redish brown	(60.32) 60.02	(5.01) 4.86	(16.21) 16.14

Table (3) : Infrared spectral data (cm^{-1}) for the starting materials and the ligand (HL)

Compound	$\upsilon_{asy}NH_2$ $\upsilon_{sy}NH_2$	υC=O	$\upsilon_{asy}COO^-$ $\upsilon_{sy}COO^-$	υO–H	υN=CH imine	υC–N	υN–N (ring)	υC=C arom.	υC–H arom.	υC–H aliph.	υC–C aliph.	δN–H
glyox.	-	1745 (carbox)	1462 1338	3361	-	-	-	-	-	2970	-	-
4-AAP	3433 3327	1647 (ring)	-	-	-	1345	1074	1591	2989	2889	1192	1680
Ligand (HL)	-	1724 (carbox.)	1419 1369	3421	1608	1336	1060	1586	2939	2900	1197	-

*** glyox = glyoxylic acid, 4-AAP = 4- aminoantipyrine**

Table (4): Electronic spectral data for the ligand (HL)

Compound	λnm	$\bar{\upsilon}$ (cm^{-1})	(ε_{max} molar^{-1}. L. cm^{-1})	Electronic transition
HL	276	36231	1885	$\pi\rightarrow\pi^*$
	346	28901	614	$n\rightarrow\pi^*$
	362	27624	500	$n\rightarrow\pi^*$

Table (5) : Micro elemental analysis of ligand (HL) complexes

Compound	Found (calc.)%				
	C	H	N	M	Cl
$[VO(HL)_2SO_4].3H_2O$	(42.44) 40.86	(4.35) 4.64	(11.42) 10.22	(6.93) 6.04	Nil
$[Mn(L)_2].3H_2O$	(42.79) 41.08	(4.66) 4.25	(23.04) 24.13	(7.54) 6.72	Nil
$[Co(L)_2].2H_2O$	(51.06) 49.98	(4.58) 3.64	(13.74) 14.06	(9.65) 10.12	Nil
$[Ni(L)_2].3H_2O$	(49.62) 49.18	(4.77) 4.16	(13.36) 12.24	(9.33) 9.72	Nil
$[Cu(L)_2].2H_2O$	(50.69) 49.82	(4.54) 3.84	(13.64) 12.83	(10.31) 10.86	Nil
$[Zn(L)_2].3H_2O$	(49.10) 48.68	(4.72) 3.92	(13.22) 12.46	(10.29) 9.18	Nil
$[Cd(L)_2].2H_2O$	(46.95) 46.03	(4.21) 3.63	(12.46) 13.18	(16.91) 17.25	Nil
$[Hg(L)_2].3H_2O$	(40.48) 39.68	(3.89) 4.08	(10.90) 9.96	(26.03) 25.65	Nil

Table (6): Some physical properties and molar conductance (M.C) of ligand (HL) complexes

Complexes	M-wt g/mol	Yield%	Colour	M.P°C	M.C Ohm^{-1}. cm^2.mol^{-1}
$[VO(HL)_2SO_4].3H_2O$	735	84	Reddish orange	106-113	4.27
$[Mn(L)_2].3H_2O$	625	78	Reddish orange	128-135	9.66
$[Co(L)_2].2H_2O$	611	92	Dark green	115-118	15.06
$[Ni(L)_2].3H_2O$	628.7	88	Dark orange	116-120	9.30
$[Cu(L)_2].2H_2O$	615.5	82	Bluish violet	96-100	7.70
$[Zn(L)_2].3H_2O$	635.4	79	Brownish orange	221-229	5.50
$[Cd(L)_2].2H_2O$	664.4	76	Raddish orange	135-140	5.11
$[Hg(L)_2].3H_2O$	770.6	81	Reddish orange	155-162	3.42

Table (7) :Magnetic susceptibility and $\mu_{eff.}$ (B.M) of some ligand (HL) complexes

