



Structural, Spectral and Thermal Studies of Novel Tridentate Schiff Base Ligand Type (NOO) as Donor Atoms Derived from Nalidixic Acid and 4-Aminoantipyrine and Metal Complexes and Evaluation of their Biological Activity

Hawraa K. Salloom^{1*}, Sajid M. Lateef², Shaimaa A.Hassan³

¹. Ministry of Education, Karkh 1 Directorate of Education/Iraq.

². Department of Chemistry, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Baghdad, Iraq.

³. Al-Karkh University of Science/Iraq.

*Corresponding Author: Hawraa K. Salloom

Abstract

In this study, a novel Schiff base (E)-4-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-1-ethyl-7-methyl-1,4-dihydro-1,8-naphthyridine-3-carboxylic acid [HL] was synthesized from nalidixic acid 4-Aminoantipyrine and its metal complexes for metal ions M=VO, Mn, Co, Ni, Cu, Zn, Pd and Pt in ethanol and acetic acid with mole ratio (M:L) (1:2). All complexes have general composition [VO (L) (SO₄) H₂O], [Mn(L)₂], [Co(L)₂] H₂O, [Ni(L)₂] H₂O, [Cu(L)₂] H₂O, [Zn(L)₂].H₂O, [Pd(KL)₂] and [Pt(KL)Cl₂] Cl₂ where L = C²³H₂₂N₅O₃. The ligand and all complexes were characterized by modern spectroscopic (FT-IR, UV Vis, ¹HNMR, Mass spectroscopy, atomic absorption), along with elemental microanalysis, magnetic susceptibility measurements, thermal analyses, chloride content and molar conductance. In addition to evaluated their biological activity against one type of bacterial and one type fungus. Based on date for all techniques we suggested that all the prepared complexes have octahedral geometry accept [[VO (L) (SO₄) H₂O] square pyramidal geometry and [Pd (KL) ₂] Square planer geometry. The value of antibacterial activity of this prepared complexes showed higher inhibition activity compared to the free ligand and starting material.

Keywords: Nalidixic Acid, 4-Aminoantipyrine, Metal complexes, Biological activity.

Introduction

Schiff's base is a nitrogen analogue of an aldehyde or ketone in which C=O group is substituted by a C=N-R group. It is also known as an azomethine. The first Schiff's base was prepared by Schiff by condensation of an aldehyde with a primary amine in 1864 [1]. Schiff bases are usually bi and tri-dentate ligands capable of forming very stable complexes with transition metals. Many diverse Schiff bases structures have been synthesized. These Schiff bases find versatile uses in chemistry [2]. Schiff bases appear to be important intermediates in a number of enzymatic reactions involving interaction of an amino group of the enzyme with a carbonyl group of the substrate. Many Schiff bases possess antibacterial [3], antifungal [4], antiviral [5], anticancer [6], antitubercular [7], anticonvulsant [8], anti-inflammatory [9],

antitumor [10], anti-HIV [11] and anthelmintic [12] cardiovascular. Nalidixic acid has been used in the treatment of several diseases as a powerful antibiotic drug for decontamination of the gut infections [13-20]. Nalidixic acid is effective primarily against gram-negative bacteria, with minor anti-gram-positive activity. In lower concentrations, it acts in a bacteriostatic manner; that is, it inhibits growth and reproduction. In higher concentrations, it is bactericidal, meaning that it kills bacteria instead of merely inhibiting their growth [21]. It has historically been used for treating urinary tract infections, caused, for example, by Escherichia coli, Proteus, Shigella, Enterobacter, and Klebsiella. It is no longer clinically used for this indication in the USA as less toxic and more effective

agents are available [22]. The Chemical name is 4-Aminoantipyrine, synonyms are 4-AAP; Solnapyrin-A.; Solvapyrin-A.; Minoazophene; Aminoazophene and Aminoantipyrin; Formula is $C_{11}H_{13}N_3O$, and molecular weight = 203.24. G/mol. 4-AAP has large scale of applications in biological, clinical, analgesics, antifungal, antibacterial, anticancerous and pharmacological areas [23-26]. Schiff bases of 4-AAP and its complexes have a variety of applications in clinical, biological, analytical and pharmacological areas [27]. Properties of 4-AAP to coordinate with metal is varied by condensing it with aldehydes, ketones, thiosemicarbazides and carbazides etc., Metal complexes of 4-AAP and biological behavior involving the amino group of 4-AAP has been studied exhaustively, when compared to the work carried out on the chemistry of transition metal complexes and biological behavior involving the amino group of 4-AAP [28, 29].

Experimental

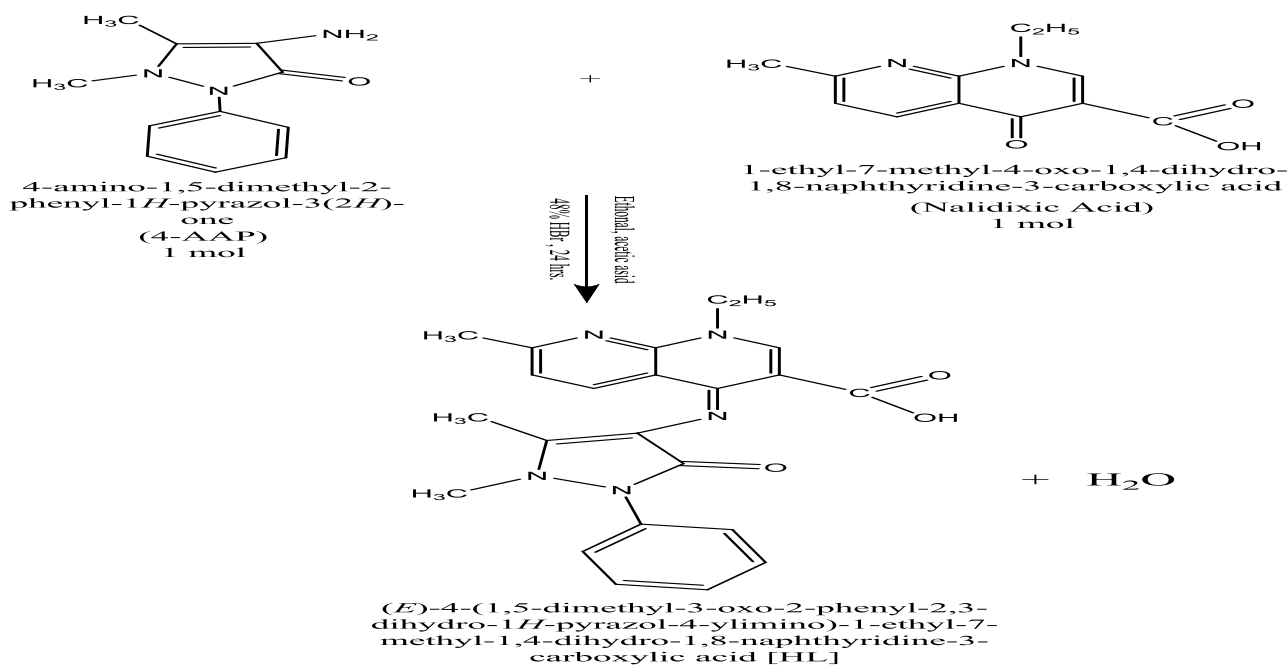
Martial's and Methods of Characterization

