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Mn **(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with new tetra dentate schiff base ligand type N_4 : synthesis and characterization**

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معقدات Mn(II)، Cu(II) ، Zn(II) ، Cd(II) و Hg(II) مع قاعدة شف جديدة رباعية نوع N_4 : تحضير وتشخيص

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المستخلص

تم تحضير معقدات جديدة للـ Mn(II) ، Cu(II) ، Zn(II) ، Cd(II) و Hg(II) بمفاعله أملاح الفلزات الثنائية مع قاعدة شف جديدة رباعية السن نوع N_4 المشتقة من 2,4- ثنائي كيتو بنتان ، 1,2- ثنائي امينوبنزين و الانلين.
($C_{28}H_{30}N_4$) N,N'-Bis-(1-methyl-3-phenylimino-butylidene)-benzene-1,2-diamine
وتم تشخيص كل المعقدات المبينة أعلاه بواسطة الطرق الطيفية (تقنية الأشعة تحت الحمراء، الاشعة فوق البنفسجية المرئية ، الامتصاص الذري للعناصر) وطيف الرنين المغناطيسي النووي لليكاند المحضر بالإضافة إلى الحساسية المغناطيسية للمعقدات المحضرة، تعيين درجة الانصهار و التوصيلة المولارية.
وقد افترضنا من معطيات كل التقنيات المذكورة أعلاه بان التركيب لجميع المعقدات هو رباعي السطوح حول الايون الفلزي المركزي.

الكلمات ألمفتاحيه : قواعد شف ، 2,4- ثنائي كيتو بنتان ،استايل استون، 1,2- ثنائي امينوبنزين و الانلين

Abstract

A new complexes of Mn(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been synthesized by reaction of the divalent metal salts with a new tetra dentate Schiff base ligand type N_4 as donor atoms derivative from 2,4-diketopentane, 1,2-diamino benzene and aniline, ($C_{28}H_{30}N_4$) N,N'-Bis-(1-methyl-3-phenylimino-butylidene)-benzene-1,2-diamine. All these complexes were characterized by the spectroscopic methods (FT.IR, UV-Vis, and Atomic Absorption) and H^1NMR for the free ligand and, along with the magnetic susceptibility, melting point and molar conductivity. From all above measurements data, we suggested the tetrahedral geometry around the central metal ions for the all neutral complexes.

Key words: Schiff base, 2, 4-diketopentane, acetyl acetone, tetra dentate ligand.

Introduction

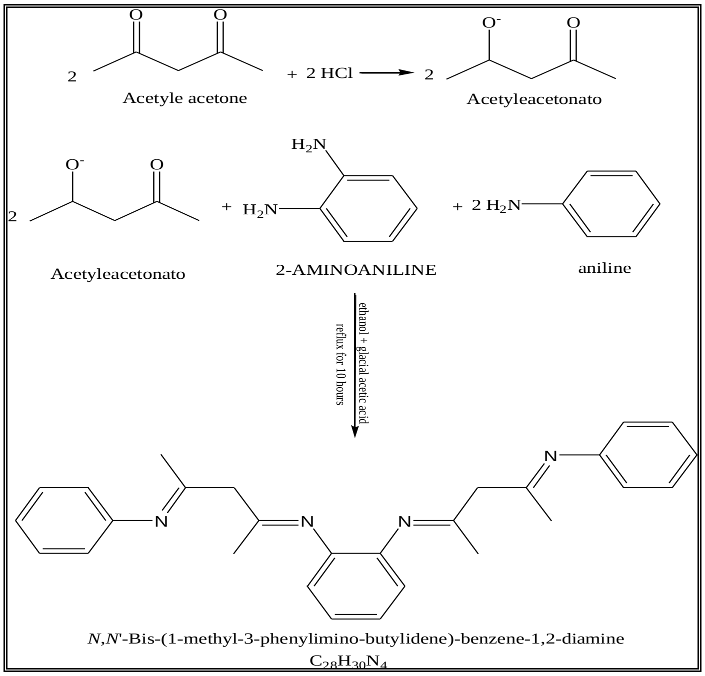
Metal complexes of Schiff base are playing an important role in the development of coordination chemistry, which is evident by the massive number of publication, including physiochemical studies [1]. Schiff base metal complexes have been widely studied because they have industrial, antibacterial, anticancer and herbicidal application [2]. They are useful in health and skin care[3], and previously reported as corrosion inhibitors for steel, copper and aluminum[4]. Schiff bases also have many applications in high performance of liquid crystal polymers [5], and sandwich complexes, half sandwich complexes [6]. The present paper reports synthesis and characterization of new Schiff base ligand N,N'-Bis-(1-methyl-3-phenylimino-butylidene)-benzene-1,2-diamine, which were prepared from reacting of acetyl acetone, o-amino anline and aniline and its complexes with Mn(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions.

Materials and Instrumentation

All chemicals are from Fluka and Redial- Dehenge 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. IR spectra were recorded as KBr discs by using Shimadzu 8300 FT-IR spectrophotometer in the range (4000-400)cm^{-1}. Electronic spectra of the prepared compounds were measured in the range (200-900) nm for 10^{-3} M solution in methanol at 25^{o}C by using Shimadzu 160 spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Electrical molar conductivity measurements of the complexes were recorded at 25^{o}C for 10^{-3} M solution of samples in methanol by using PW 526 digital conductivity meter. Melting points were recorded by using Sturat melting point apparatus.