Complexes*	$X_g\times10^{-6}$	$X_M\times10^{-6}$	$X_A\times10^{-6}$	$\mu_{eff.}$ (B.M)	Suggested structure
$[Mn(L)_2].3H_2O$	20.21	1263.58	12857.7	5.52	high spin octahedral
$[Co(L)_2].2H_2O$	15.60	9536.68	9762.8	4.81	high spin octahedral
$[Ni(L)_2].3H_2O$	4.94	3105.78	3331.9	2.81	high spin octahedral
$[Cu(L)_2].2H_2O$	1.70	1051.38	1277.5	1.74	high spin octahedral

*** D= - 226.12×10^{-6}**

Table (8) :Infrared spectral data (wave number υ^-) cm^{-1} for the ligand (HL) and it's complexes

Compound	υOH	υC=O ring	υC=O carbox.	υN=C imine	υCOO$^-$ asy.	υCOO$^-$ sy.	υC=C arom.	υC–H arom.	υC–N	υN–N	υC–C aliph.	υC–H aliph.	υM–N	υM–O
(HL)	3421	1645	1724	1608	1419	1369	1586	2939	1336	1159	1197	2900	-	-
$[VO(HL)_2SO_4].3H_2O$	3342	1614	1734	1558	1408	1370	1525	2981	1344	1165	Overlap	2920	538	503
$[Mn(L)_2].3H_2O$	3421	1635	1734	1589	1436	1373	1521	2974	1330	1157	1199	2918	547	439
$[Co(L)_2].2H_2O$	3414	1620	1724	1589	1436	1377	1521	2980	1336	1159	1203	2908	572	501
$[Ni(L)_2].3H_2O$	3373	1622	1722	1589	1436	1377	1521	2937	1396	1159	1199	2900	589	472
$[Cu(L)_2].2H_2O$	3369	1608	1739	1593	1409	1375	1523	2978	1328	1160	1209	2935	538	457
$[Zn(L)_2].3H_2O$	3415	1616	1735	1558	1436	1386	1521	2987	1338	1157	1192	2939	549	457
$[Cd(L)_2].2H_2O$	3446	1624	1734	1589	1456	1375	1521	2970	1338	1159	1190	2937	538	457
$[Hg(L)_2].3H_2O$	3415	1618	1734	1591	1456	1317	1521	2980	1338	1157	1195	2920	567	459

Carbox.= carboxylate, asy.= asymmetric, sy.= symmetric, arom.= aromatic, aliph.= aliphatic $\Delta\upsilon = \upsilon_{asy}.COO^- - \upsilon_{sy}.COO^-$

