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Synthesis and characterization of the new Tetradentate schiff base ligand type N_4 derived From 4-animoantipyrine,4-dimethylaminobenzaldehyde, ethylenediamine and furfural, towards Fe(III), Co(II), Cu(II), Zn(II) and Hg(II) Ions

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تحضير وتشخيص ليكاند قاعدة شف جديدة رباعية السن نوع N_4 مشتقة من 4- امينوانتي بايرين، 4- ثنائي مثيل امينو بنزلديهايد، ثنائي مثيل امين و الفورفورال مع Fe(III) ، Co(II) ، Cu(II)، Zn(II) و Hg(II)

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المستخلص

تم تحضير معقدات الحديد (III) ، الكوبالت (II) ، النحاس (II)، الخارصين (II) و الزئبق(II) بمفاعلة املاح كلوريدات الفلزات المذكورة مع ليكاند قاعدة شف جديدة رباعية السن نوع N_4 :

(N^1Z,N^2Z)-N^1-(4-((Z)-4-(dimethylamino) benzylideneamino)-2,3-dimethyl-1-phenyl-1,2dihydropyrazol-5-ylidene)-N^2(4((Z)-furan-2-ylmethyleneamino)-2,3-dimethy l-1-phenyl-1,2dihydropyrazol-5-ylidene)ethane1,2–diamine

وتم تشخيص كل المعقدات المحضرة بواسطة الطرق الطيفية (تقنية الأشعة تحت الحمراء، الأشعة فوق البنفسجية – المرئية و الامتصاص الذري للعناصر) الحساسية المغناطيسية ، تعيين نقطة الانصهار ، التحليل الدقيق للعناصر و التوصيلية المولارية. بالإضافة إلى طيف الرنين النووي المغناطيسي لليكاند الحرة. ومن خلال النتائج والمعطيات المتحصل عليها من التقنيات اعلاه تم استنتاج بنية ثماني السطوح لمعقد الحديد وبنية رباعي السطوح لبقية معقدات الكوبالت ، النحاس، الخارصين و الزئبق . ذوات الصيغة العامة $[FeLCl_2]Cl$ ، $[CoL]Cl_2$، $[CuL]Cl$، $[ZnL]Cl_2$ و $[HgL]Cl_2$.

الكلمات المفتاحية : قاعدة شف ، 4- امينوانتي بايرين، 4- ثنائي مثيل امينو بنزلديهايد، ثنائي مثيل امين و الفورفورال.

Abstract

Iron(III), Cobalt(II), Cupper(II), Zinc(II) and Mercury(II) complexes have been synthesized by reaction of their chloride salt with a new tetradentate Schiff base ligand type N_4: (N^1Z,N^2Z)-N^1-(4-((Z)-4-(dimethylamino)benzylideneamino)-2,3-dimethyl-1-phenyl-1,2dihydropyrazol-5-ylidene)-N^2(4((Z)-furan-2-ylmethyleneamino)-2,3-dimethyl-1-phenyl-1,2dihydropyrazol-5-ylidene)ethane1,2–diamine. All the prepared complexes were characterized by the spectroscopic methods (FT.IR, UV-Vis) Atomic Absorption, Magnetic Susceptibility, Melting Point, Elemental Analysis and Molar Conductivity, as well as the H^1NMR for the free ligand. According to the resulted data from the above mentioned techniques, the octahedral structure geometry was proposed for Fe(III) complex with the formula $[FeLCl_2]Cl$, and tetrahedral geometry was proposed for the rest with a general formula $[ML]Cl_2$.

Key words: Schiff Base, 4-Aminoantipyrine, 4-Dimethylaminobenzaldehyde, Furfural.

Introduction

It is well known that the preparation of new ligands is perhaps the most important step in the development of metal complexes, which exhibit unique properties and novel reactivity (1). Schiff bases of aromatic aldehydes or aromatic ketons are more stable than aliphatic aldehydes or ketons because of the conjugation system (2). Schiff bases derived from 4-aminoantipyrine, and their complexes having a wide variety of applications in many fields of biological, clinical, analytical, organic, inorganic and pharmacological areas (3). They are also used as pigments and dyes, catalysis intermediates in organic synthesis and as polymer stabilizer (4). During the past years a considerable attention has been paid to the chemistry of the metal complexes of Schiff base containing nitrogen as donor atoms. This may be attributed to their high stability (5). The coordination property of the 4-aminoantipyrine ligands was modified to give flexible ligands systems formed by condensation with a variety of reagents such as aromatic aldehydes and aromatic amines (6). The present paper reports the synthesis and characterization of new Tetradentate Schiff base Ligand Type N_4 (N^1Z,N^2Z)-N^1-(4-((Z)-4(dimethylamino) benzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-ylidene)-N^2(4((Z)-furan-2ylmethyleneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-ylidene)ethane1,2–diamine and its Fe(III), Co(II), Cu(II), Zn(II) and Hg(II) complexes.

Experimental

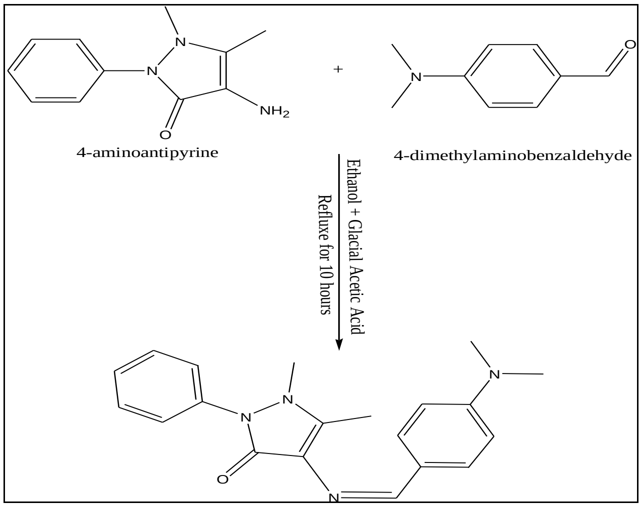
Materials and Instrumentation

All chemicals supplied by Fluka, Redial- Dehenge, Gainland Chem, B D H and Thomas Baker companies. Elemental microanalysis was carried out by C.H.N analyzer, model 1106 (Calo-Ebra). Metal contents of the complexes were determined by Shimadzu-A-A- 680G Atomic Absorption Spectrophotometer. The FT.IR spectra were recorded as KBr disc technique by using Shimadzu 8300 FT-IR Spectrophotometer in the range (4000-250)cm^{-1}. Electronic Spectra of the prepared complexes were measured in the range (200-900) nm for 10^{-3}M solution of DMSO at room temperature by using Shimadzu 160 Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Electrical molar conductivity measurements of the complexes were recorded at room temperature for 10^{-3}M solution of samples in DMSO by using PW 526 digital conductivity meter. Melting points were recorded by using Sturat Melting Point Apparatus. Magnetic Moments were measured with a magnetic susceptibility balance (Jonson Matty Catalytic System Division) and finally H^1NMR spectrum was acquired in DMSO-d_6 solution using a Brucker AMX400 MHZ spectrometer with existed of TMS as an internal standard for H^1NMR.

Synthesis of Compounds and Complexes

1- Synthesis of 4-[(4-Dimethylamino-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2 dihydro-pyrazol-3-one: ($C_{20}H_{22}N_4O$).

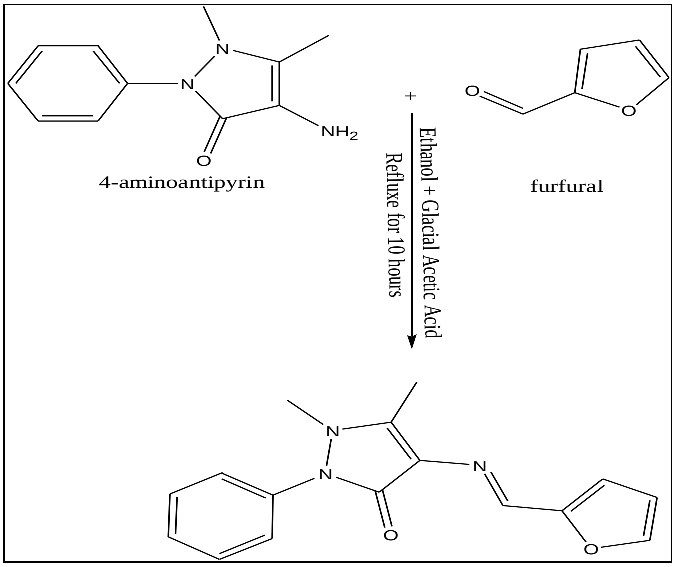
(0.0003 mole, 0.609gm) of 4-aminonatipyrine dissolved in 25ml of absolute ethanol, and added dropwise with stirring to 25ml of ethanol solution containing (0.003mole, 0.447gm) of 4-dimethylaminobenzaldehyde and few drops of glacial acetic acid as catalyst (7). The mixture of the reaction refluxed for 10hours at $75C^0$ (scheme-1), and then filtered to remove the unreacted starting materials. The solvent was left to evaporate at room temperature, the resulted yellow crystals washed several times with ethanol and left dry. The yield was 0.952g (95%), ($220C^0$-$222C^0$) (table-1).