Synthesis of ligand

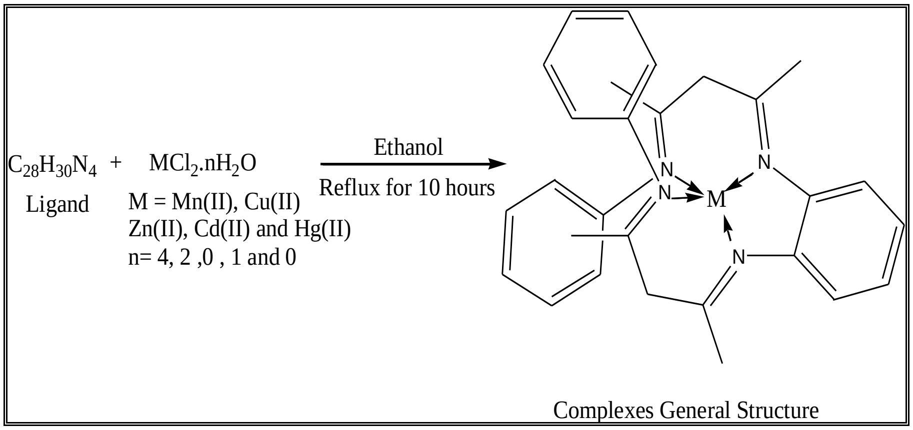
1,2- diamino benzene (0.324gm, 3 mmole) was dissolved in (30ml) of ethanol a pale yellowish pink solution formed, (0.006ml, 6mmole) of acetyl acetone solution which is dissolved in (30ml) of ethanol in presence of a few drops of concentrated hydrochloric acid[7] was added gradually to 1,2- diamino benzene solution to obtain a very dark solution. Then (0.229ml, 6mmole) of anilne in (30ml) of ethanol was added to the solution of 1,2- diamino benzene and acetyl acetone. The mixture was allowed to reflux process for (10hours) at (60C^{0}) (Scheme-1) , then cooled at room temperature and filtered many times to let the no reacted starting materials to be moved. A dark reddish brown precipitate was recrystallized by methanol to give dark reddish brown crystals, yield (95.3%), (1.207gm) mp(78C^{0}-80C^{0}) (table-1).



Scheme (1): Synthesis of The Free Ligand

Synthesis of [ML]Cl_2 Complexes

A mixture of the ligand [L] (0.0844gm, 0.0002mole) in ethanol (30ml) and a few drops of glacial acetic acid were added drop wise with stirring to (100ml) round bottom flask containing a solution of $MCl_2.nH_2O$ (n= 0 – 4) (0.0002mole) in (30ml) of ethanol. The reaction mixture was allowed to reflux for (10 hours), during reflux time the solution colors turned to more darkness. The solvent was evaporated to give a dark (reddish, greenish, and brownish) solids. The precipitates were recrystallized and washed several times using methanol to give the complexes with yields of (62-82%).



Scheme (2): Synthesis of Mn(II), Cu(II), Zn(II), Cd(II) and Hg(II) Complexes

Results and Discussion

Ligand [L]

The ligand [L] was prepared by condensation reaction of (1:2:2) mole ratio of 1,2-diamino benzene, acetyl acetone and aniline in presence of drops of HCl_{con} according to the general method in (scheme-1). The free ligand dissolved in methanol, ethanol and DMSO. Some of the physical properties and micro analysis of the elements for the free ligand and its complexes are listed in the (table-1). The FT.IR spectrum of the free ligand (fig-1) displayed many band changing, appearing and disappearing in comparison with the starting materials. The most important band in (1633)cm^{-1} due to the iminc group (ʋC=N) which is a good evidence refer to Schiff base compound formation[8]. The other bands at (2966)cm^{-1}, (2918)cm^{-1}, (1220)cm^{-1}, (1039)cm^{-1}, (1491)cm^{-1}, (1516)cm^{-1}, (1373)cm^{-1}, (1437)cm^{-1} and (750)cm^{-1}. Due to the functional groups (ʋC-H)aromatic, (ʋC-H) aliphatic, (ʋC-C), (ʋC-N)[9], ($ʋ_{sym}$C=C), ($ʋ_{Asym}$C=C), (ʋCH_3), (ʋCH_2) and aromatic (ʋC-H) out of plane ring[10]. The UV-Vis spectrum of the free ligand (fig-2) exhibit a high intense absorption peak at (245nm, 40816cm^{-1}, ε_{max}= 1234 $L.mol^{-1}.cm^{-1}$) due to ($\pi \rightarrow \pi^*$) electronic transition while the second peak at (305nm, 32786.6 cm^{-1}, ε_{max}= 423 $L.mol^{-1}.cm^{-1}$) due to ($n \rightarrow \pi^*$) electronic transition[11]. The data of electronic spectrum for the free ligand are listed in the (table-3). The predicated H^1NMR of the free ligand (fig-3) showed three main peaks at δ_{ppm} : 7.59 (5H), 1.837 (2H), 0.8 (3H)[12]. Anal. Calc. for the free ligand $C_{28}H_{30}N_4$ (422): C, 79.59; H, 7.16; N, 13.26. Found C, 78.93; H, 6.98, N, 13.22 %.

Complexes

The reaction of the free ligand [L] with metal chloride salt Mn(II), Cu(II), Zn(II), Cd(II) and Hg(II) were carried out in ethanol solvent under reflux in presence of glacial acetic acid. All announced complexes are stable and dissolved in methanol, ethanol and DMSO. On the basis of elemental analysis data (table-1) the molecular formula for prepared complexes were assigned to be $[MnL]Cl_2$, $[CuL]Cl_2$, $[ZnL]Cl_2$, $[CdL]Cl_2$ and $[HgL]Cl_2$. The suggested molecular formula have been also supported by the spectral measurements as well as molar conductivity, metal determination and magnetic moment.

Molar conductivity

The molar conductivity for the prepared complexes in methanol solvent 0.001 M solution at

298^0 K (table-1) indicated 1:2 electronic nature[13,14].

Magnetic moment

The values of measured magnetic susceptibility and effective magnetic moment (μ_{eff}) for the prepared complexes are shown on (table-1), Mn(II), Cu(II) exhibit μ_{eff} (5.0, 2.32) BM for the single unpaired electron[15]. While μ_{eff} for Zn(II), Cd(II) and Hg(II) complexes showed that all the remaining complexes are diamagnetic[16].