Nalidixic Acid, 4-Aminoantipyrine, vanadyl (II) sulfate mono hydrate, manganis (II) chloride tetrahydrate, cobalt (II) chloride hexahydrate, nickel (II) chloride hexahydrate, cupper (II) chloride dehydrate, Palladium chloride, zinc (II) chloride and Hydrogen hexachloroplatinum (IV), DMSO acetic acid and ethanol were provide from Aldrich company. Melting points for prepared complexes were measured by electro thermal

(Stuart melting point apparatus). Infrared spectra were performed using a Shimadzu (FT-IR)-8400S, The electronic spectra of the compounds were recorded by using double-beam (U.V-Vis) spectrophotometer type U.V 160A (Shimadzu), Elemental micro analysis recorder by using Euro Vector, model EA 3000 single V.3.Osinglein.The Chloride contents were determined using (686-Titro processor-665. Dosimat Matron Swiss), Electrical conductivity measurements of the complexes were recorder at (25°C) for (10⁻³ mole. L⁻¹) solution of the samples in DMSO by using (conductivity meter, model 4070), Magnetic measurements of the metal complexes were performed on a Magnetic Susceptibility Balance Mode (MSB_MKI), ¹HNMR, acquired using a Bruker-400 MHz and 200 MHz for thermogravimetric analysis (TGA) was carried out using STA PT-1000 Linseis company /Germany.

Synthesis of ligand [HL]

A Solution of 4- amino antipyrine (0.203g, 1mmol) in (10ml) ethanol was added to a solution of nalidixic acid (0.232 g, 1 mmol) in (5 ml) ethonal and (5ml) acetic acid then heated to complete dissolving with (3) drops of HBr (48%). The mixture was refluxed for overnight with stirring. The yellow crystal precipitate was formed during refluxing, which was cooled at room temperature then filtered and washed with ethanol and acetic acid then recrystallized by methanol to get a pure sample, yield 80% m.p. (198-200)°C and M.wt = 417 g/mol (C₂₃H₂₃N₅O₃). As displayed in Scheme (1).



Scheme 1: synthesis route of the ligand [HL]

Synthesis of Ligand [HL] Complexes

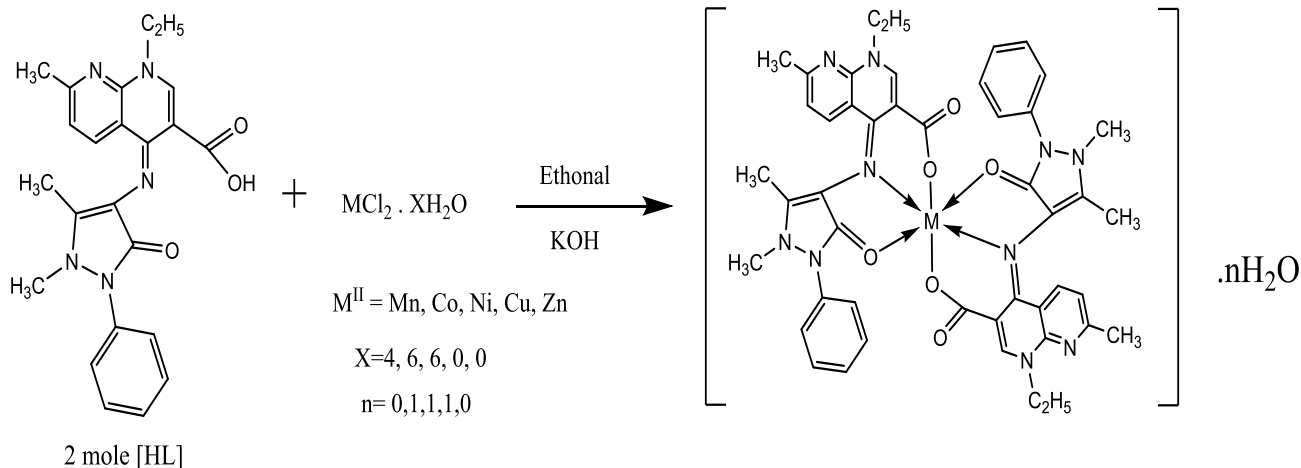
Synthesis of [Cu (L) ₂] H₂O

A solution of KOH (0.056 g, 1 mmol) in (5 ml) ethanol was added to a solution of Schiff bases ligand [HL] (0.417 g, 1 mmol) in (10 ml) ethanol in order to form [KL]. A solution of CuCl₂ (0.1345 g, 1 mmol) in (10ml) ethanol was added to a solution of [KL] ligand. The reaction mixture was allowed to refluxed for (3hrs). A reddish brown precipitate was formed which was filtered off, washed several times with Absolut ethanol and dried. Yield

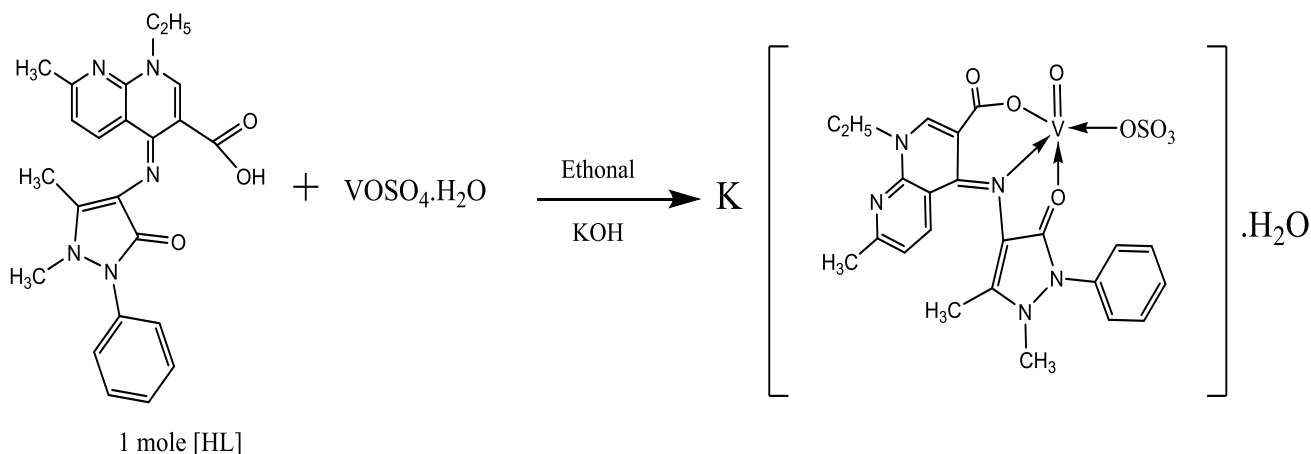
78% m.p. (206°-208°) C. See scheme (2)

Syntheses of Complexes [(VO (L) (SO₄)) H₂O, [Mn(L)₂], [Co(L)₂] H₂O, [Ni(L)₂] H₂O, [Zn(L)₂].H₂O, [Pd(KL)₂], [Pt(KL)Cl₂] Cl₂)