Table (9) :Electronic spectral data for the ligand (HL) and it's complexes

Compound	λ(nm)	$\bar{\upsilon}$(cm^{-1})	(ε_{max} mol^{-1}. L.cm^{-1})	Electronic transition	Suggested structure
(HL)	276	36231	1885	$\pi\rightarrow\pi^*$	-
	346	28901	614	$n\rightarrow\pi^*$	
	362	27624	500	$n\rightarrow\pi^*$	
$[VO(HL)_2SO_4].3H_2O$	281	35587	2144	Intra- ligand	oh
	345	28986	1423	Intra- ligand	
	354	28249	1000	Intra- ligand	
	454	22026	190	$^{2}B_{2}g\rightarrow{}^{2}A_{1}g$	
	654	15291	209	$^{2}B_{2}g\rightarrow{}^{2}B_{1}g$	
	746	13409	14	$^{2}B_{2}g\rightarrow{}^{2}Eg$	
$[Mn(L)_2].3H_2O$	280	35714	2202	Intra- ligand	oh
	344	29070	1704	Intra- ligand	
	357	28011	1072	Intra- ligand	
	415	24096	462	$^{6}A_{1}g\rightarrow{}^{2}T_{2}g_{(G)}$	
	500	20000	114	$^{6}A_{1}g\rightarrow{}^{4}A_{1}g,{}^{4}Eg_{(G)}$	
	711	14665	7	$^{6}A_{1}g\rightarrow{}^{4}T_{1}g_{(G)}$	
$[Co(L)_2].2H_2O$	281	35587	2202	Intra- ligand	oh
	345	28986	1748	Intra- ligand	
	362	27624	1076	Intra- ligand	
	523	19120	76	$^{4}T_{1}g\rightarrow{}^{4}T_{1}g_{(P)}$	
	661	15129	24	$^{4}T_{1}g\rightarrow{}^{4}A_{2}g$	
	745	13423	14	$^{4}T_{1}g\rightarrow{}^{4}T_{2}g$	
$[Ni(L)_2].3H_2O$	274	36496	1853	Intra- ligand	oh
	345	28986	766	Intra- ligand	
	354	28249	576	Intra- ligand	
	588	17007	25	$^{3}A_{2}g\rightarrow{}^{3}T_{1}g_{(P)}$	
	783	12771	19	$^{3}A_{2}g\rightarrow{}^{3}T_{1}g$	
	962	10395	16	$^{3}A_{2}g\rightarrow{}^{3}T_{2}g$	
$[Cu(L)_2].2H_2O$	276	36232	1969	Intra- ligand	Distorted oh
	355	28169	1228	Intra- ligand	
	377	26525	992	C.T	
	815	12270	33	$^{2}Eg\rightarrow{}^{2}T_{2}g$	
$[Zn(L)_2].3H_2O$	281	35587	2236	Intra- ligand	Distorted oh
	347	28818	1462	Intra- ligand	
	363	27548	1018	Intra- ligand	
$[Cd(L)_2].2H_2O$	280	35714	2120	Intra- ligand	-
	344	29070	1902	Intra- ligand	
	357	28011	1127	Intra- ligand	
$[Hg(L)_2].3H_2O$	281	35587	2120	Intra- ligand	-
	345	28986	1902	Intra- ligand	
	356	28090	1127	Intra- ligand	

Table (10) :Showed the inhibition circle diameter in millimeter for the bacteria after 24 hour in cubation paid (37°C) for ligand (HL) and it's and mated complexes

Compounds	E. Coli	*Pesudomonas*	*Bacillus*	*Staphylococcus*
DMSO	5	7	-	5
Ligand (HL)	13	14	12	11
$[VO(HL)_2SO_4].3H_2O$	15	11	-	7
$[Mn(L)_2].3H_2O$	-	8	-	9
$[Co(L)_2].2H_2O$	14	9	-	13
$[Ni(L)_2].3H_2O$	14	35	18	25
$[Cu(L)_2].2H_2O$	-	-	18	12
$[Zn(L)_2].3H_2O$	-	9	15	13
$[Cd(L)_2].2H_2O$	17	14	29	13
$[Hg(L)_2].3H_2O$	17	20	25	20