Scheme (1): Synthesis of 4-[(4-Dimethylamino-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2 dihydro-pyrazol-3-one: ($C_{20}H_{22}N_4O$).

2- Synthesis of 4-[(Furan-2-ylmethylene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one: ($C_{16}H_{15}N_3O_2$).

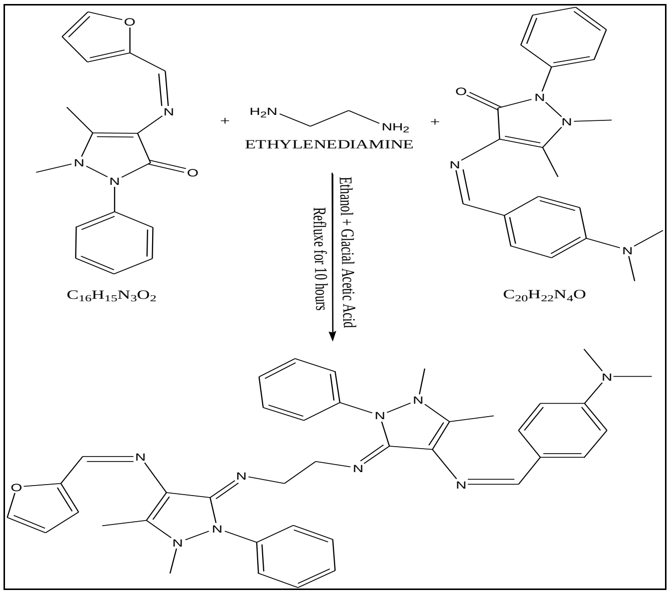
(0.0003 mole, 0.609gm) of 4-aminonatipyrine was dissolved in 25ml of absolute ethanol and added dropwise with stirring to 25ml of ethanol solution containing (0.003mole, 0.288gm) of Furfural, and few drops of glacial acetic acid as catalyst (7). The mixture of the reaction refluxed for 10hours at $75C^0$ (scheme-2), and then filtered to remove the unreacted starting materials. The solvent was left to evaporate at room temperature, the resulted brown crystals washed several times with ethanol and left dry. The yield was 0.6921g (82%), mp ($210C^0$-$212C^0$) (table-1).



Scheme (2): Synthesis of 4-[(Furan-2-ylmethylene)-amino]-1,5-dimethyl-2-phenyl 1,2-dihydro-pyrazol-3-one: ($C_{16}H_{15}N_3O_2$).

3- Synthesis of the Free Ligand (L): ($C_{38}H_{41}N_9O$).

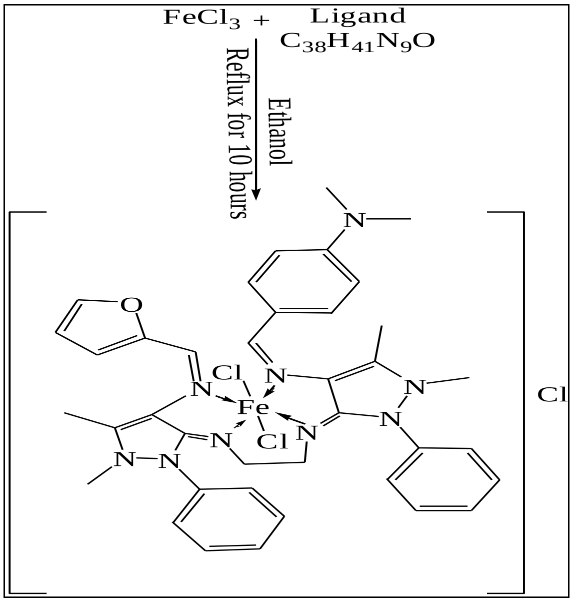
(0.003mole, 0.18gm) of Ethylenediamine which dissolved in 25ml of hot ethanol was added dropwise with stirring to a mixture of (0.003mole, 1.002gm) of ($C_{20}H_{22}N_4O$), and (0.003mole, 0.843gm) of ($C_{16}H_{15}N_3O$) in 100ml of hot ethanol containing a few drops of glacial acetic acid. The mixture was refluxed for 10hours at 75C^0 (scheme-3), then the mixture filtered to remove the unreacted starting materials. The solvent was left to evaporate at room temperature, the resulted brown crystals washed several times with ethanol and left dry. The yield was 1.764g (92%), mp (165C^0-167C^0) (table-1).



Scheme (3): Synthesis of the Free Ligand (L): ($C_{38}H_{41}N_9O$).

4- Synthesis of Iron(III) Complex.

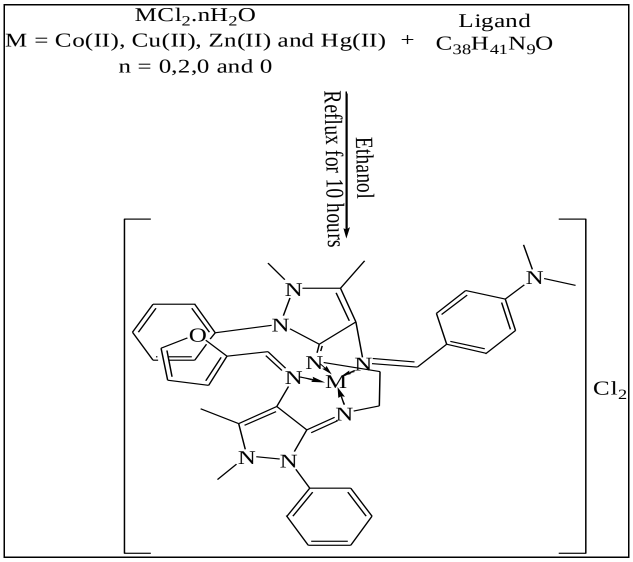
A brownish solution of the ligand [L] ($C_{38}H_{41}N_{9}O$) (0.0004mole, 0.2556gm) in hot ethanol 50ml was added dropwise with stirring to (0.0004mole, 0.06492gm) of $FeCl_3$ reddish solution in 50ml of ethanol. The reaction mixture was allowed to reflux for 10hours at 75C^{0} (scheme-4). During reflux time the solution color turned to dark reddish brown. The solvent was left to evaporate at room temperature, the resulted reddish brown crystals washed several times with ethanol and left dry. The yield was 0.2179g (68%), mp (179C^{0}-177C^{0}) (table-1).



Scheme (4): Synthesis of Iron(III) Complex [$FeLCl_2$]Cl

5- Synthesis of Cobalt(II), Cupper(II), Zinc(II) and Mercury(II) Complexes.

A brownish solution of the ligand [L] ($C_{38}H_{41}N_{9}O$) (0.0004mole, 0.2556gm) in hot ethanol 50ml was added dropwise with stirring to (0.0004mole) (0.05196gm, 0.0682gm, 0.0545gm and 0.1084gm) of ($CoCl_2$, $CuCl_2.2H_2O$, $ZnCl_2$ and $HgCl_2$) (reddish, greenish and colorless) solutions in 50ml of ethanol. The reaction mixture was allowed to reflux for 10hours at 75C^{0} (scheme-5). During reflux time the solution colors turned to more darkness (reddish, greenish and brownish). The solvent was left to evaporate at room temperature; the resulted crystals washed several times with ethanol and left dry to give dark (reddish, greenish and brownish) complexes with yields (61%-89%) mp (90C^{0}-184C^{0}) (table-1).



Scheme (5): Synthesis of [CoL]Cl$_2$, [CuL]Cl$_2$, [ZnL]Cl$_2$ and [HgL]Cl$_2$ Complexes.