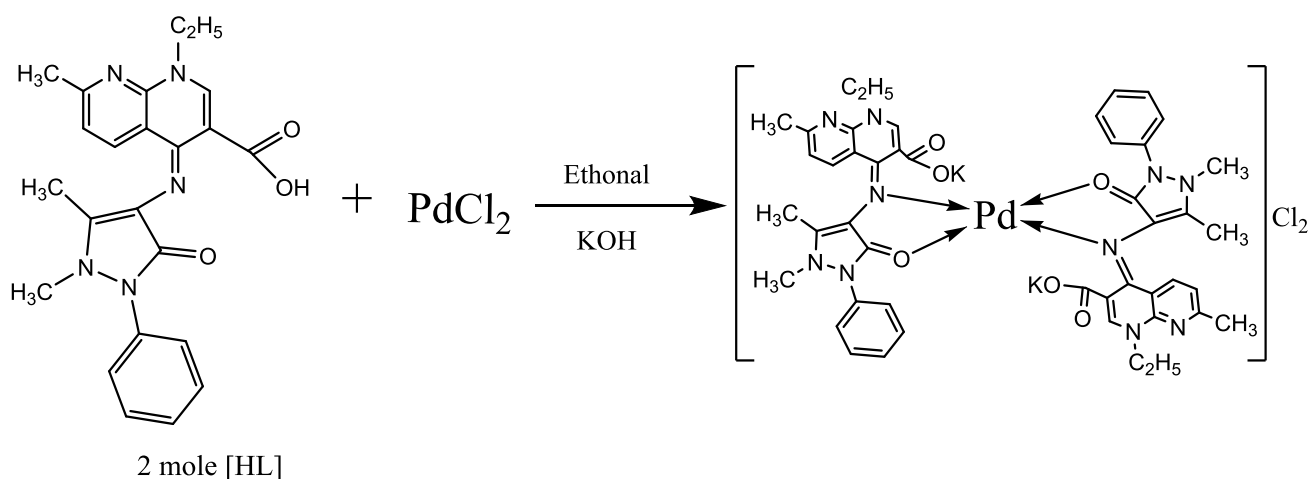
Similar method to that mentioned in [2.4.2.1] in synthesizing of Cu (II) complex was used to synthesized the complexes of [HL] with VOSO₄.H₂O and with MCl₂.xH₂O M (II) = [Mn (x=4), Co (x=6), Ni (x=6), Zn (x=0), Pd (x=0) and H₂PtCl₆]. The physical properties of the complexes and their reactant quantity displayed. See Scheme (2-5).



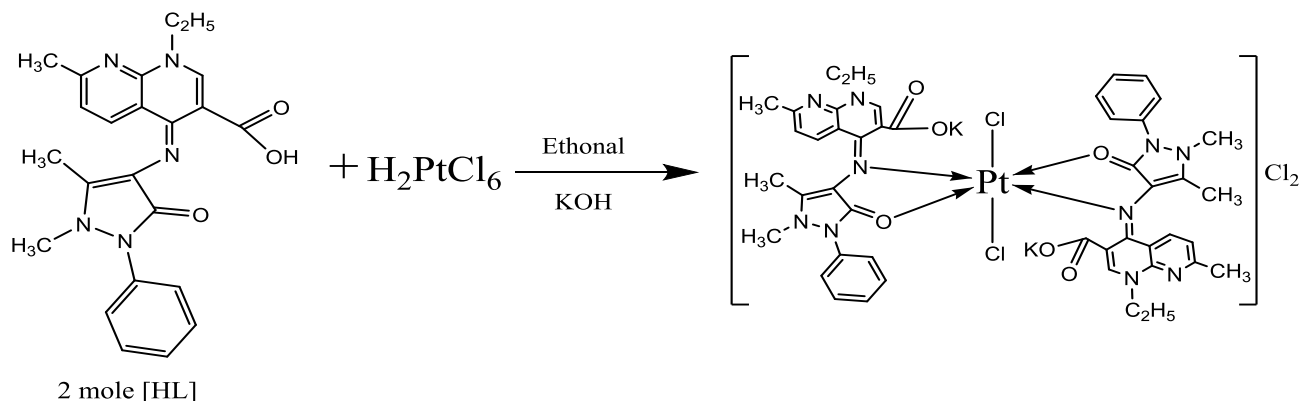
Scheme 2: Synthesis route of [M (L)₂]



Scheme 3: Synthesis route of K [VO (L) SO₄] H₂O



Scheme 4: Synthesis route of [Pd (KL) ₂] Cl₂

Scheme 5: Synthesis route of [Pt (KL)₂ Cl₂] Cl₂

Results and Discussion

FT-IR Spectrum of Ligand [HL]

The FT-IR Spectrum of ligand [HL] fig. (3.6) showed a band at (3205) cm^{-1} refers to (O-H) stretching frequency of carboxylic group. The two bands at (1712) cm^{-1} and (1375) cm^{-1} can be attributed to (ν asy – COO⁻) and (ν asy-COO⁻). The strong band at (1616) cm^{-1} was assigned to (ν C=O) for 4-AAP. The new weak band at (1562) cm^{-1} can be attributed to (ν C=N) of azomethine group [30]. Appearance of this band (azomethine) and disappearance of (ν asy) and (ν sy.) of NH₂ for 4-AAP and ν C=O (ketonic) of nalidixic acid, in the IR spectrum of ligand [HL] confirms the formation of schiff bases ligand [31]. The observed bands at (1518, 1473) cm^{-1} and (3045) cm^{-1} can be assigned to aromatic (ν C=C) and (ν C-H) respectively. The characteristic bands were summarized.

The Electronic Spectrum of ligand [HL]

Fig (3).The U.V-Vis spectra data of ligand [HL] were given. The U.V-Vis spectrum of this ligands, Fig. (3-8) exhibits three intense absorption peaks. The first and second at (270) nm (37037) cm^{-1} and (301) nm (33223) cm^{-1} were assigned to $\pi \rightarrow \pi^*$ electronic transition [32]. The third peak at (338) nm (29586) cm^{-1} was attributed to $n \rightarrow \pi^*$ electronic transition [33].

¹H-NMR Spectrum of ligand [HL]

The singlet signal observed at (δ =2.70 ppm) in the spectrum of free Schiff base [HL], was assigned to the methyl group (C-CH₃), singlet signal showed at (δ =2.08 ppm), was attributed to the (N-CH₃), triplet showed at (δ =1.38-1.42 ppm), was attributed to the group (N-CH₂-CH₃), multiple a ranged between (δ =7.20-7.59 ppm) were assigned to the aromatic protons of the phenyl, singlet signal showed at (δ =14.90 ppm), was attributed to the methyl of O-H carboxylic group (O-H), quart showed at (δ =5.22 ppm), was attributed to the ethyl group (N-CH), The singlet signal appeared at (δ =2.50 ppm) in fig (4). Can be assigned to the solvent (DMSO) [34].