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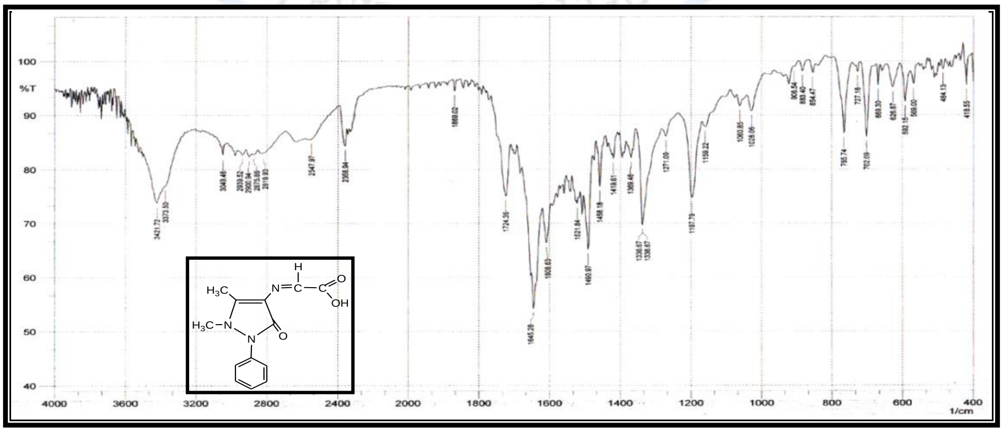
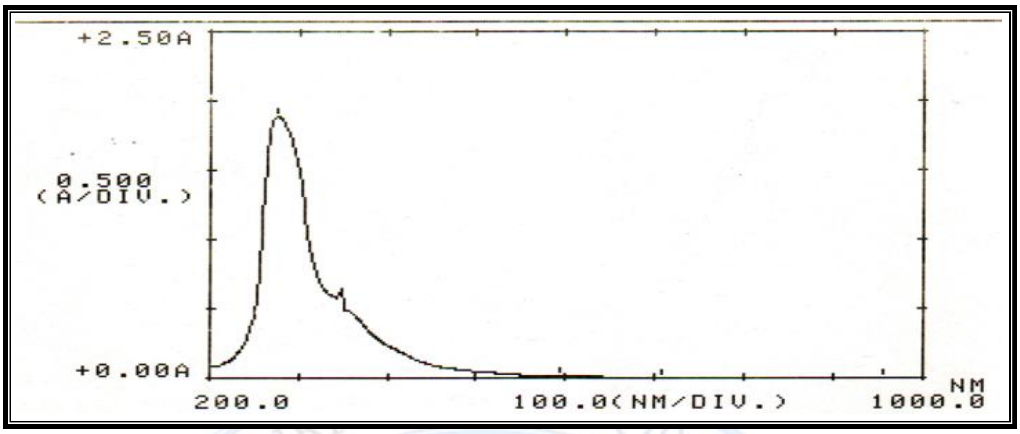
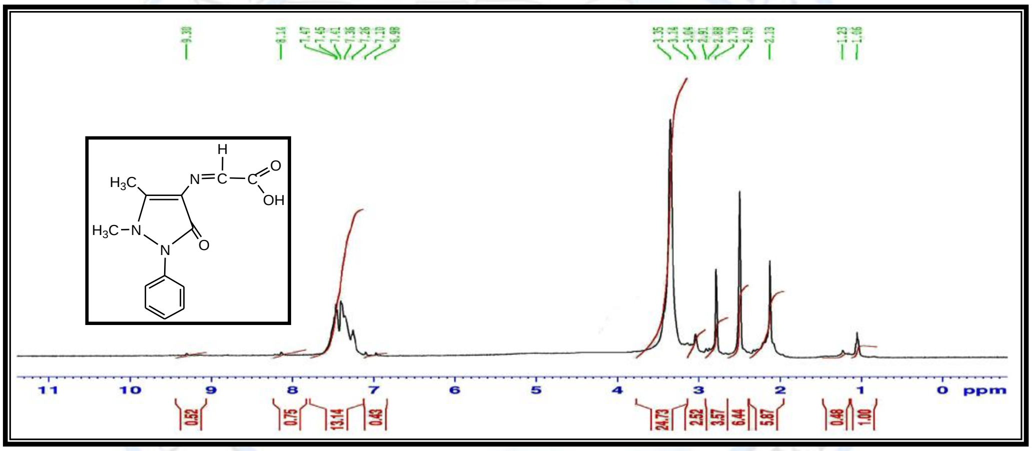