Results and Discussion

a. Characterization of 4-[(4-Dimethylamino-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2 dihydro-pyrazol-3-one: ($C_{20}H_{22}N_4O$).

The condensation reaction of 4-aminonatipyrine and 4-dimethylaminobenzaldehyde give yellow crystals, which characterized with spectroscopic methods. The FT.IR spectrum (Fig.1) showed many changing of peaks shifting, appearing and disappearing in comparison with the starting materials. The most important band at (1641.49)cm^{-1} are due to iminc group (υC=N) which is a strong evidence of Schiff base formation(8). The other bands at (3045)cm^{-1}, (2958)cm^{-1}, (1681.9)cm^{-1}, (1589)cm^{-1}, (1301)cm^{-1}, (1134)cm^{-1} and (758)cm^{-1} due to functional groups (υC-H) aromatic, (υC-H) aliphatic, (υC=O), (υC=C), (υCH_3) (υC-O)(9) and aromatic (υC-H) out of plane ring (100. The UV-Vis spectrum exhibited two absorption peak at (235nm, $\bar{\upsilon}$ = 24553cm^{-1}, ε_{max}= 510 L.mol^{-1}.cm^{-1}) due to ($\pi \rightarrow \pi^*$) electronic transition while the second peak at (369nm, $\bar{\upsilon}$ = 10752 cm^{-1}, ε_{max}= 930 L.mol^{-1}.cm^{-1}) due to ($n \rightarrow \pi^*$) electronic transition (11). And finally the micro analysis of the elements Cal. (334): C, 71.85; H, 6.58; N, 16.76; O, 4.79. Found: C, 72; H, 6.3; N, 16.70; O, 4.8 %.

b. Characterization of 4-[(Furan-2-ylmethylene)-amino]-1,5-dimethyl-2-phenyl-1,2 dihydro-pyrazol-3-one: ($C_{16}H_{15}N_3O_2$).

The condensation reaction of 4-aminonatipyrine and furfural give brown crystals which characterized with spectroscopic methods. The FT.IR spectrum (Fig.2) showed many changing of peaks shifting, appearing and disappearing in comparison with the starting materials. The most important band at (1643.41)cm^{-1} due to iminc group (υC=N) which is a strong evidence of Schiff base formation (8). The other bands at (2920)cm^{-1}, (2860)cm^{-1}, (1696)cm^{-1}, (1577)cm^{-1}, (1365)cm^{-1}, (1130)cm^{-1} and (771)cm^{-1} due to functional groups (υC-H)aromatic, (υC-H) aliphatic, (υC=O), (υC=C), (υCH_3) (υC-O)(9) and aromatic (υC-H) out of plane ring (10). The UV-Vis spectrum exhibited two absorption peak at (258nm, $\bar{\upsilon}$ = 38759cm^{-1}, ε_{max}= 490 L.mol^{-1}.cm^{-1}) due to ($\pi \rightarrow \pi^*$) electronic transition while the second peak at (382nm, $\bar{\upsilon}$ = 26178 cm^{-1}, ε

$_{max}$= 1100 L.mol^{-1}.cm^{-1}) due to (n→π*) electronic transition (11). And finally the micro analysis of the elements Cal. (281) : C, 68.32; H, 5.35; N, 14.94; O, 11.38. Found: C, 86.1; H, 5.4; N, 15.1; O, 11.4 %.

c. Characterization of the Free Ligand (L): ($C_{38}H_{41}N_9O$).

The proligand was prepared with condensation reaction of (1:1:1) mole ratio of $C_{20}H_{22}N_4O$, $C_{16}H_{15}N_3O_2$ and Ethylenediamine according to method in (scheme-3). The free ligand is soluble in methanol, ethanol and DMSO. The FT.IR spectrum of the free Ligand (Fig.3) displayed many bands changing, appearing and disappearing in comparison with the starting compounds. The most important notes disappear of carbonyl groups (υC=O) at (1681.98)cm^{-1} and (1696)cm^{-1} which it is a strong evidence of Schiff base formation and appearing of two new bands at (1647)cm^{-1} and (1608)cm^{-1} due to iminc groups (υC=N) (12). However the other bands at (3043)cm^{-1}, (2924)cm^{-1}, (1585)cm^{-1}, (1485)cm^{-1}, (1369)cm^{-1}, (1134)cm^{-1} and (698)cm^{-1} due to functional groups (υC-H)aromatic, (υC-H) aliphatic, (υC=C), (υCH_2), (υCH_3), (υC-O) (9) and aromatic (υC-H) out of plane ring (10). The UV-Vis spectrum (Fig.4) exhibit two absorption peak at (260nm, ῡ = 38461cm^{-1}, ε $_{max}$= 410 L.mol^{-1}.cm^{-1}) due to (π→π*) electronic transition while the second peak at (360nm, ῡ = 27777 cm^{-1}, ε $_{max}$= 867 L.mol^{-1}.cm^{-1}) due to (n→π*) electronic transition (11). The predicated H^1NMR of the free Ligand (Fig.5) showed main peaks at d_{ppm}: 8.07(1H), 7.60(5H), 6.21(2H), 3.44(3H), 2.76(3H), 1.78(3H) and 1.48(2H)(13). And finally the micro analysis of the elements Cal. (639): C, 71.3; H, 6.41; N, 19.7; O, 2.5. Found: C, 71.1; H, 6.5; N, 19.69; O, 2.48 %.

Complexes

The reaction of the free ligand [L] with metal chloride salt Fe(III), Co(II), Cu(II), Zn(II), and Hg(II) were carried out in refluxed ethanol. All the prepared complexes are stable and soluble in methanol, ethanol and DMSO. On the basis of elemental analysis data (table-1) the molecular formula for prepared complexes were assigned to be [$FeLCl_2$]Cl, [CoL]Cl_2, [CuL]Cl_2, [ZnL]Cl_2 and [HgL]Cl_2. The suggested molecular formula has been also supported by the spectral measurements, molar conductivity, elemental analysis and magnetic susceptibility.

Molar Conductivity

The molar conductivity for the prepared complexes in DMSO at ambient temperature using 0.001 M solution from the complexes the results in (table-1) indicated 1:1 metal to Ligand mole ratio (14,15).

Magnetic Susceptibility

The values of measured magnetic susceptibility and effective magnetic moment (μ_{eff}) for the prepared complexes are shown in (table-1). Depending on the tabulated μ_{eff} values, complexes of Fe(III), Co(II) and Cu(II) are paramagnetic, while the Zn(II) and Hg(II) are diamagnetic (16-18).

Atomic Absorption

The atomic absorption measurements (table-1) for all complexes were in comparable with the theoretical values.

FT.IR Spectra

The FT.IR spectra for all prepared complexes showed different spectral data in comparison with the free ligand spectrum (table-3). All spectra exhibited shifting in the two iminc group (υC=N) at rang (1647-1658)cm^{-1} and (1593-1608)cm^{-1} in comparing with that in the free ligand at (1647)cm^{-1} and (1608)cm^{-1}(19). This shift in frequency in the position of the iminic group (υC=N) suggests a coordination between N atoms of the free ligand with metal ions (20). The other bands in Fe(III), Co(II), Cu(II), Zn(II) and Hg(II) complexes at (2924)cm^{-1}, (3047)cm^{-1}, (2927)cm^{-1} , (3047)cm^{-1} and (2942)cm^{-1} Due to the functional groups (υC-H) aromatic. (2854)cm^{-1}, (2924)cm^{-1}, (2870)cm^{-1}, (2924)cm^{-1} and (2854)cm^{-1} due to the functional group (υC-H) aliphatic(20). (1546)cm^{-1}, (1546)cm^{-1}, (1535)cm^{-1}, (1581)cm^{-1} and (1585)cm^{-1} due to the frequency of (υC=C) group (21). (1492)cm^{-1}, (1489)cm^{-1}, (1492)cm^{-1}, (1489)cm^{-1} and (1485)cm^{-1} due to the frequency of (υCH_2) group (22,23). (1369)cm^{-1}, (1373)cm^{-1}, (1373)cm^{-1}, (1369)cm^{-1} and (1369)cm^{-1} due to the frequency of (υCH_3) group (22,23). (1165)cm^{-1}, (1165)cm^{-1}, (1168)cm^{-1}, (1139)cm^{-1} and (1139)cm^{-1} due to the frequency of (υC-O) group(22,23). The most important peak appearance in complexes FT.IR charts in comparing with the free ligand charts its (υM-N) in the range (420- 439)cm^{-1}. (420)cm^{-1}, (424)cm^{-1}, (425)cm^{-1}, (439)cm^{-1} and (439)cm^{-1}(22,23). And finally the unique band at (390)cm^{-1} for Fe(III) complex which it is a strong evidence of (M-Cl) coordination linkage (24).