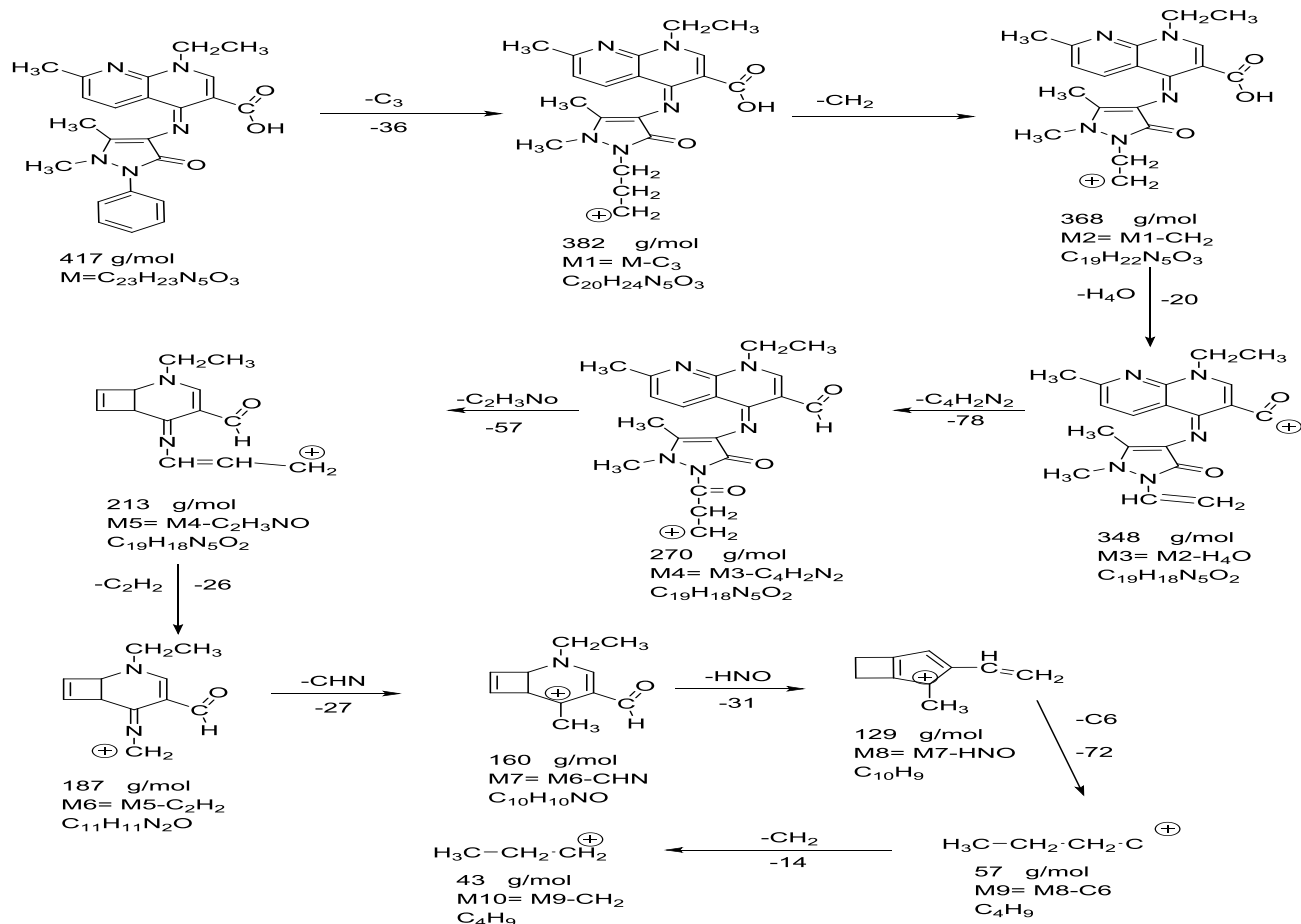
GC-Mass Spectrum of ligand [HL]

Is depicted in Figure (5).The electrospray (+) mass spectrum of [HL] is presented. The spectrum exhibits successive fragments related to ligand structure [35]. The molecular ion peak for the ligand is observed at $m/z = 417$ which corresponds to M⁺ (50%) for [C₂₃H₂₃N₅O₃]; requires = 417, other fragments and their relative abundance and fragmentation pattern are shown in Table (1).

The suggested mass fragmentation of (L) is shown in scheme (6).

Table 1: The fragmentation pattern of ligand [HL]

Ligand	Assignment	Peak m/z	Relative abundance%
[HL]	M = (C ₂₃ H ₂₃ N ₅ O ₃)	417	50
	M - C ₃ ⁺ = M ₁	382	15
	M ₁ - CH ₂ ⁺ = M ₂	368	14
	M ₂ - OH ₄ ⁺ = M ₃	348	11
	M ₃ - C ₄ H ₂ N ₂ ⁺ = M ₄	270	25
	M ₄ - C ₂ H ₃ NO ⁺ = M ₅	213	12
	M ₅ - C ₂ H ₂ ⁺ = M ₆	187	13
	M ₆ - CHN ⁺ = M ₇	160	32
	M ₇ - HNO ⁺ = M ₈	129	60
	M ₈ - C ₆ ⁺ = M ₉	57	100
M ₉ - CH ₂ ⁺ = M ₁₀	43	85	



Scheme 6: Suggested mass fragmentation of ligand [HL]

Characterization of Complexes

Characterization of Complexes K [VO (L) (SO₄)]·H₂O

Dark gray, Yield: 71%. m.p. 175 °C. IR 3381 ν OH (H₂O), 1712-1375 ν asy. COO ν syCOO, 1612 ν C=O₄AAP, 1560 ν C=N_{iminic}, 573 M-N, 548 M-O, 970-, 1115,616 SO₄. UV/visible (DMSO, mm):270 (Intra - ligand), 319 (Intra-ligand), 408 (²B_{2g}→²A_{1g}), 605 (²B_{2g}→²B_{1g}), 808 (²B_{2g}→²E_g). (C.H.N) (found %), cala. %:(42. 85)43.39C, (3.15)3.77H, (11.26)11.00N, (7.63)8.01Metal. μ_{eff} (B.M):1.64

[Mn (L)]₂

Orange, Yield: 75%. m.p. 187°C. IR 1705-1390 ν asy. COO ν syCOO, 1624 ν C=O₄AAP, 1576 ν C=N_{iminic}, 550 M-N, 447 M-O. UV/visible (DMSO, mm):277 (Intra – ligand), 346 (MLCT), 386 ⁶A_{1g}→⁴A_{1g}, Eg (G)), 402 (⁴A_{1g}→⁴T_{2g} (G)), 477 (⁴A_{1g}→⁴T_{1g} (G)). (C.H.N) (found %), cala. %:(61.84)62.23C, (4.83)4.96H, (15.01)15.78N, (5.53)6.20 Metal. μ_{eff} (B.M):5.37

[Co (L)]₂·H₂O

Brown, Yield: 61%. m.p. 220 °C. IR 3360 ν OH (H₂O), 1705-1390 ν asy. COO ν syCOO, 1620 ν C=O₄AAP, 1572 ν C=N_{iminic}, 498 M-N, 445 M-O in Fig (6). UV/visible (DMSO, mm):