Atomic absorption

The atomic absorption measurements (table-1) for all complexes were found comparable when they are compared with theoretical values.

IR spectra

The IR spectra for all prepared complexes gave a different spectra in comparison with free ligand spectra. The IR spectra of complexes are listed in (table-2). the IR spectra of Mn(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes exhibit a shift in iminic group υC=N to lower frequency and appeared at rang (1584.8 –1633) cm^{-1} (1626.05)cm^{-1},(1584.8)cm^{-1}, (1633.76)cm^{-1}, (1629.9)cm^{-1} and (1627.97)cm^{-1} in comparing with that in the free ligand[17]. This shift to lower frequency in the position of the iminic group (C=N) suggests a coordination between N atoms of the free ligand and metal ions and delocalization of metal ion electronic density in π- orbital of the free ligand and formation of π- back bonding (dπ-pπ) which indicate the coordination between N atoms of iminic C=N groups and metal ion [17,18]. The other bands in Mn(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes at (2926)cm^{-1}, (2926)cm^{-1}, (2962)cm^{-1} , (2926)cm^{-1}, and (2924)cm^{-1} Due to the functional groups (υC-H) aromatic. (2900)cm^{-1}, (2855)cm^{-1}, (2902)cm^{-1}, (2858)cm^{-1} and (2858)cm^{-1} due to the functional group (υC-H) aliphatic. (1105)cm^{-1}, (1122)cm^{-1}, (1159)cm^{-1}, (1165)cm^{-1}, (1165)cm^{-1} due to the functional group (υC-C). (1031)cm^{-1}, (1030)cm^{-1}, (1031)cm^{-1}, (1031)cm^{-1} and (1030)cm^{-1} due to the functional group (υC-N). (1576)cm^{-1}, (1464)cm^{-1}, (1506)cm^{-1}, (1487)cm^{-1}, (1516)cm^{-1} due to the frequency of (υ_{sym}C=C) group (1600)cm^{-1}, (1512)cm^{-1}, (1525)cm^{-1}, (1599)cm^{-1}, (1599)cm^{-1} due to the frequency of (υ_{Asym}C=C) group. (1377)cm^{-1}, (1303)cm^{-1}, (1300)cm^{-1}, (1386)cm^{-1}, (1373)cm^{-1} due to the frequency of (υCH_3) group. (1483)cm^{-1} . (1370)cm^{-1} . (1367)cm^{-1} . (1464)cm^{-1} . and (1483)cm^{-1} due to the (υCH_2) functional group. And (754)cm^{-1}, (752)cm^{-1}, (756)cm^{-1} , (759)cm^{-1} and (754)cm^{-1} due to the aromatic (υC-H) out of plane ring[10]. The most important peak appears in complexes IR charts in comparing with the free ligand charts its (υM-N) in the range (470- 501)cm^{-1}.(472)cm^{-1}, (501)cm^{-1}, (472)cm^{-1}, (450)cm^{-1} and (470)cm^{-1}[18].

Electronic spectra

The electronic spectral data for all complexes are summarized in (table-3). The peak at (245) nm in the electronic for the ligand was shifted to lower absorbance for Mn (II) complex and to higher absorbance for the all remaining complexes. These shifting in ligand absorbance peak are a good indicator for coordination between the free ligand and metal ions. The electronic spectra of Mn (II) complex displayed two absorption peaks in (245nm, 40816cm^{-1}, ε_{max}= 946 L.mol^{-1}.cm^{-1}) due to ligand field electronic transition while the second peak at (305nm, 32786.6 cm^{-1}, ε_{max}= 1239 L.mol^{-1}.cm^{-1}) due to ($^6A_1 \rightarrow {}^4E$, $^4A_{1(G)}$) which overlap with charge transfer peak. In fact, these results are in good agreement with previous work of Mn(II) tetrahedral complexes. The electronic spectra of Cu(II) complex displayed three absorption peaks in (245nm, 40816cm^{-1}, ε_{max}= 1239 L.mol^{-1}.cm^{-1}) due to ligand field of electronic transition while the second peak at (310nm, 32258 cm^{-1}, ε_{max}= 955 L. mol^{-1}.cm^{-1}) due to charge transfer and the third peak at (420nm, 32809 cm^{-1}, ε_{max}= 970 L. mol^{-1}.cm^{-1}) due to ($^2B_2 \rightarrow {}^2E$), In fact, these results are in good agreement with previous work of Mn(II) and Cu(II) tetrahedral complexes[11]. Finally, the UV-Vis spectra of Zn(II), Cd(II) and Hg(II) complexes displayed two absorption peaks in (245nm, 40816cm^{-1}, ε_{max}= 1239 L.mol^{-1}.cm^{-1}), (245nm, 40816cm^{-1}, ε_{max}= 1240 L.mol^{-1}.cm^{-1}) and (245nm, 40816cm^{-1}, ε_{max}= 1239 L.mol^{-1}.cm^{-1}) due to ligand field electronic transition while the second peak at (310nm, 32258 cm^{-1}, ε_{max}= 900 L.mol^{-1}.cm^{-1}), (310nm, 32258cm^{-1}, ε_{max}= 900 L.mol^{-1}.cm^{-1}) and (315nm, 31746cm^{-1}, ε_{max}= 900 L.mol^{-1}.cm^{-1}) due to charge transfer peak[18].