Electronic spectra

The electronic data for all complexes are summarized in (table-4). The peak at (260)nm in the electronic for the free ligand was shifted to lower absorbance for all of the prepared complexes. The shifting in the ligand absorbance peak indicates the coordination between the free Ligand and metal ions. The electronic spectra of Fe(III) complex displayed four absorption peaks at (259nm, 40000cm^{-1}, ε_{max}= 979 L.mol^{-1}.cm^{-1}) due to ligand field electronic transition type ($\pi\rightarrow\pi^*$) transition, while the second peak at (341nm, 29411cm^{-1}, ε_{max}= 1732 L.mol^{-1}.cm^{-1}) due to charge transfer. In fact these results are in good agreement with previous work of Fe(III) distortion octahedral complexes, the third peak at (350nm, 28571cm^{-1}, ε_{max}= 1295 L.mol^{-1}.cm^{-1}) due to the ($n\rightarrow\pi^*$) transition. Finally the weak (d-d) transition type ($^6A_1\rightarrow$ excited state)(24) at (430nm, 23255cm^{-1}, ε_{max}= 200 L.mol^{-1}.cm^{-1}). The electronic spectra of Co(II) complex displayed three absorption peaks at (259nm, 40000cm^{-1}, ε_{max}= 280 L.mol^{-1}.cm^{-1}) due to ligand field electronic transition while, the second peak at (342nm, 29411 cm^{-1}, ε_{max}= 621 L. mol^{-1}.cm^{-1}) due to charge transfer and the third peak at (510nm, 19607 cm^{-1}, ε_{max}= 180 L. mol^{-1}.cm^{-1}) due to ($^4A_2\rightarrow{}^4T_{1P}$) . The electronic spectra of Cu(II) complex displayed three absorption peaks at (258nm, 40000cm^{-1}, ε_{max}= 622 L.mol^{-1}.cm^{-1}) due to Ligand field electronic transition while the second peak at (340nm, 29411 cm^{-1}, ε_{max}= 340 L. mol^{-1}.cm^{-1}) due to charge transfer and the third peak at (715nm, 62500 cm^{-1}, ε_{max}= 160 L. mol^{-1}.cm^{-1}) due to ($^2T_2\rightarrow{}^2E$),, In fact these results are in good agreement with previous work of Co(II) and Cu(II) Tetrahedral complexes[11]. Finally, the UV-Vis spectra of Zn(II) and Hg(II) complexes displayed two absorption peaks at (260nm, 38461cm^{-1}, ε_{max}= 505 L.mol^{-1}.cm^{-1}) and (260nm, 38461cm^{-1}, ε_{max}= 463 L.mol^{-1}.cm^{-1}) due to ligand field electronic transition while the second peak at (346nm, 29411 cm^{-1}, ε $_{max}$= 1177 L.mol^{-1}.cm^{-1}) and (344nm, 29411cm^{-1}, ε $_{max}$= 787 L.mol^{-1}.cm^{-1}) due to charge transfer peak (11).

Table (1): Physical measurement results of the prepared compounds, free ligand and its complexes

Compound	M.Wt	Molar Conductance Ohm^1.cm^2.mol^{-1}	Yield % Weight(gm)	mp C^0	C%	H%	N%	O%	M%	μ$_{eff}$ B.M
$C_{20}H_{22}N_4O$	334		95 (0.951gm)	220-222	72 (71.85)	6.3 (6.58)	16.70 (16.76)	4.8 (4.79)		
$C_{16}H_{15}N_3O_2$	281		82 (0.691gm)	210-212	68 (68.3)	5.4 (5.35)	15.1 (14.94)	11 (11.38)		
Ligand $C_{38}H_{41}N_9O$	639		92 (1.764gm)	165-167	71 (71.3)	6.5 (6.41)	19.69 (19.7)	2.48 (2.5)		
[FeLCl$_2$]Cl	801.3	32	68 (0.217gm)	168-170	56 (56.9)	5.19 (5.11)	16.1 (15.72)	2.2 (1.99)	7 (6.963)	5.67
[CoL]Cl$_2$	768.9	75	73 (0.224gm)	165-167	61 (59.3)	5.22 (5.33)	16.4 (16.38)	2 (2)	7 (7.660)	4.60
[CuL]Cl$_2$	773.5	73	68 (0.213gm)	90-92	60 (58.95)	5.22 (5.3)	16.49 (16.28)	1.96 (2)	7.89 (8.209)	2.04
[ZnL]Cl$_2$	775.3	78	61 (0.186gm)	180-182	58 (58.81)	5.22 (5.28)	16.4 (16.25)	1.96 (2)	8.12 (8.43)	Diamagnetic
[HgL]Cl$_2$	910.5	78	89 (0.324gm)	182-184	50 (50.08)	5.1 (4.50)	14.1 (13.83)	1.5 (1.75)	21.90 (22.02)	Diamagnetic

Table (2): FT. IR spectral data for the proligands (cm^{-1}).

Compound	$_{Ar}$υC-H	$_{Al}$υC-H	υC=O	υC=N	υC=C	υCH$_3$	υC-O	υC-H
$C_{20}H_{22}N_4O$	3045	2958	1681.9	1641.49	1589	1301	1134	758
$C_{16}H_{15}N_3O_2$	2920	2860	1696	1643.41	1577	1365	1130	771

Table (3): FT. IR spectral data for the free ligand and its complexes (cm^{-1}).

Compound	$_{Ar}$υC-H	$_{Al}$υC-H	υC=N	υC=N	υC=C	υCH$_2$	υCH$_3$	υC-O	υC-H	υM-N	υM-Cl
Free Ligand $C_{38}H_{41}N_9O$	3043	2924	1647	1608	1585	1485	1369	1134	698		
[FeLCl$_2$]Cl	2924	2854	1658	1593	1546	1492	1369	1165	698	420	390
[CoL]Cl$_2$	3047	2924	1647	1593	1546	1489	1373	1165	759	424	
[CuL]Cl$_2$	2927	2870	1654	1597	1535	1492	1373	1168	759	425	
[ZnL]Cl$_2$	3047	2924	1647	1608	1581	1489	1369	1139	759	439	
[HgL]Cl$_2$	2942	2854	1647	1608	1585	1485	1369	1139	698	439	

Table (4): Electronic spectral data for the prepared compounds and complexes

Compound	λ (nm)	Absorbance	ύ (cm^{-1})	ε_{max} L.M^{-1}.cm^{-1}	Assignment	Structure
$C_{20}H_{22}N_4O$	235	0.51	24553	510	$\pi\rightarrow\pi^*$	
	369	0.93	10752	369	$n\rightarrow\pi^*$	
$C_{16}H_{15}N_3O_2$	258	0.49	38759	490	$\pi\rightarrow\pi^*$	
	382	1.1	26178	1100	$n\rightarrow\pi^*$	
Free Ligand	260	0.41	38461	410	$\pi\rightarrow\pi^*$	
$C_{38}H_{41}N_9O$	360	0.867	27777	867	$n\rightarrow\pi^*$	
$[FeLCl_2]Cl$	259	0.979	40000	979	$\pi\rightarrow\pi^*$	Octahedral
	341	1.732	29411	1732	C.T	
	350	1.295	28571	1295	$n\rightarrow\pi^*$	
	430	0.2	23255	2000	d-d	
$[CoL]Cl_2$	259	0.280	40000	280	L.F	Tetrahedral
	342	0.621	29411	621	C.T	
	510	0.18	19607	180	$^4A_2\rightarrow{}^4T_{1P}$	
$[CuL]Cl_2$	258	0.622	40000	622	L.F	Tetrahedral
	340	0.90	29411	900	C.T	
	715	0.16	62500	160	$^2T_2\rightarrow{}^2E$	
$[ZnL]Cl_2$	260	0.50	38461	505	L.F	Tetrahedral
	346	1.177	29411	1177	C.T	
$[HgL]Cl_2$	260	0.463	38461	463	L.F	Tetrahedral
	344	0.787	29411	787	C.T	