270 (Intra – ligand), 332(Intra – ligand), 345 (Intra - ligand), 423(^{(v₃)⁴Tig(F)→⁴T_{2g}(P)), 683 (^{(v₂)⁴Tig(F) →⁴A_{2g}(F)), 803 (^{(v₁)⁴Tig(F)→⁴T_{2g}(F)). Fig. (7) (C.H.N) (found %), cala. %:(59.83) 60.72C, (4.67)5.06H, (15.40)16.02N, (6.11)6.49Metal. μ_{eff} (B.M):4.33}}}

[Ni (L)]₂·H₂O

Orange, Yield: 71%. m.p. 122-125 °C. in fig. (6) IR 3275 ν OH (H₂O), 1705-1398 ν asy. COO ν syCOO, 1620 ν C=O₄AAP, 1572 ν C=N_{iminic}, 579 M-N, 440 M-O. in fig (7) UV/visible (DMSO, mm):268 (Intra – ligand), 345 (Intra – ligand), 406 (^{(v₃)³A_{2g}(F)→³T_{1g}(P)), 726 (^{(v₂)³A_{2g}(F)→³T_{1g}(F)), 978 (^{(v₁)³A_{2g}(F)→³T_{2g}(F)). (C.H.N) (found %), cala. %:(60.16) 60.74C, (4.53) 5.06H, (14.68)15.40N, (6.31)6.45 Metal. μ_{eff} (B.M):2.68}}}

[Cu (L)]₂·H₂O

Yellow, Yield: 70%. m.p. 206-208 °C. IR 3390 ν OH (H₂O), 1704-1387 ν asy. COO ν syCOO, 1620 ν C=O₄AAP, 1558 ν C=N_{iminic}, 515 M-N, 472 M-O. UV/visible (DMSO, mm):270 (Intra – ligand), 346 (Intra – ligand), 368 (MLCT), 727 (²E_g→²T_{2g}). (C.H.N) (found %), cala. %:(59.88) 60.42C, (4.63)5.03H, (14.72)15.32N, (6.27)6.95Metal. μ_{eff} (B.M):1.74

[Zn (L) ₂]

Dark brown, **Yield:** 76%. **m.p.** 195 °C.

IR 1704-1383 ν asy. COO⁻ ν _{asy}COO, 1624 ν C=O_{4-AAP}, 1574 ν C=N_{iminic}, 575 M-N, 442 M-O. UV/visible (DMSO, mm):366 (Intra-ligand), 335 (Intra – ligand). (C.H.N) (found %), cala. % : (60.84)61.53C, (4.56) 4.90H, (15.92) 15.60N, (6.87)7.28 Metal.

[Pd (KL) ₂] Cl₂

Brown, **Yield:** 72%. **m.p.** 240°C IR 1714-1367 ν asy. COO⁻ ν _{asy}COO, 1628 ν C=O_{4-AAP}, 1560 ν C=N_{iminic}, 552 M-N, 445 M-O. UV/visible (DMSO, mm):375 (Intra – ligand), 331 (Intra – ligand), 351 (MLCT), 468 (¹A_{1g}→¹B_{1g}), 572 (¹A_{1g}→¹A_{2g}). (C.H.N) (found %), cala. %: (49.18) 50.76C, (3.67) 4.04H, (11.58)12.87N, (8.95)9.78Metal, (6.01) 6.52 Cl.

Thermal Analyses for [Zn(L)₂]

Figure (8) TGA peak observed at 376 °C indicated the loss of (C₂₃H₂₅N₅O₃) fragment, (det. = 48.288 mg, calc. =46.920 mg).

The two step occurred at 519 °C revealed the loss of (-C₁₂H₁₂N₂O) portion, (det. = 20.789 mg, calc. = 22.949 mg) Wight experimental loss(69.071)% , final (30.929)% , Wight theoretical loss (69.414)% and final(30.586)% with (C₁₁H₇N₃O₂Zn).

[Pt (KL) Cl₂] Cl₂

Dark gray, **Yield:** 71%. **m.p.** 230 °C. IR 1712-1377 ν asy. COO⁻ ν _{asy}COO, 1620 ν C=O_{4-AAP}, 1571 ν C=N_{iminic}, 570 M-N, 489 M-O. UV/visible (DMSO, mm):266 (Intra – ligand), 323(Intra – ligand), 385(MLCT), 506 (¹A_{1g}→¹T_{2g}), 848 (¹A_{1g}→¹T_{1g}). (C.H.N) (found %), cala. % : (43.57) 44.26C, (3.01)3.52H, (10.78) 11.22N, (15.22)15.63 Metal, (10.94) 11.83 Cl

Results and Discussion of Complexes Chemistry

A novel Schiff base and eight complexes were synthesized by direct reaction between ligand [HL] and metalions, this complex were synthesis to confirm the suggested structures of complexes.

FT-IR Spectra of ligand [HL] Complexes

The FT-IR spectral data were summarized in table (3-14). The band at (1562) cm⁻¹ in the spectrum of free ligand [HL], which referred to ν C=N of imine group was shifted to lower or higher frequency and appeared at range

(1558-1576) cm⁻¹ in spectra of all complexes. This shift in ν C=N of imine group confirming the coordination of ligand [HL] through N atom of this group with metal ions [36]. On the other hand, the two bands related to carboxyl a to moiety at (1712) cm⁻¹ and (1375) cm⁻¹, which were assigned to ν asy. COO⁻ and ν sy. COO⁻ modes respectively, in the IR spectrum of free ligand [HL], were shifted to lower or higher frequency at range (1635-1707) cm⁻¹ and (1363-1398) cm⁻¹ in the spectra of all complexes (except Pd(II) and Pt(IV) two complexes) $\Delta\nu$ values refer to the COO⁻ group behaves as monodentate. This shift suggested the coordination between COO⁻ group with metal ion (VO (II), Mn(II), Co(II), Ni(II), Cu(II) and Zn (II) via oxygen atom.

The band at (1616) cm⁻¹ which refers to ν C=O for 4-AAP ring in spectrum of free ligand [HL], was shifted to lower or higher frequency at range (1612-1628) cm⁻¹ in the spectra of all complexes, showing that the coordination was happened via oxygen atom of this group (C=O) with metal ions. In complexes the band of ν asy. COO⁻ which was shifted to lower or higher frequency, as previously passed, was appeared as shoulder and overlap with band of ν C=O of 4-AAP ring.

The new bands in IR spectrum of VO (II) (9) complex at frequencies (901) cm⁻¹ and (1115, 970, 616) cm⁻¹ were attributed to (ν V=O) group and (ν SO₄, δ SO₄) monodentate ligand of SO₄²⁻. The FR spectra of VO(II), Co(II), Ni(II) and Cu(II) complexes exhibited abroad band at (3381, 3360, 3275 and 3390), was assigned to hydrated H₂O [37]. At the lower frequency region, the IR spectra of all complexes showed new bands which are not present in spectrum of free ligand, these band, were noted at range (498-579) cm⁻¹ and (440-548) cm⁻¹, were attributed to ν M-N and ν M-O respectively.