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

Compound	**M.Wt**	**Molar Conductance Ohm^1.cm^2.mol^{-1}**	**Yield %**	**mp C^0**	**C%**	**H%**	**N%**	**M%**	**μ_{eff} B.M**
$C_{28}H_{30}N_4$	**422**		**95.3**	**78-80**	**78.93** **(79.59)**	**6.98** **(7.16)**	**13.22** **(13.26)**		
[MnL]Cl_2	**548**	**72**	**67**	**125-127**	**61.4** **(61.31)**	**5.3** **(5.47)**	**10.00** **(10.21)**	**10.3** **(10.03)**	**5.00**
[CuL]Cl_2	**556.5**	**79**	**66**	**129-130**	**61.00** **(60.37)**	**5.31** **(5.39)**	**10.00** **(10.06)**	**11.60** **(11.41)**	**2.33**
[ZnL]Cl_2	**583.4**	**90**	**62**	**130-132**	**57.2** **(57.59)**	**5.00** **(5.142)**	**10.20** **(9.598)**	**11.00** **(11.21)**	**Diamagnetic**
[CdL]Cl_2	**605.4**	**95**	**77**	**158-160**	**55.00** **(55.50)**	**5.01** **(4.955)**	**9.00** **(9.250)**	**18.23** **(18.56)**	**Diamagnetic**
[HgL]Cl_2	**693.59**	**100**	**82**	**138-104**	**48.00** **(48.44)**	**4.03** **(4.325)**	**8.00** **(8.07)**	**27.92** **(28.90)**	**Diamagnetic**

Table (2): IR spectral data for the free ligand and its complexes (cm^{-1})

Compound	**υC=N**	**$_{Ar}$υC-H**	**$_{Al}$υC-H**	**υC-C**	**υC-N**	**υ$_{sy}$(C=C)**	**υ$_{asy}$(C=C)**	**υCH_3**	**υCH_2**	**υC-H**	**υM-N**
$C_{28}H_{30}N_4$	**1633**	**2966**	**2918**	**1220**	**1039**	**1491**	**1516**	**1373**	**1437**	**750**	
[MnL]Cl_2	**1626**	**2926**	**2900**	**1105**	**1031**	**1576**	**1600**	**1377**	**1480**	**754**	**472**
[CuL]Cl_2	**1584**	**2926**	**2858**	**1122**	**1030**	**1464**	**1512**	**1303**	**1370**	**752**	**501**
[ZnL]Cl_2	**1633**	**2926**	**2902**	**1159**	**1031**	**1506**	**1525**	**1300**	**1367**	**756**	**472**
[CdL]Cl_2	**1629**	**2926**	**2858**	**1165**	**1031**	**1487**	**1599**	**1386**	**1466**	**759**	**450**
[HgL]Cl_2	**1627**	**2924**	**2858**	**1165**	**1030**	**1516**	**1599**	**1373**	**1485**	**754**	**470**

Table (3): Electronic spectral data of the free ligand and its complexes

Compound	λ (nm)	ύ (cm^{-1})	ε$_{max}$ L.M^{-1}.cm^{-1}	Assignment	Structure
$C_{28}H_{30}N_4$	245 305	40816 32786.6	1234 423	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	
$[MnL]Cl_2$	245 305	40816 32786.6	946 1239	L.F C.T	Tetrahedral
$[CuL]Cl_2$	245 310 420	40816 32258 23809.5	1239 955 970	L.F C.T $^2B_2\rightarrow{}^2E$	Tetrahedral
$[ZnL]Cl_2$	245 310	40816 32258	1239 900	L.F C.T	Tetrahedral
$[CdL]Cl_2$	245 310	40816 32258	1240 900	L.F C.T	Tetrahedral
$[HgL]Cl_2$	245 315	40816 31746	1239 900	L.F C.T	Tetrahedral

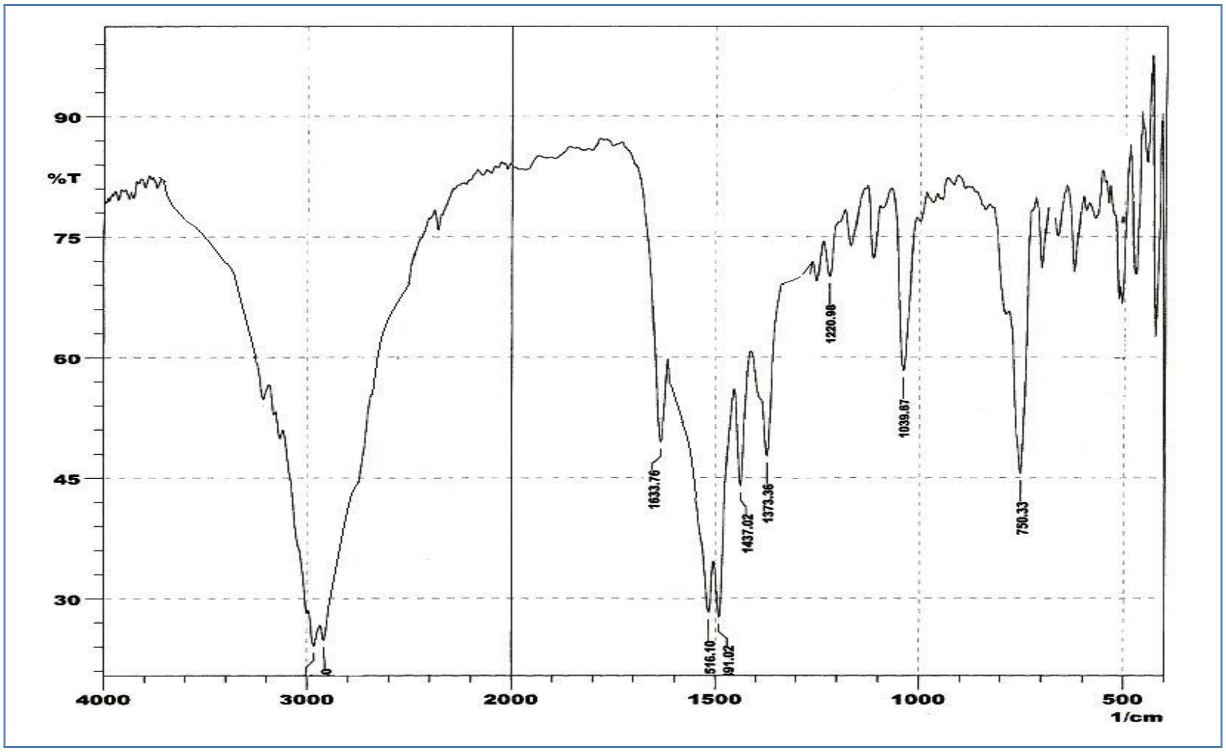


Figure (1): The IR spectrum of free ligand ($C_{28}H_{30}N_4$).

