Synthesis, Thermogravimetric and Spectroscopic Characterizations of New Tetraazamacrocyclic Schiff Base Ligand and Some Metal Complexes

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Abstract

In the present study, metal complexes of Mn(II), Ni(II), Co(II), Cu(II) and Hg(II) were synthesized using new Tetraazamacrocyclic Schiff Base (5E,8E,14E,17E)-6,8,15,17-tetramethyl-1,2,3,4,4a,7,9a,10,11,12,13,13a,16,18a-tetradecahydrodibenzo [b,i][1,4,8,11]tetraazacyclotetradecine (L) derived from 1,2-diamino cyclo hexane with the acetyl acetone. Compounds have been exanimated and confirmed by fourier-transform infrared (FT-IR), ultraviolet-visible (UV-visible), proton nuclear magnetic resonance (^{1}HNMR), carbon nuclear magnetic resonance (^{13}CNMR), microelemental analyses (CHN), thermal analysis (TG), conductivity and magnetic susceptibility. The propose geometry for all complexes [$MLCl_2$] structures were octahedral. Thermogravimetric of cobalt complex was carried out in two steps by fission into several small aggregates.

Key Words: Macrocyclic, Ligand, Tetraazamacrocyclic, Thermogravimetric, Metal Complexes

1. Introduction

Macrocyclic compounds are defined as cyclic molecules with nine or more atoms in their ring, three of which are electron pair donors [1]. Macrocycles are important and useful cyclic compounds that are mainly made up of organic frames with heteroatoms that can chelate to substrates interleaved. They belong to a branch of inorganic chemistry known as coordination chemistry, which is concerned with the investigate of the structures, properties and reactions of macrocyclic ligands when they are coordinated to a transition metal core [2]. Because of some of the unique features afforded by the macrocyclic environment, macrocyclic ligands have gotten a lot of interest in recent years. These include extremely high thermodynamic stability, the ability of the central metal to exist in unusual oxidation states and their ability to mimic naturally occurring macrocyclic molecules in their structural and functional features [3, 4]. The variety and scope of macrocyclic chemistry's applications have continued to grow as the field has progressed. This final section aims to provide high-level overview applications of synthetic macrocyclic. A particularly insightful treatment can be found in the Nobel Lecture of Jean-Marie Lehn, [5] which describes the concept of supramolecular chemistry from simple recognition, to cation and anion receptors, multiple recognition, catalysis, transport, and molecular devices.

This study is concerned with synthesizing and characterizing five complexes of the ligand (L), obtained by reaction 1,2-diamino cyclohexane with acetylacetone using transition metal ions such as Mn(II), Ni(II), Co(II), Cu(II), and Hg(II).

2. Experimental

2.1. Materials

The chemicals, o-diamino cyclohexane (Sigma Aldrich), acetyl acetone (Thomas Baker), were used as received. The metal salts $CoCl_2.6H_2O$ (Oxford), $NiCl_2$, $MnCl_2$, $HgCl_2$ and $CuCl_2\cdot 2H_2O$ (CDH), were commercially available pure samples. Ethanol (Honey well) was used as solvent.