The band which due to ν C=N (ring) could be overlap with the band of ν C=O (4-AAP) at range (1612-1628) cm⁻¹ From these observation, we conclude that the ligand [HL]behaves as tridentate with [VO(II), Co (II), Ni (II), Cu(II) and Zn(II)]complexes via N atom of iminic group (C=N) and two oxygen atoms of carboxylic group (-COO⁻) and (C=O) group of 4-AAP ring [38], while it behaves bidentate with [Pd(II) and (Pt(IV))] complexes via N atom of iminic group(C=N) and oxygen

atom of (C=O) group of 4-AAP ring.

The Electronic Spectra

The electronic spectrum of Zn (II), complex showed that no (d-d) transition because it contains a full d sub shell [39]. (UV_Vis) electronic transitions for all complexes have good agreement for octahedral geometry accept $[VO(L)(SO_4)] \cdot H_2O$ square pyramidal geometry and $[Pd(KL)_2]$ Square planer geometry, around the metal ion. The TGA Data of $[Zn(L)_2]$ has agreement with their molecular formula [40].

Elemental Analysis

Elemental microanalysis results also have a good agreement with the calculated values. At last the molar conductance showed that all complexes non- electrolytic behavior show Table (2).

Magnetic Moment (μ_{eff})

The (μ_{eff}) values for Mn(II) Co(II), Ni(II) and Cu(II) refer to high-spin octahedral geometry, while for VO(II) complexes refers to square pyramidal. But $\mu_{eff} = 0.00$ for Pd(II) -4d⁸ square planer and Pt (IV) -5d⁶(octahedral) because this two ions diamagnetic in nature.

Table 2: The molar conductivity the complexes

Compounds	\square_m S.cm ² .mole ⁻¹
K[VO (L) (SO ₄) H ₂ O]	33.61
[Mn(L) ₂]	8.95
[Co(L) ₂] H ₂ O	13.7
[Ni(L) ₂] H ₂ O	14.26
[Cu(L) ₂] H ₂ O	8.58
[Zn(L) ₂]	11.48
[Pd(KL) ₂] Cl ₂	71.63
[Pt(KL)Cl ₂] Cl ₂	72.54

Biological Activity

In Fig (9).The biological activity of prepared ligand and its complexes were evaluated in vitro, E. coli and C. albicans aeruginosa which described in Table.(3) The ligand and

all complexes give higher inhibition activity against one type of bacterial (Escherichia coli) and one type of fungus (Candida albicans) was compared with the control DMSO and the starting materials.

Table 3: Bacterial activity of the starting material, ligands and its complexes

No.	Compound	<i>Esherichia Coli</i>	<i>Bacillus subtilis</i>
	HL	13	20
9	K[VO (L) (SO ₄) H ₂ O]	14	22
10	[Mn(L) ₂]	12	17
11	[CO(L) ₂] H ₂ O	14	25
12	[Ni(L) ₂] H ₂ O	13	23
13	[Cu(L) ₂] H ₂ O	11	23
14	[Zn(L) ₂].H ₂ O	13	26
15	[Pd(KL) ₂] Cl ₂	11	18
16	[Pt(KL)Cl ₂] Cl ₂	12	22

Conclusion

The Schiff base [HL] behave as tridentate ligand through two oxygen atoms of Carboxylic group and carbonyl group of 4-AAP and N atom of iminic group with the

central metal ions: VO(II) (Mn(II), Co(II), Ni(II), Cu(II), Zn(II) accept (Pd(II) and Pt(IV) bidentate via oxygen atom of C=O of 4-AAP ring and N atom of iminic group forming complexes with geometrical structure as in Fig.(1):

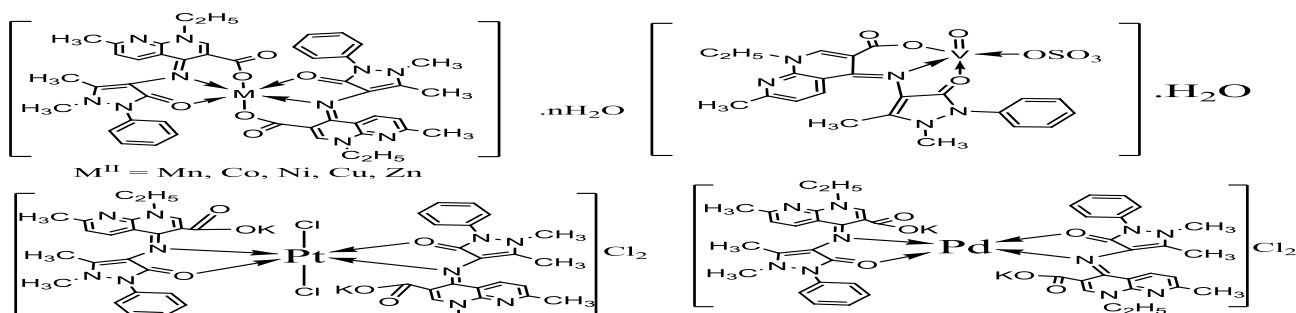


Fig 1: Suggested structure of complexes

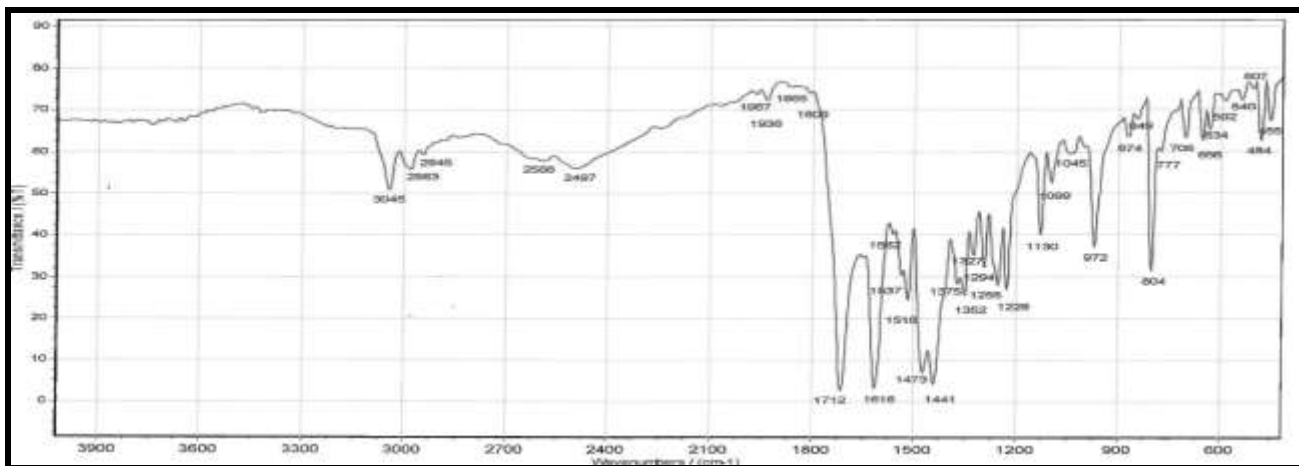


Fig.2: Infrared spectrum of Schiff base ligand (HL)