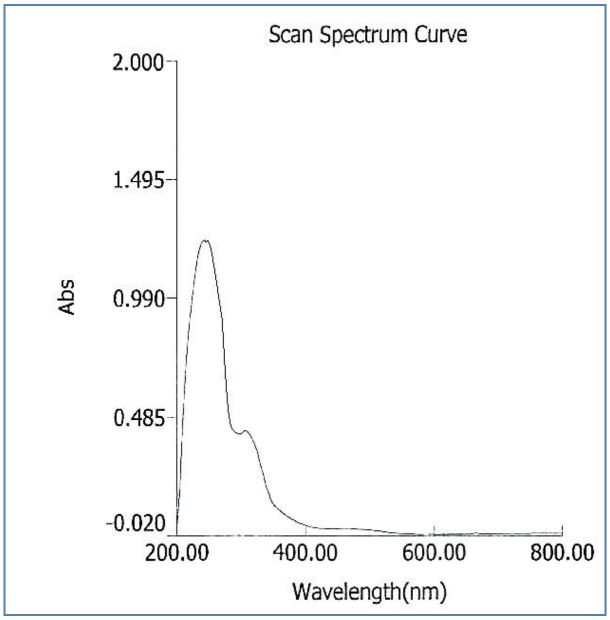
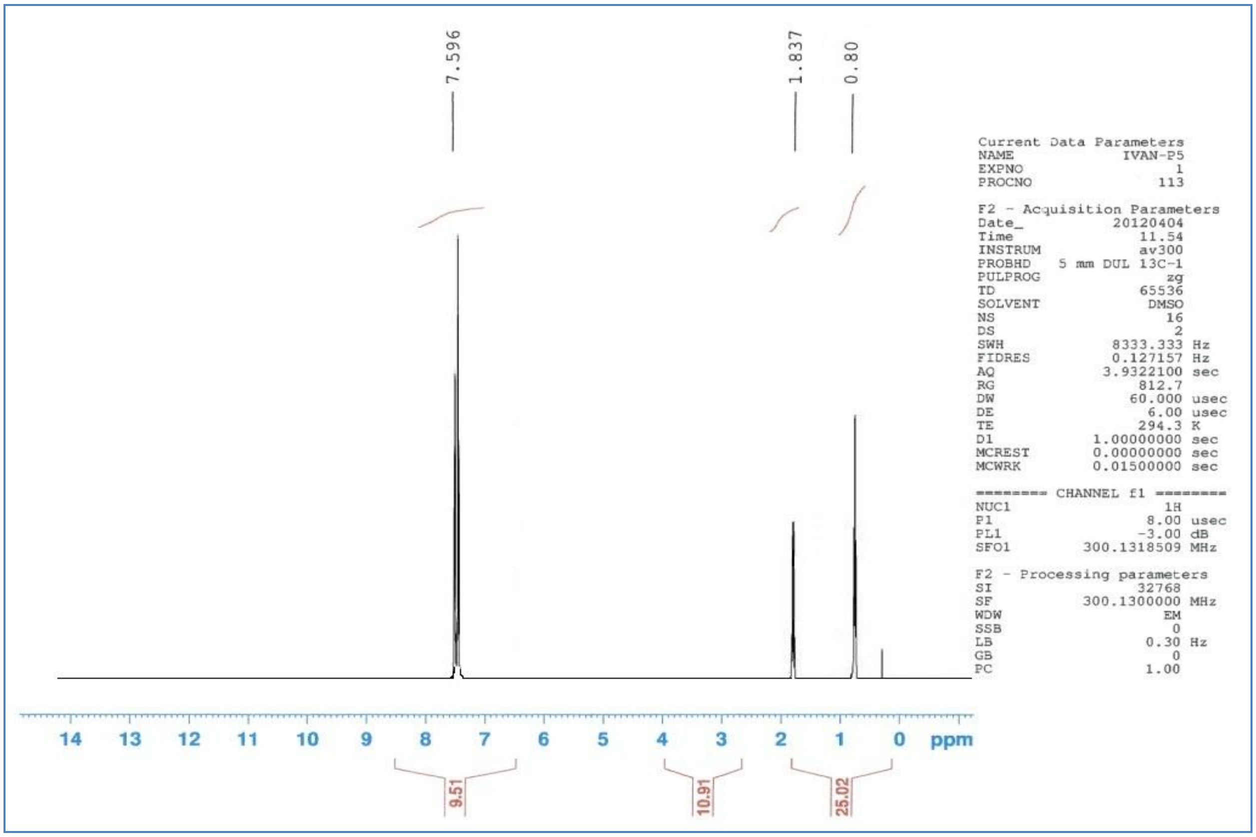


Figure (2): The (UV-Vis) of free ligand ($C_{28}H_{30}N_4$).



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PULPROG               zg
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SOLVENT             DMSO
NS                    16
DS                     2
SWH             8333.333 Hz
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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SF           300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
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PC                  1.00
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Figure (3): H^1NMR of the free ligand ($C_{28}H_{30}N_4$).