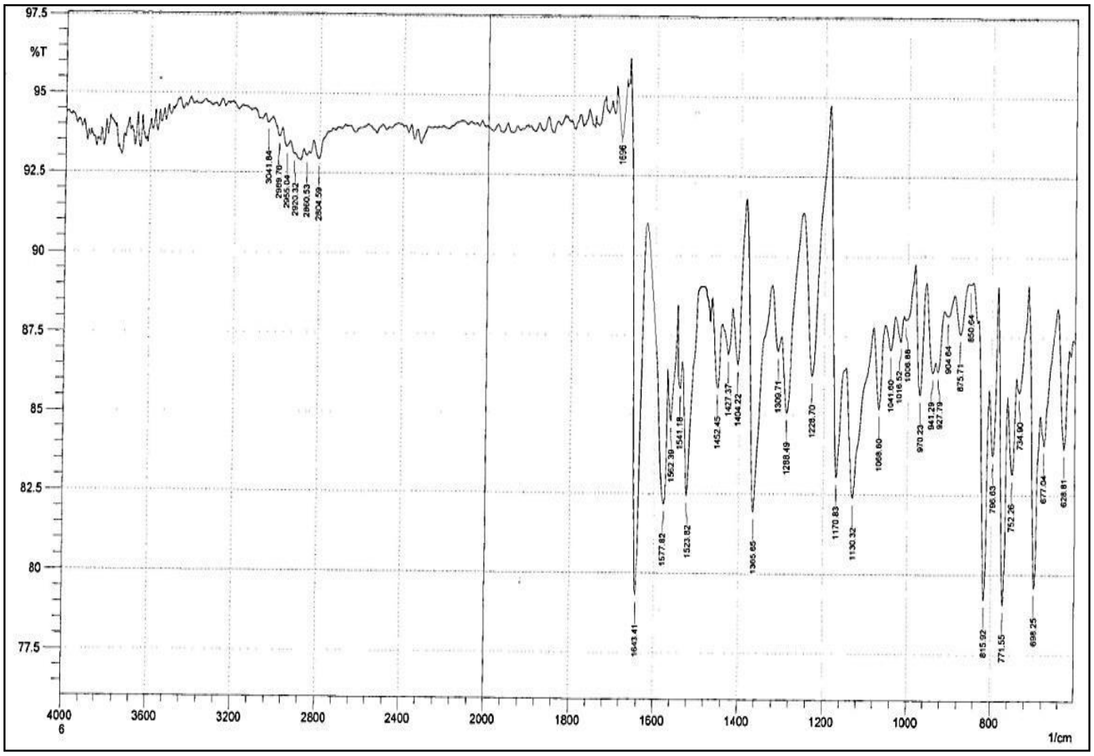


Figure (1): (FT.IR) spectrum of 4-[(4-Dimethylamino-benzylidene)-amino]-1,5-dimethylphenyl-1,2 dihydro-pyrazol-3-one.

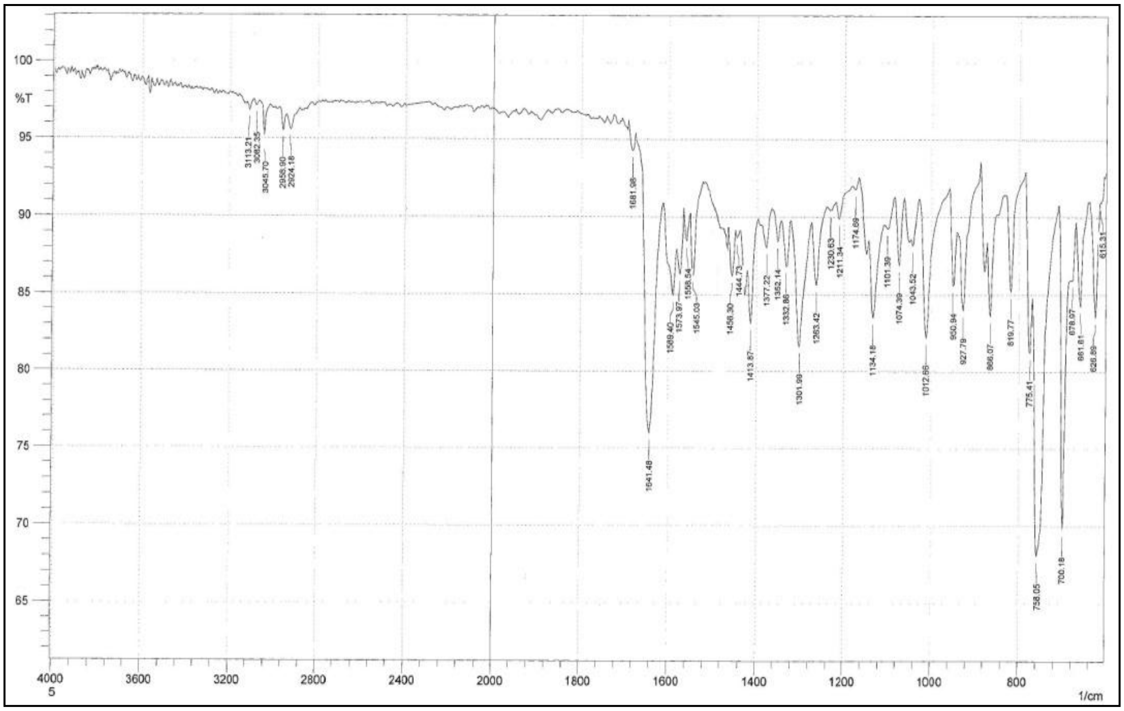


Figure (2): (FT.IR) spectrum of 4-[(Furan-2-ylmethylene)-amino]-1,5-dimethyl-2-phenyl-1,2 dihydro-pyrazol-3-one.

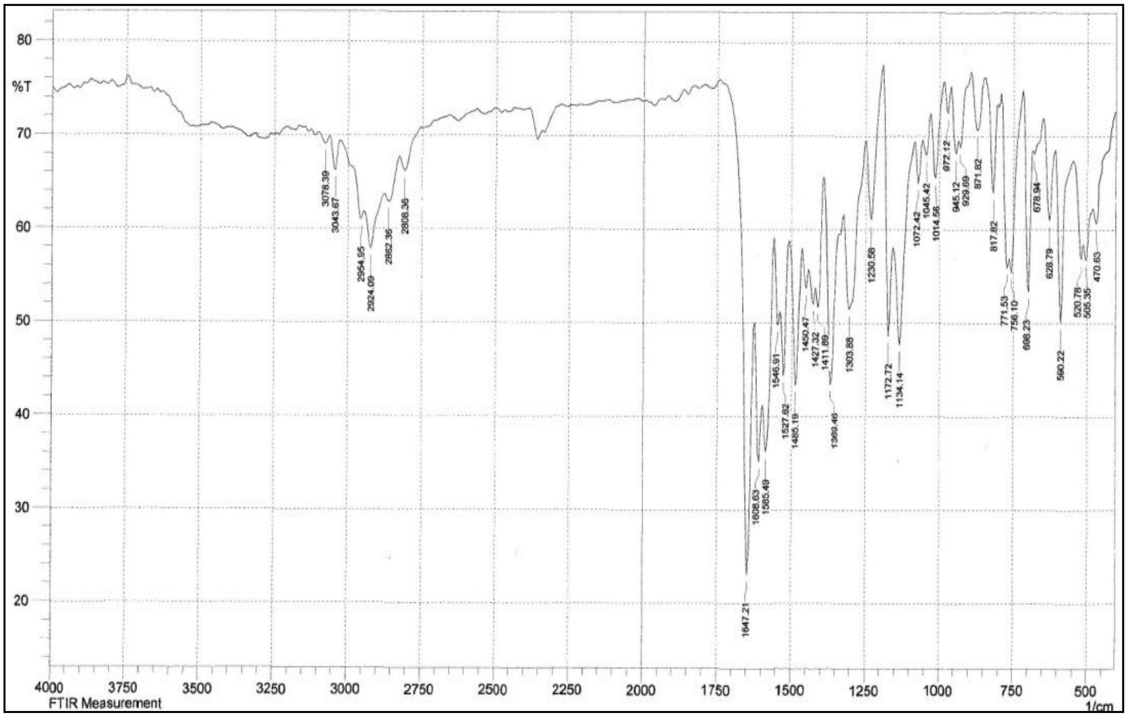


Figure (3): (FT.IR) spectrum of the free ligand ($C_{38}H_{41}N_9O$).