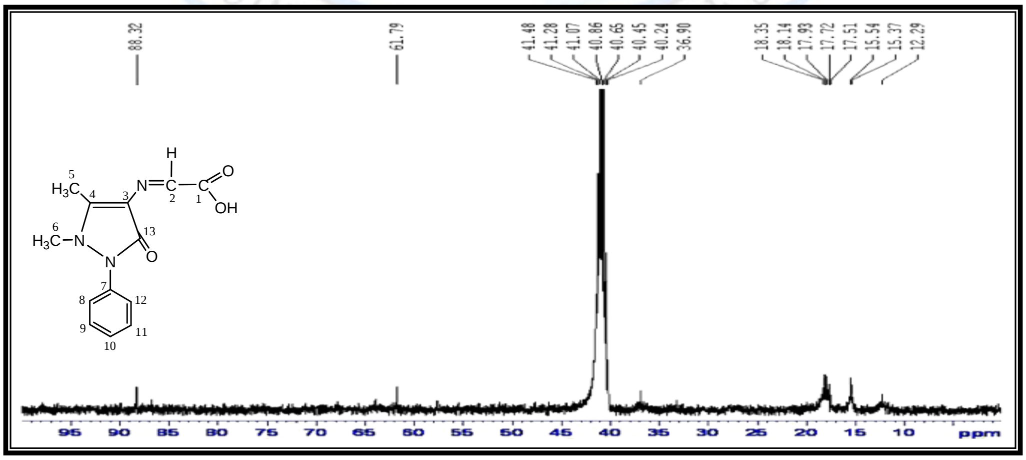
(Fig. 1): FT- IR spectrum of the ligand (HL)

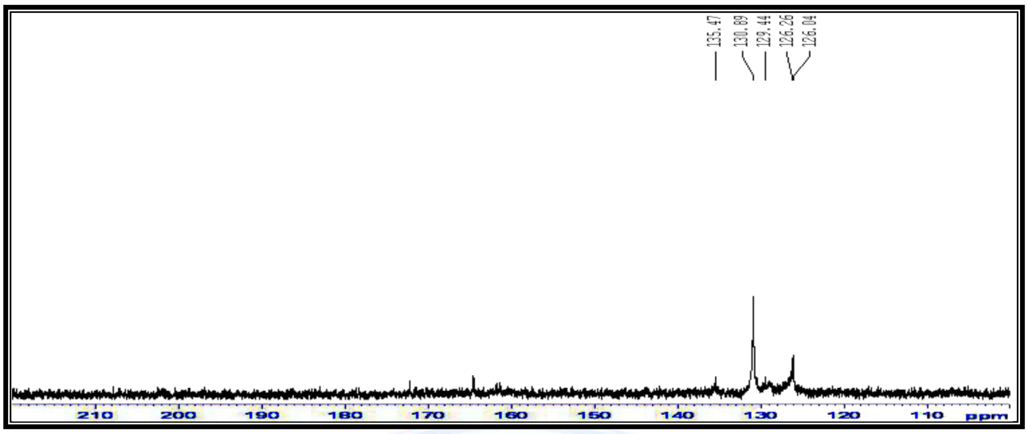


(Fig. 2): U.V- Vis spectrum of the ligand (HL)

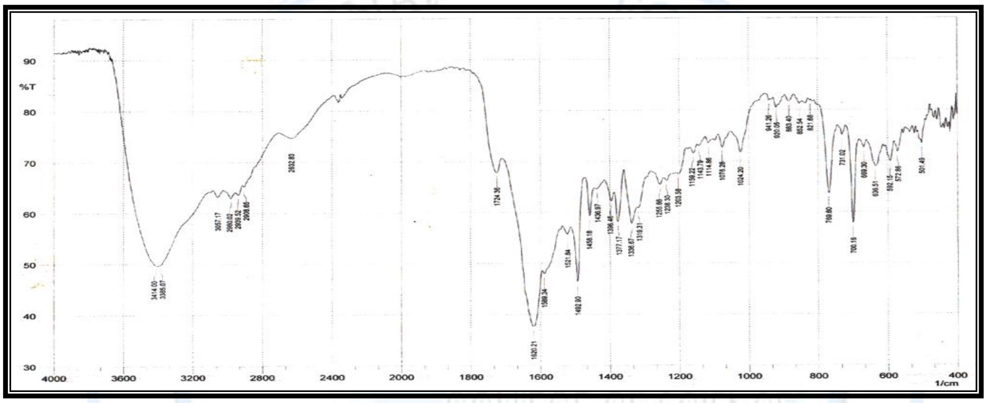


(Fig. 3): ^{1}H-NMR spectrum of the ligand (HL)