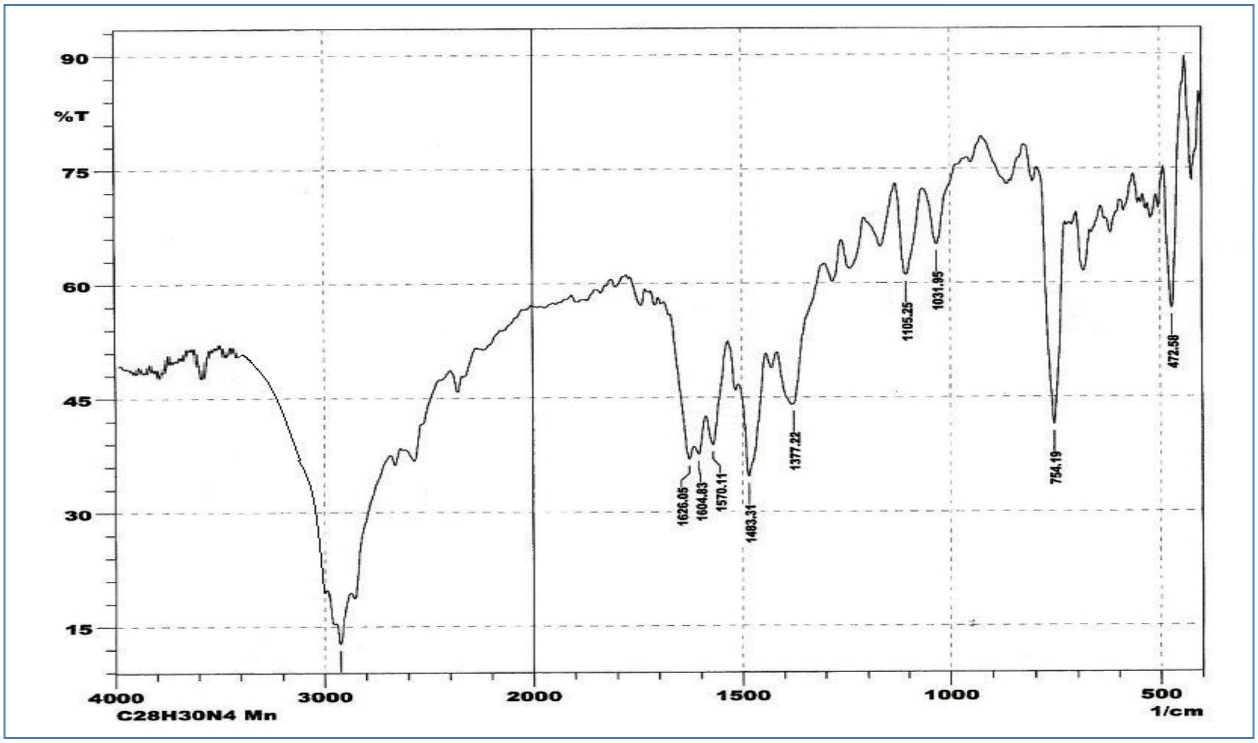

Figure (4): IR chart of $[MnL]Cl_2$ complex

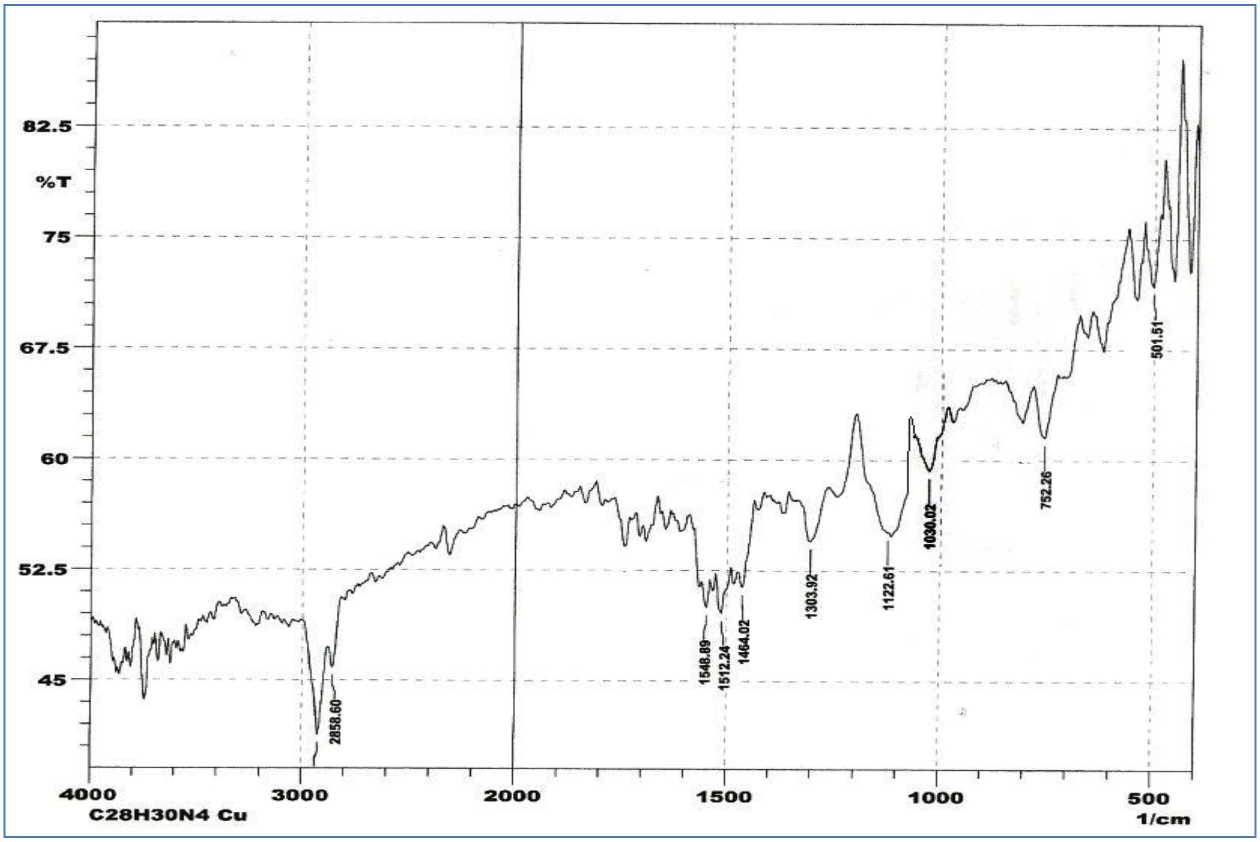

Figure (5): IR chart of $[CuL]Cl_2$ complex

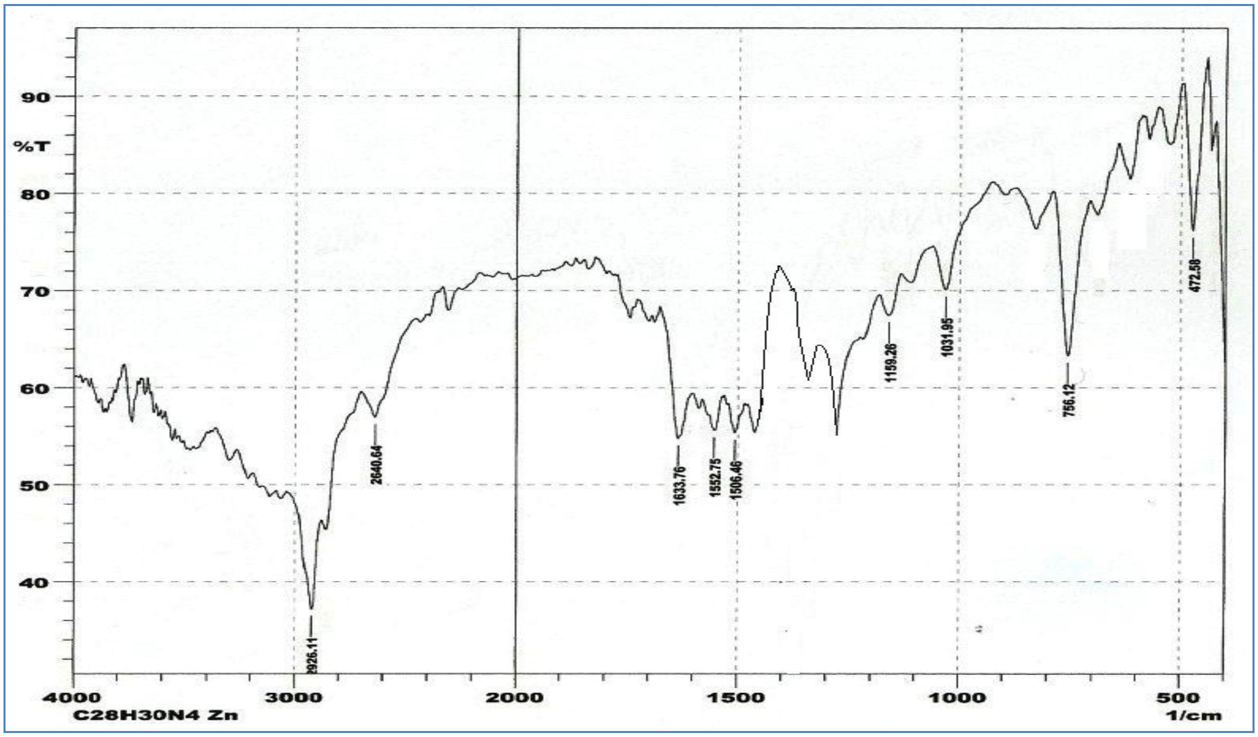