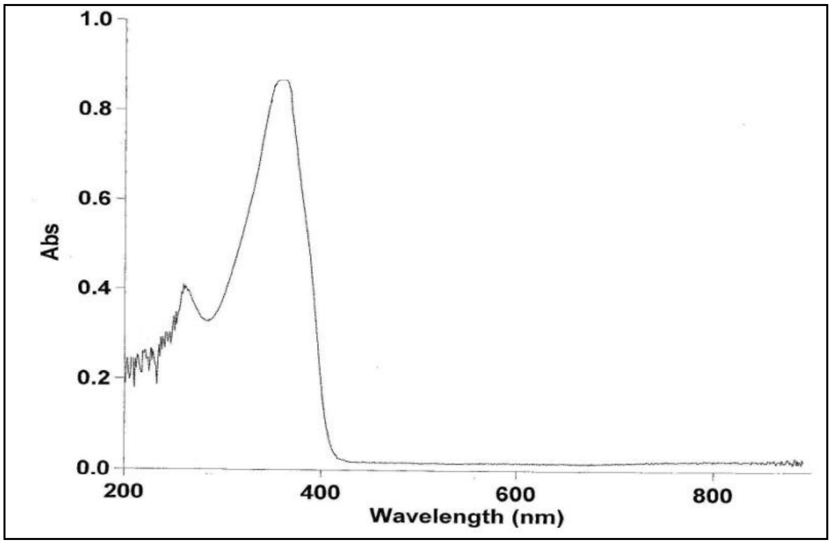
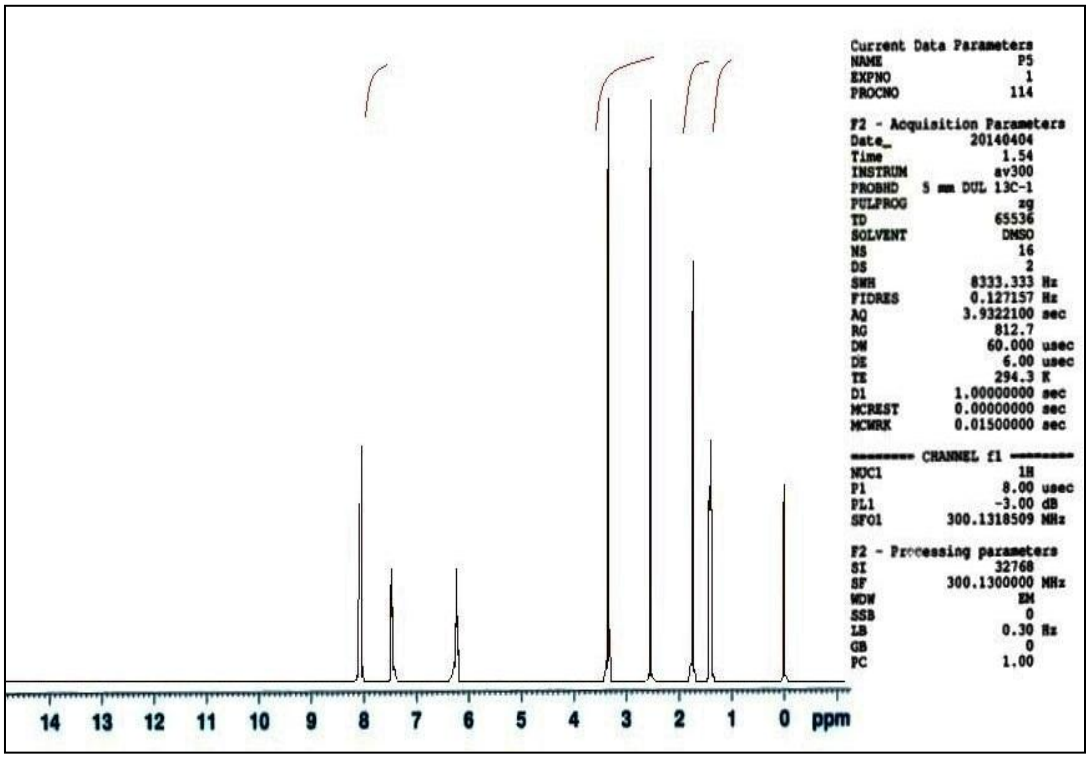


Figure (4): The (UV-Vis) spectrum of the free ligand ($C_{38}H_{41}N_9O$).



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PULPROG               zg
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NS                    16
DS                     2
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FIDRES          0.127157 Hz
AQ             3.9322100 sec
RG                 812.7
DW                60.000 usec
DE                  6.00 usec
TE                 294.3 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
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P1                  8.00 usec
PL1                -3.00 dB
SFO1         300.1318509 MHz

F2 - Processing parameters
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WDW                   EM
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Figure (5): (H^1NMR) spectrum of the free ligand ($C_{38}H_{41}N_9O$).