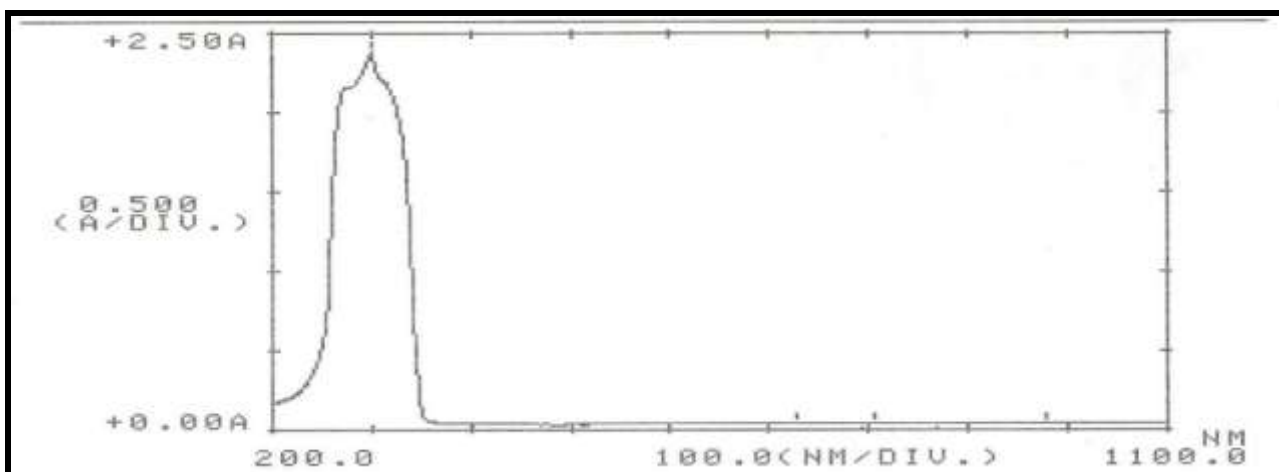


Fig.3: Electronic spectrum of ligand [HL]

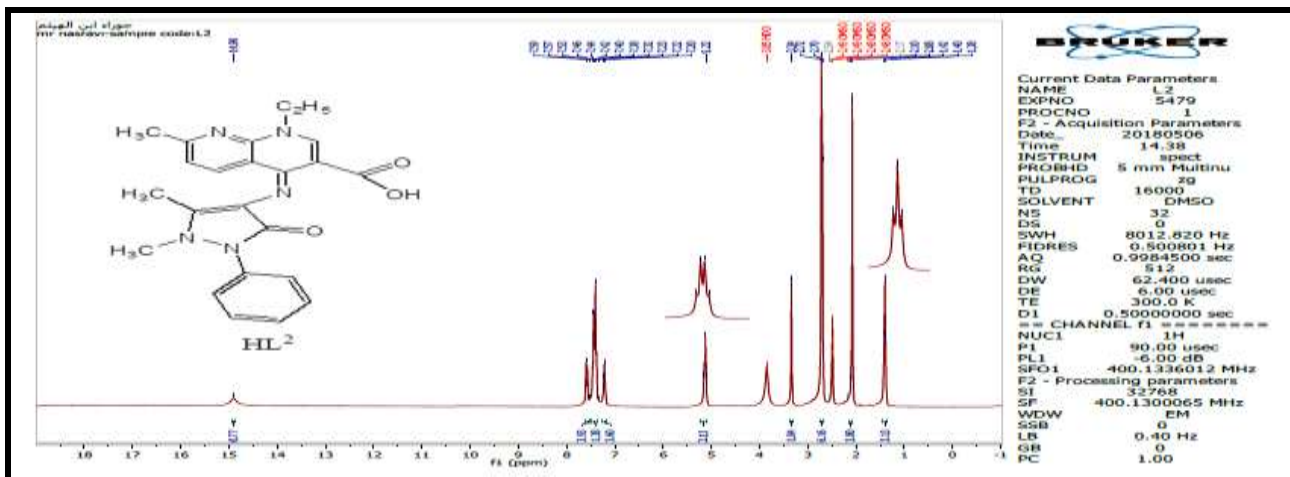


Fig.4: ¹H-NMR spectrum of ligand [HL]

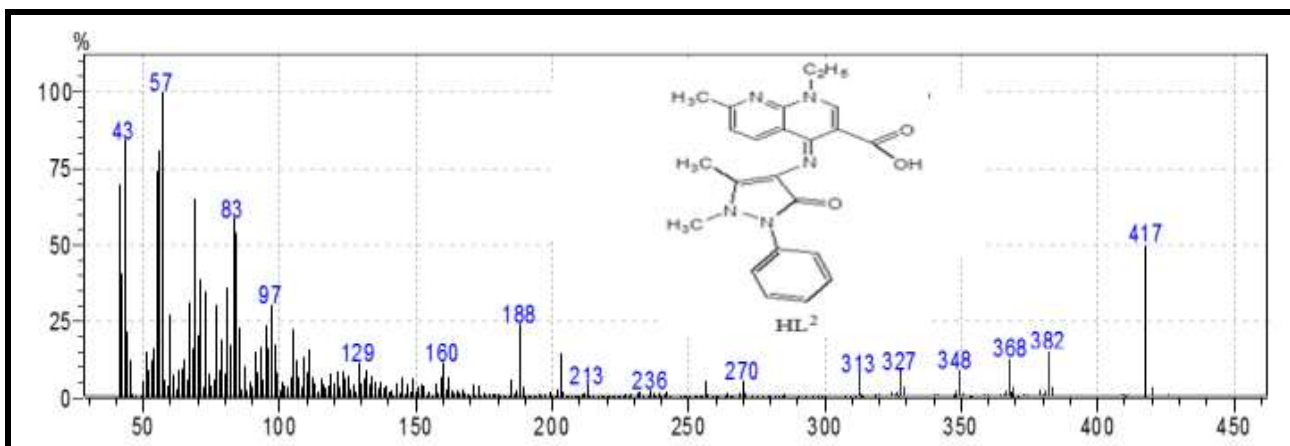


Fig.5: GC-Mass spectrum of ligand [HL]

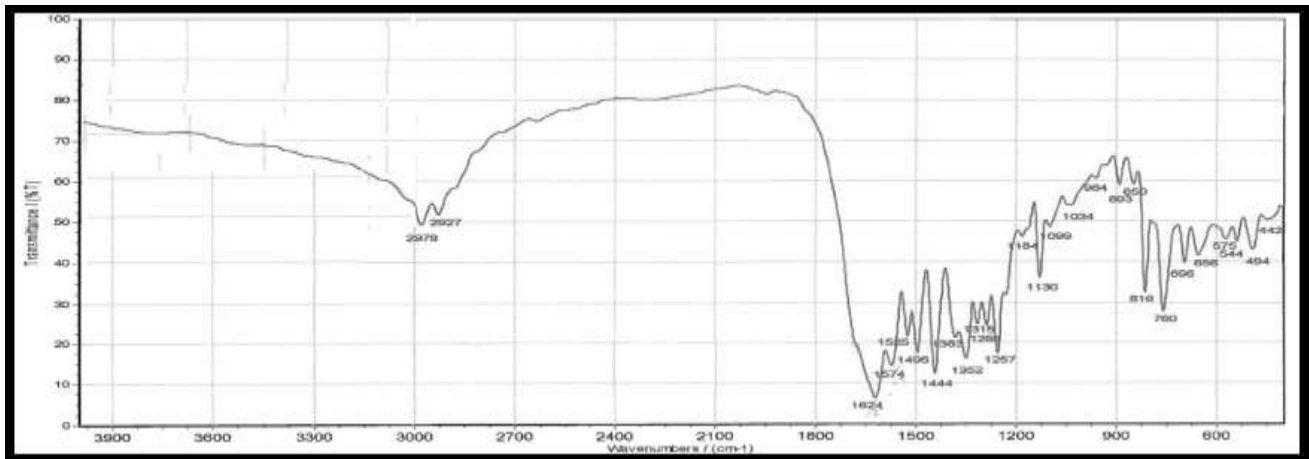


Fig.6: Infrared spectrum of ligand complex [Zn (L) ₂]