2.2. Instrumentation

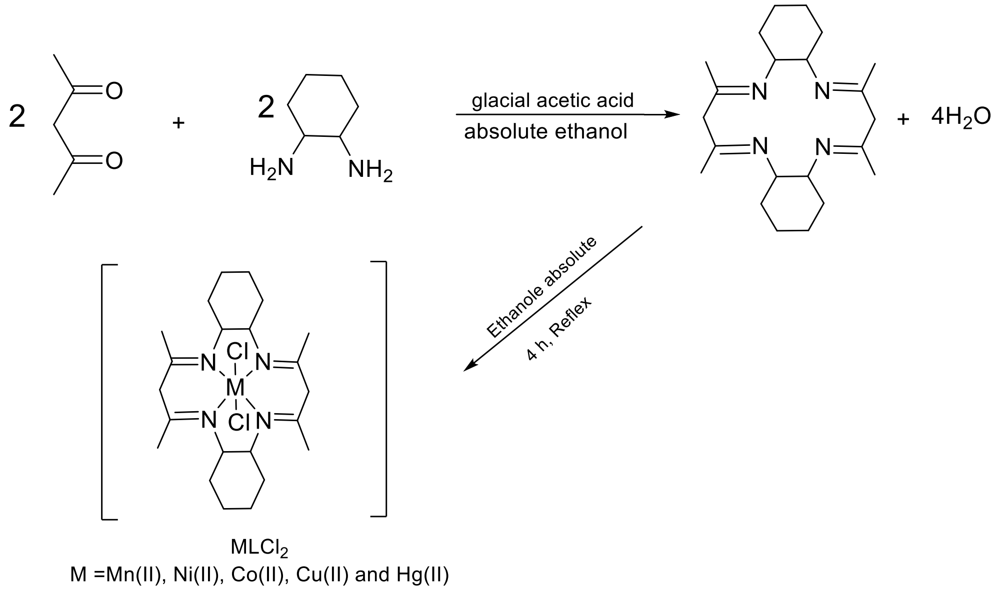
All of the chemicals and Reagents inside in synthesis of the (L) and its complexes were from pure grade and purchased from Fluka, BDH and Merck chemical companies. Infrared spectroscopy was measured using the device (Shimadzu 8400s FT-IR) and CsI disc within the range (200-4000) cm^{-1}. Through the use of an electro-thermal melting point device (SMP10 Stuart), the melting point of the compounds prepared in an open tube was determined. Using (Shimadzu UV-1800) visible ultraviolet spectrophotometer with a concentration of 10^{-3} M samples in DMSO solvent at room temperature and a quartz cell length of 1.0 cm, the electron spectra of the prepared compounds were measured. Using the device (Bruker 300 MHz NMR spectrometer), the chemical displacements were recorded in (NMR spectra ^{1}H and ^{13}C) in (DMSO-d6 with TMS). Using a device (Shimadzu (AA 680)), to determine the content of the metals in the complexes. Using a device (Philips pw-Digital conductivity meter), the molar conductivity of the prepared compounds was measured with a concentration of (10^{-3}M) in (DMSO) and at room temperature. Using a device (magnetic sensitivity balance (Sherwood Scientific)), (μeff B.M) of complexes were measured at room temperature. Using a device (Euro EA 300), (%M, %C, %H, %N) was determined for the prepared compounds. A STA PT-1000 Linseis at the temperature range of 0-1000℃ and used argon gas, thermal gravity analysis (TGA) was performed.

2.3. Synthesis of tetraazamacrocyclic schiff base ligand

An equimolar amounts of 1,2-diamino cyclo hexane (**1 g**, **8.8 mmol**) with the acetyl acetone (**0.9 g**, **8.8 mmol**), both dissolved in absolute ethanol was refluxed in the presence of a catalytic amount of acetic acid glacial for **8h**, the mixture let to cool at room temperature, the precipitate was filtered then washed with cool ethanol, and let to dry, and finally recrystallized with ethanol [6, 7].

2.4. Synthesis of the complexes

To an ethanolic solution **(20 mL)** of metal salts **(8.6×10^{-1} mmol)**, the ethanolic solutions of 6,8,15,17-tetramethyl-1,2,3,4,4a,7,9a ,10,11,12,13, 13a,16,18a-tetra-decahydro dibenzo [b,i][1,4,8,11] tetraazacyclotetradecine: **L (3×10^{-1} g, 8.6×10^{-1} mmol)** were added simultaneously with constant stirring. The reaction mixture was then refluxed for **0.5 h**. The mixture let to cool at room temperature; the precipitate was filtered then washed with hot ethanol and dried in vacuum [8, 9]. **Table (1)** displays some physical properties of the prepared complexes, weight of metal salts and yield. Where M^{II}= Co, Cu, Mn, Ni and Hg., **Scheme (1)**



Scheme (1): The preparation route of complexes [$MLCl_2$]

3. Result and Discussion

Thermal stability and the nature of the colored solid are the most important characteristics of the prepared metal complexes. The theoretical and practical data of (CHN) Microanalysis for all prepared complexes were approximated, Table (1).