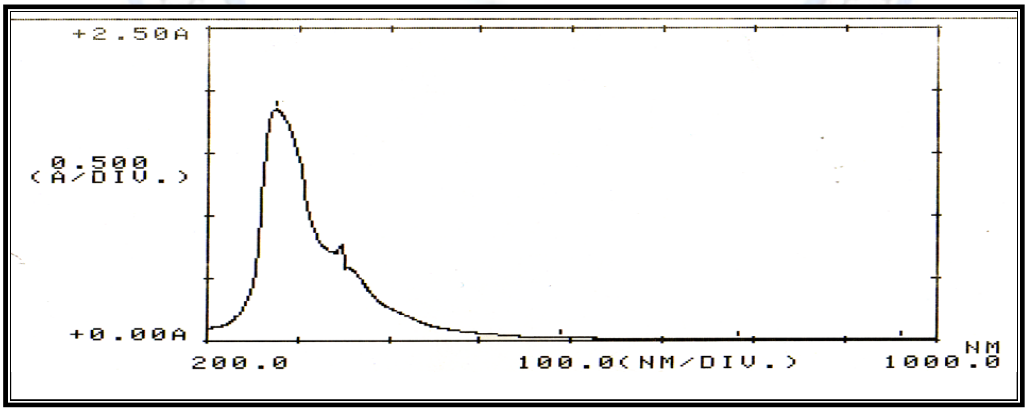


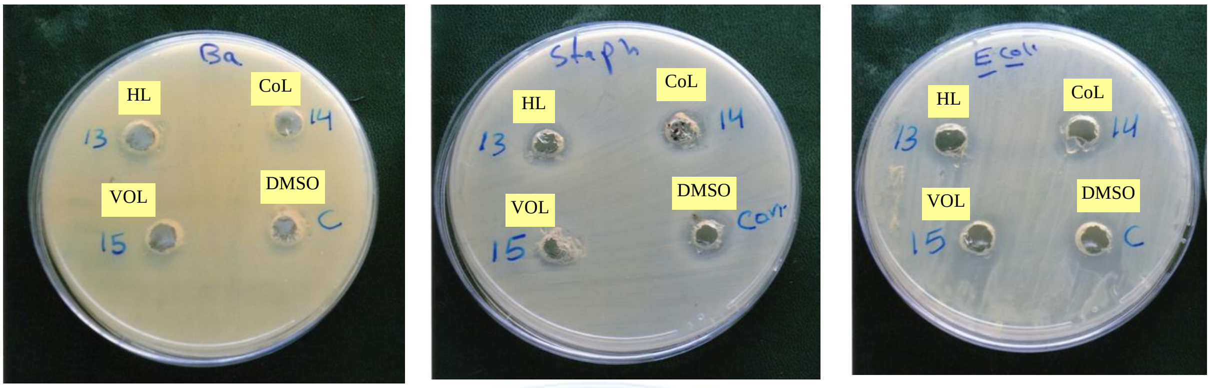


(Fig. 4): ^{13}C-NMR spectrum of the ligand (HL)