Figure (6): IR chart of $[ZnL]Cl_2$ complex

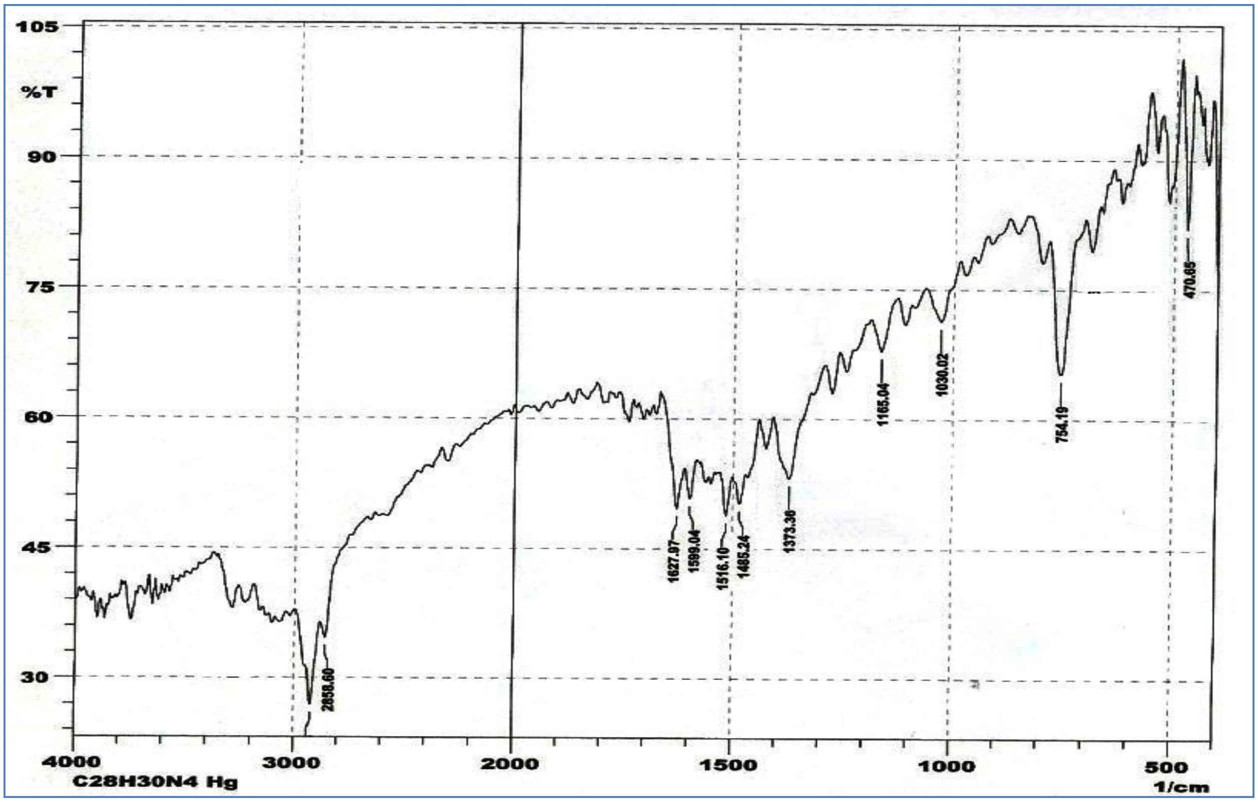

Figure (7): IR chart of $[HgL]Cl_2$ complex

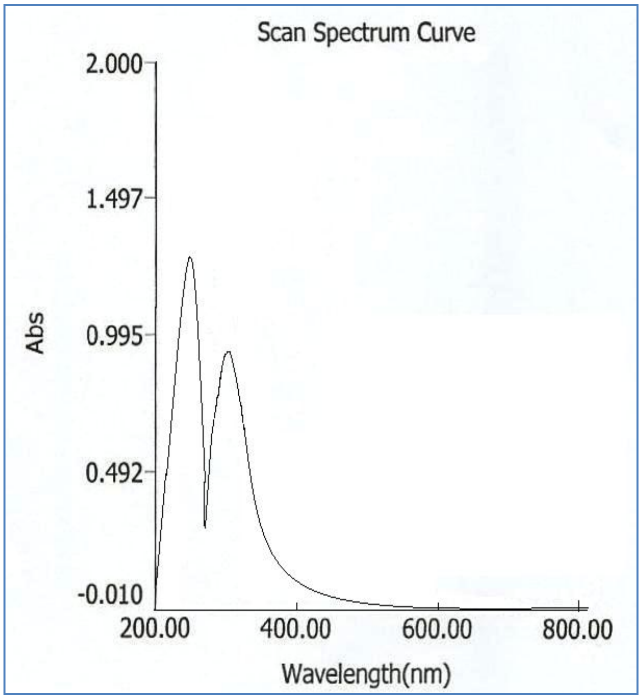

Figure (8): UV-Vis chart of [MnL]Cl$_2$ complex