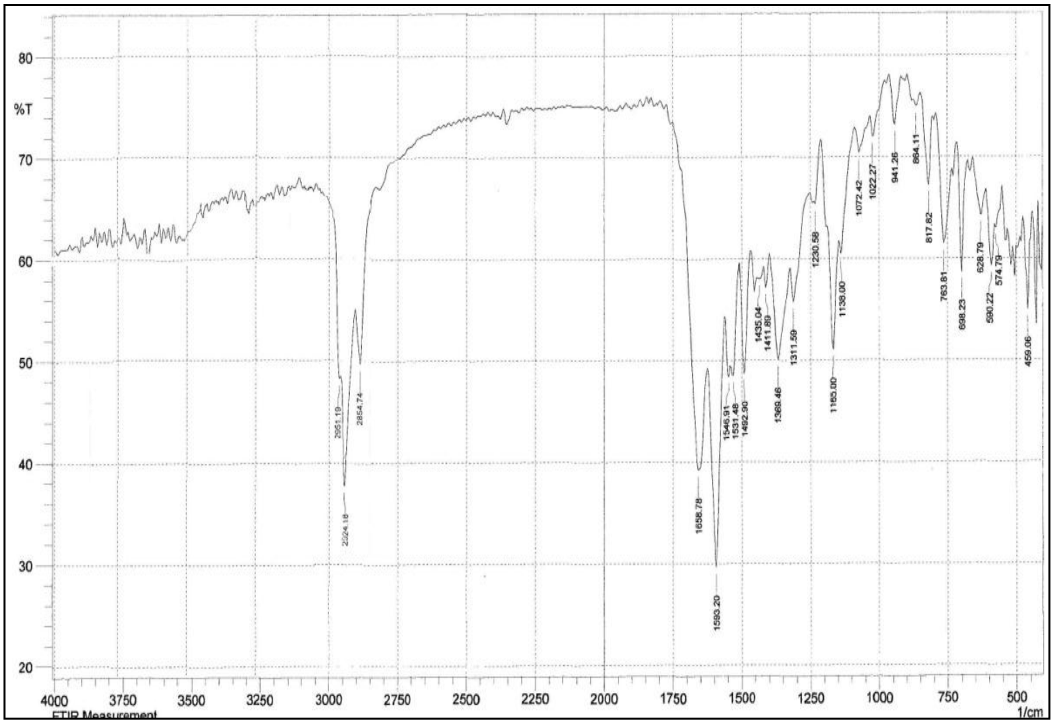

Figure (6): (FT.IR) spectrum of $[FeLCl_2]Cl$ complex

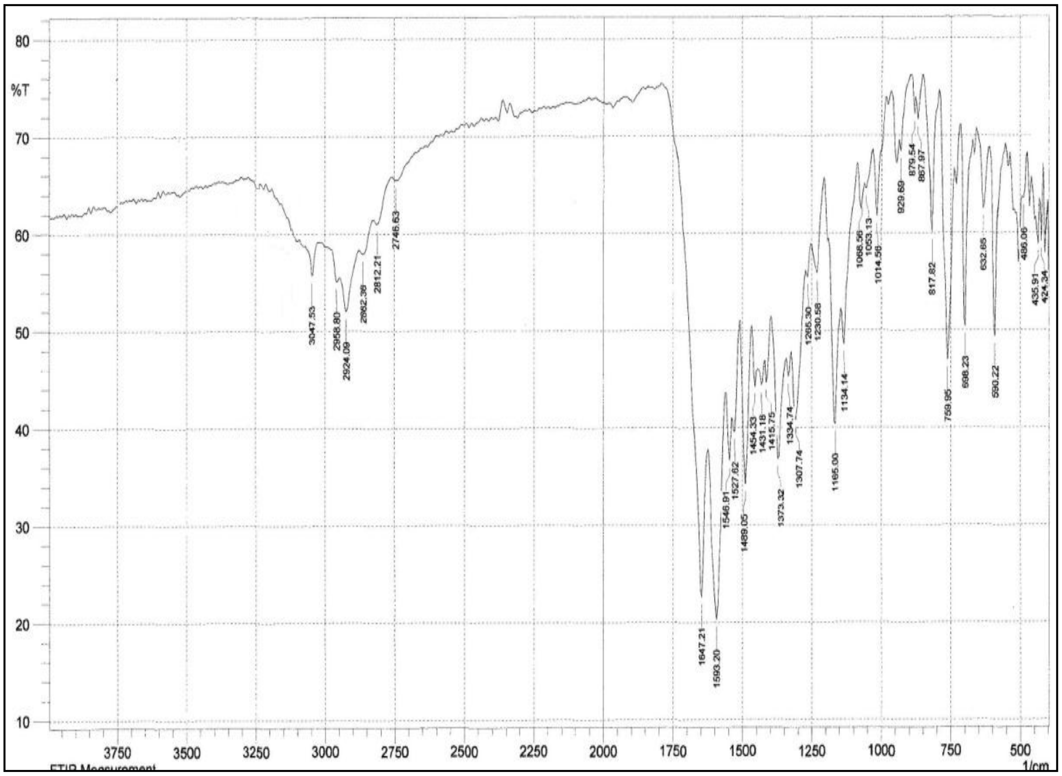

Figure (7): (FT.IR) spectrum of $[CoL]Cl_2$ complex

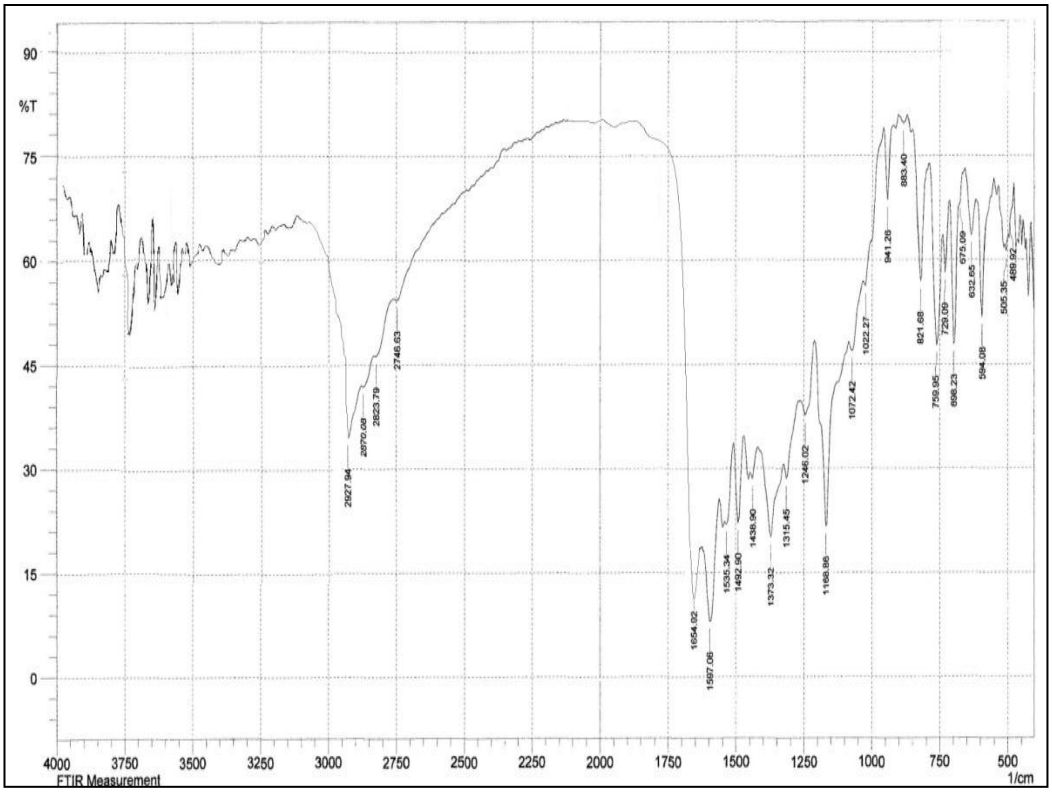

Figure (8): (FT.IR) spectrum of [CuL]Cl_2 complex

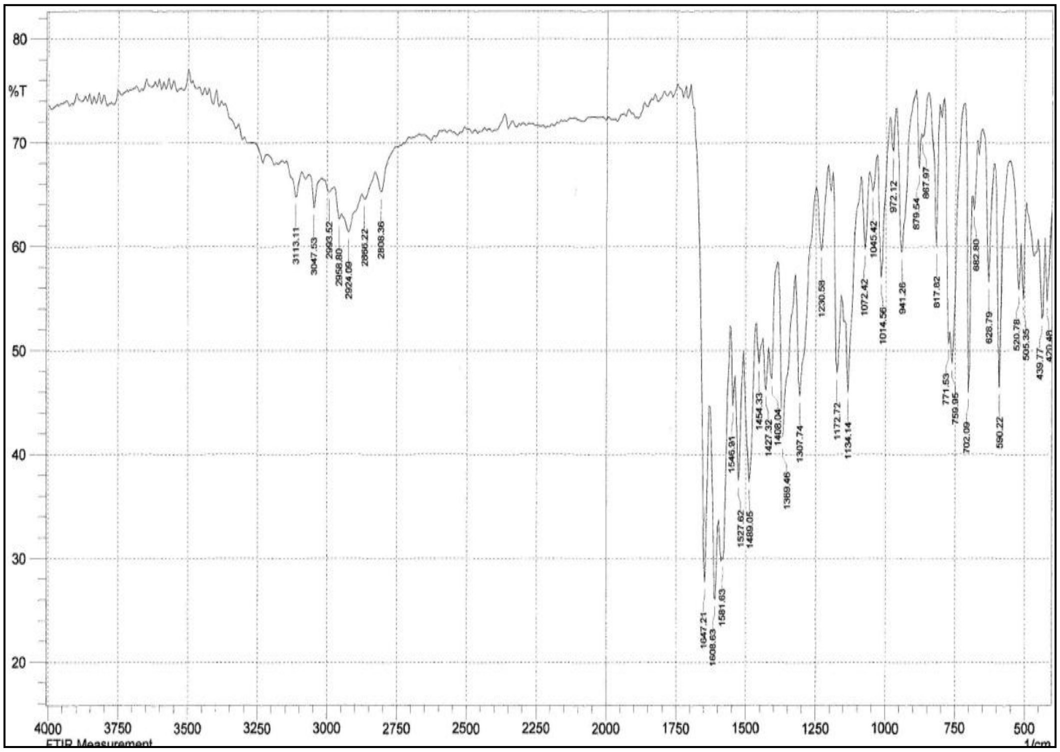

Figure (9): (FT.IR) spectrum of [ZnL]Cl_2 complex

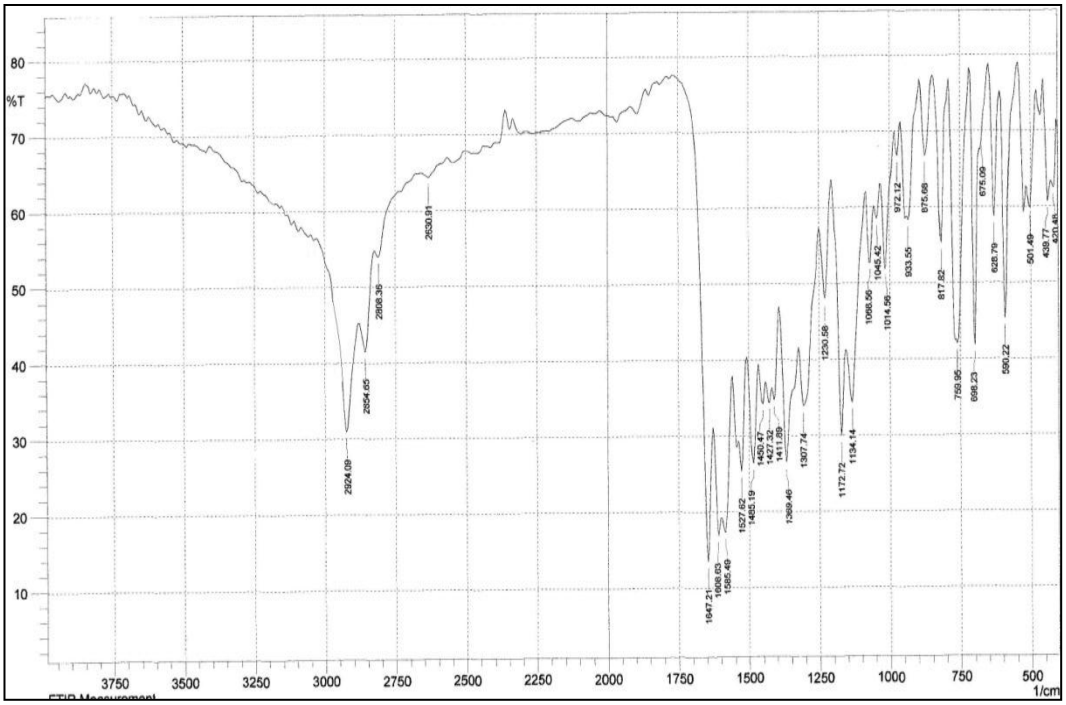

Figure (10): (FT.IR) spectrum of $[HgL]Cl_2$ complex

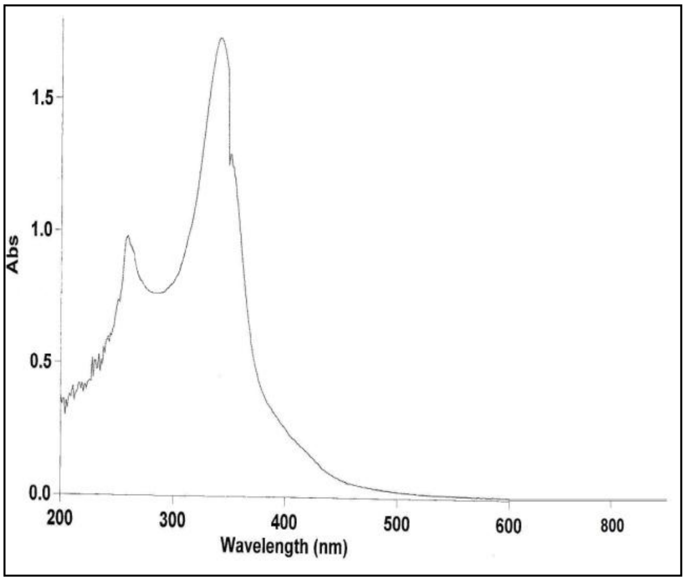