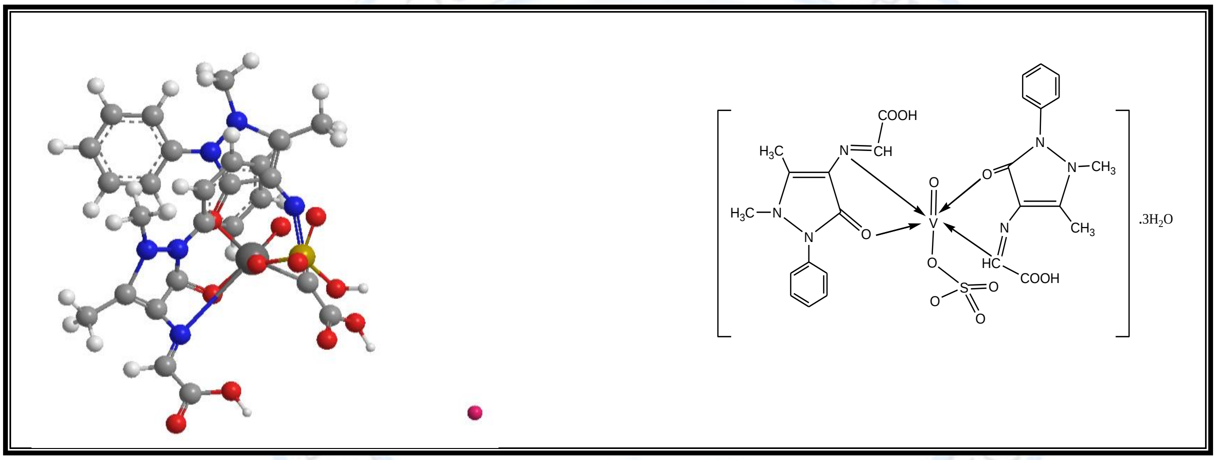


(Fig. 5): FT- IR Spectrum of [Co(L)$_2$]. 2H$_2$O complex

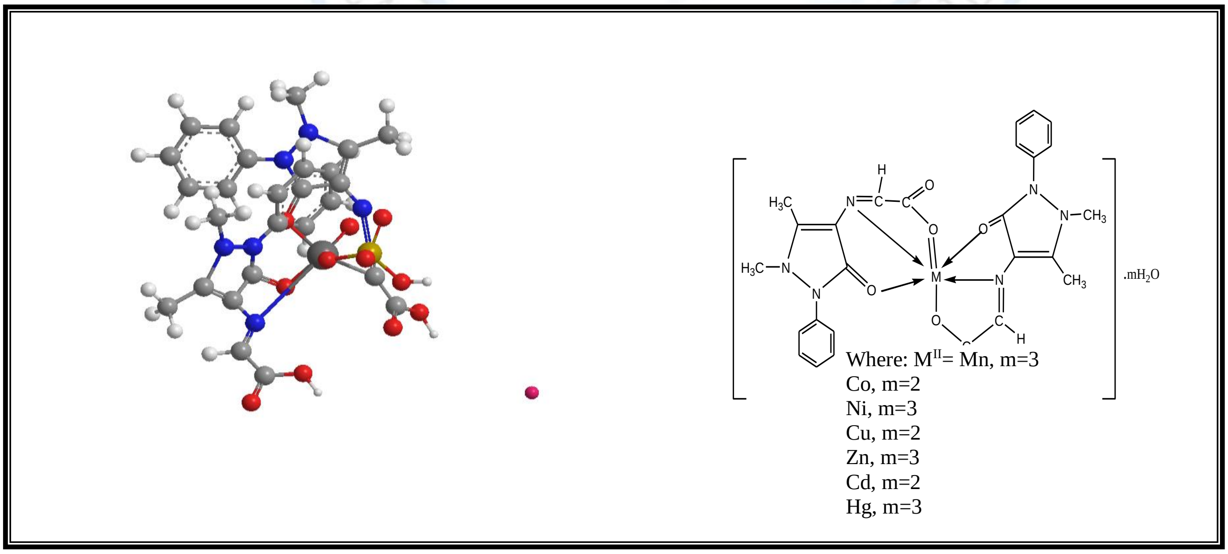




(Fig. 7) :Inhibition diameter for ligand (HL) and complexes
Ecoli= *Escherichia coli*, Staph= *Staphylococcus aurens*, Bacil= *Bacillus*



(Fig. 8): Structure of $[VO(HL)_2SO_4].3H_2O$ complex



Where: M^{II}= Mn, m=3
Co, m=2
Ni, m=3
Cu, m=2
Zn, m=3
Cd, m=2
Hg, m=3

(Fig. 9): Structure of ligand (HL) complexes