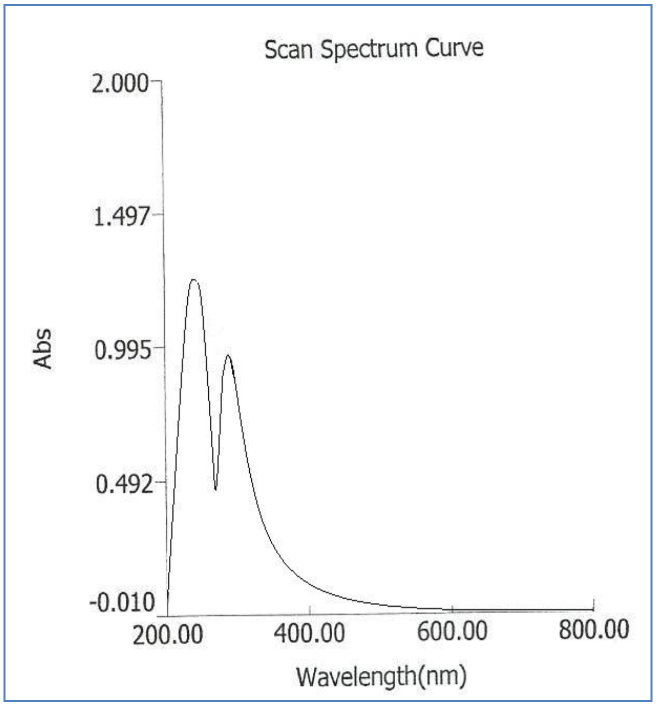

Figure (9): UV-Vis chart of [ZnL]Cl$_2$ complex

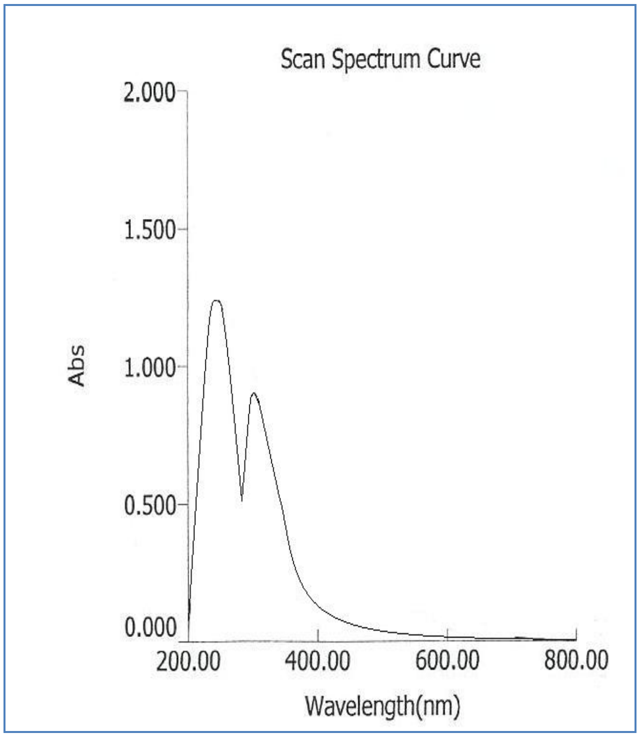

Figure (10): UV-Vis chart of $[CdL]Cl_2$ complex

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