Figure (11): (UV-Vis) spectrum of $[FeLCl_2]Cl$ complex

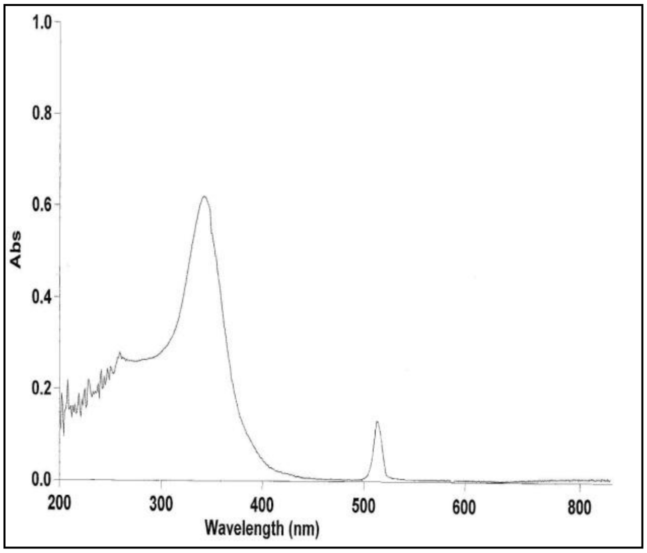

Figure (12): (UV-Vis) spectrum of $[CoL]Cl_2$ complex

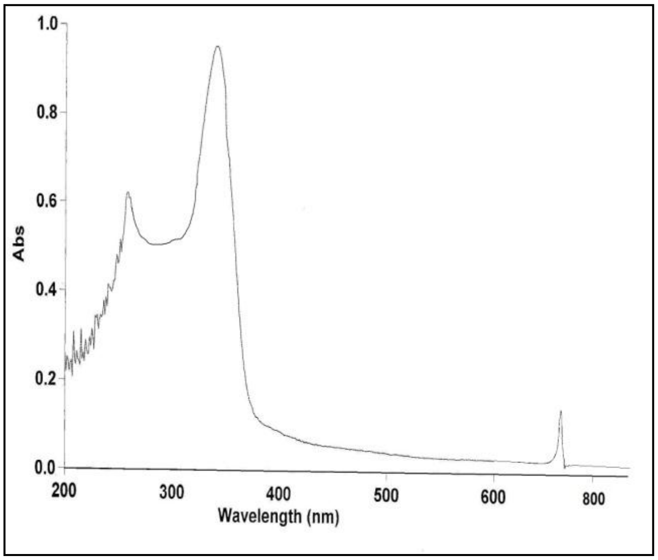

Figure (13): (UV-Vis) spectrum of $[CuL]Cl_2$ complex

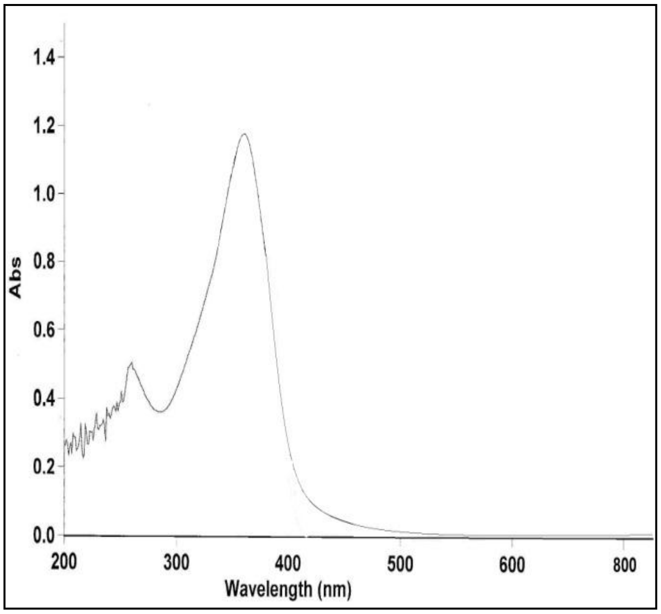

Figure (14): (UV-Vis) spectrum of $[ZnL]Cl_2$ complex

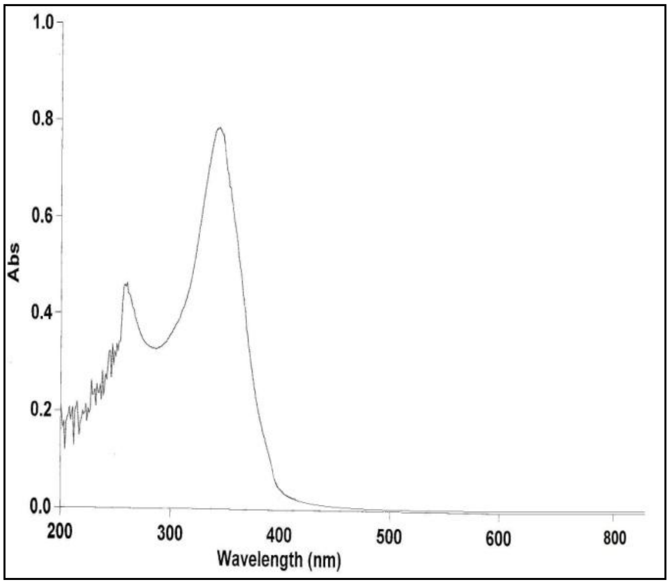

Figure (15): (UV-Vis) spectrum of $[HgL]Cl_2$ complex

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