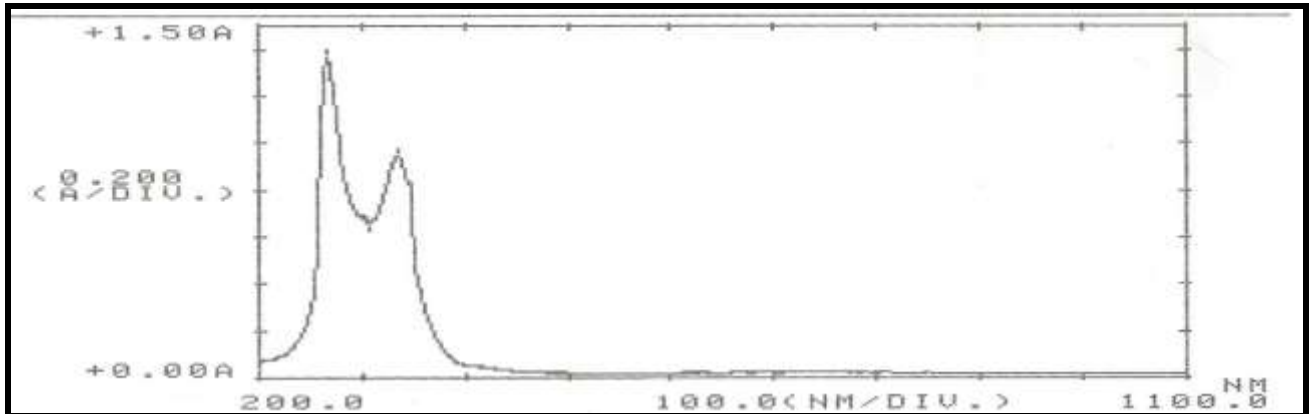


Fig. 7: Electronic spectrum of mono - ligand complex [Zn (L)₂]

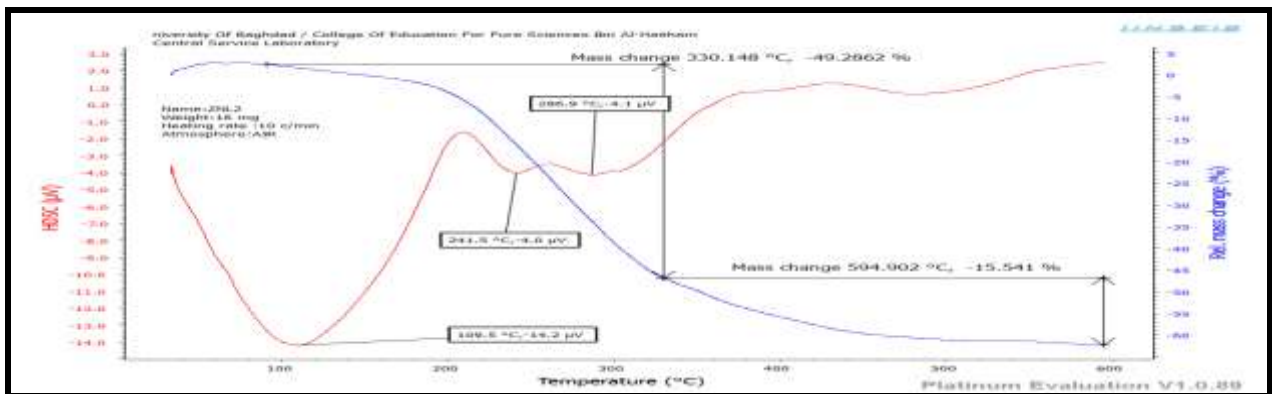


Fig.8: (TGA and DSC) thermo gram of [Zn (L) ₂] in an argon atmosphere

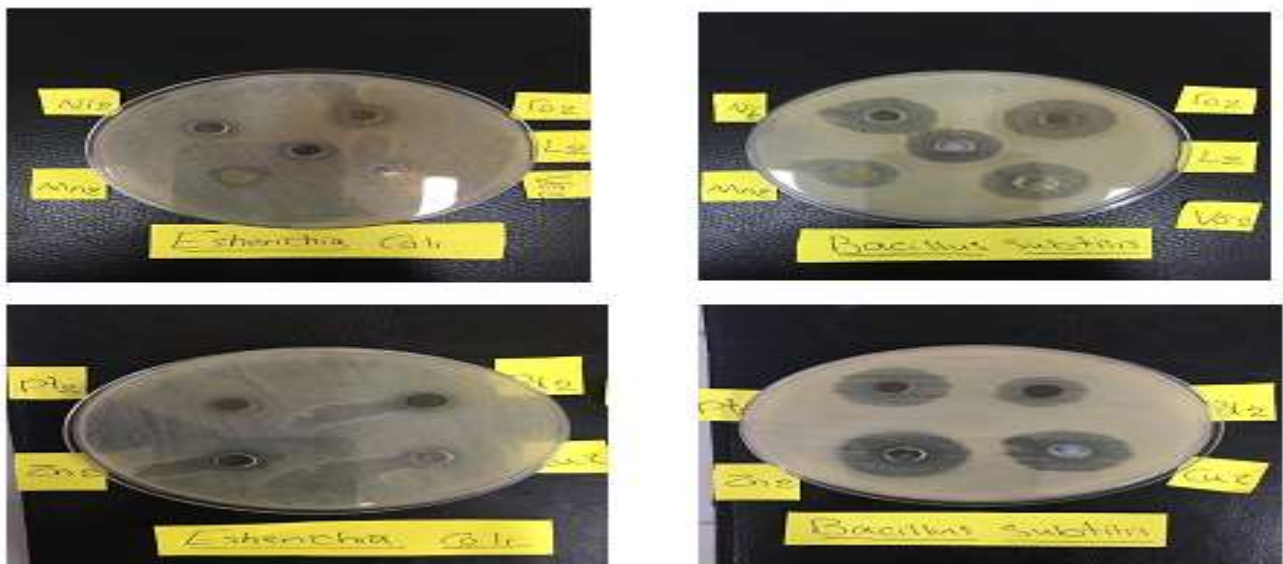


Fig.9: Inhibition diameter for ligands and complexes E coli=Escherchia coli baci=bacillus

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