Table (1): Different physical properties of (L) and its complexes

No.	Empirical formula	M.wt g/mol.	Yield %	color	m.p.°C	Microanalysis found, (Calc.) %		
						C	H	N
1	[$C_{22}H_{36}N_4$] L	356.56	59.7	Light brown	160	74.11	10.18	15.71
2	[$NiC_{22}H_{36}N_4Cl_2$]	486.15	69.2	Light green	282*	54.48 (54.35)	7.59 (7.46)	11.67 (11.52)
3	[$MnC_{22}H_{36}N_4Cl_2$]	482.40	53.1	Pale brown	267	54.89 (54.78)	7.74 (7.52)	11.82 (11.61)
4	[$CuC_{22}H_{36}N_4Cl_2$]	491.00	70.4	Brown	234	53.95 (53.82)	7.62 (7.39)	11.64 (11.41)
5	[$CoC_{22}H_{36}N_4Cl_2$]	486.39	71.6	Turquo-ise	248	54.49 (54.33)	7.74 (7.46)	11.74 (11.52)
6	[$HgC_{22}H_{36}N_4Cl_2$]	628.05	76.3	Pale brown	290*	42.26 (42.07)	5.95 (5.78)	9.10 (8.92)

3.1. IR spectrum of tetraazamacrocyclic schiff base ligand

Regarding the IR spectrum of the ligand, no signals in the domain 3390-3200 cm^{-1} related to ν(NH$_2$) amino group or near 1716 cm^{-1} characteristic to C=O group were observed. This indicated the total condensation of the NH$_2$ group with the C=O group then apparition of a macrocyclic Schiff's base. That statement will be confirmed by the occurrence of a strong signal at 1575 cm^{-1} characteristic of the υ (C=N) stretching vibration [10-14]. The stretching vibrations of aliphatic CH$_2$ were characterized by strong signals at 2933 and 2858 cm^{-1} [15, 16]. The bands at 923-891 cm^{-1} are due to C-C groups, **Figure (1)** [17, 18].

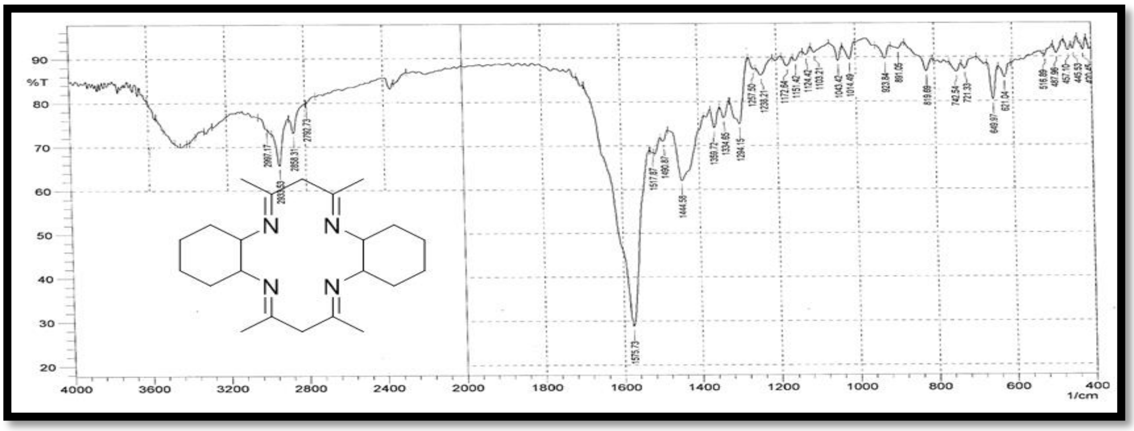


Figure (1): FTIR spectrum of L

3.2. IR spectrum of macrocyclic complexes

The IR spectra of all the tetra aza macrocyclic complexes showed band within the region of 1608–1589 cm^{-1} assigned to the coordinated imine group ν(C=N) with the metal ions [19-21]. Far Infra-Red spectrum of the complexes shows band in the region 491–420 cm^{-1} corresponds which may be due to M-N vibration confirming the coordination through the nitrogen of azomethine group [22-24]. The band observed at 310–225 cm^{-1} in all chloride complexes were consigned to metal-chlorine, **Figure (2)**, **Table (2)** [25-27].

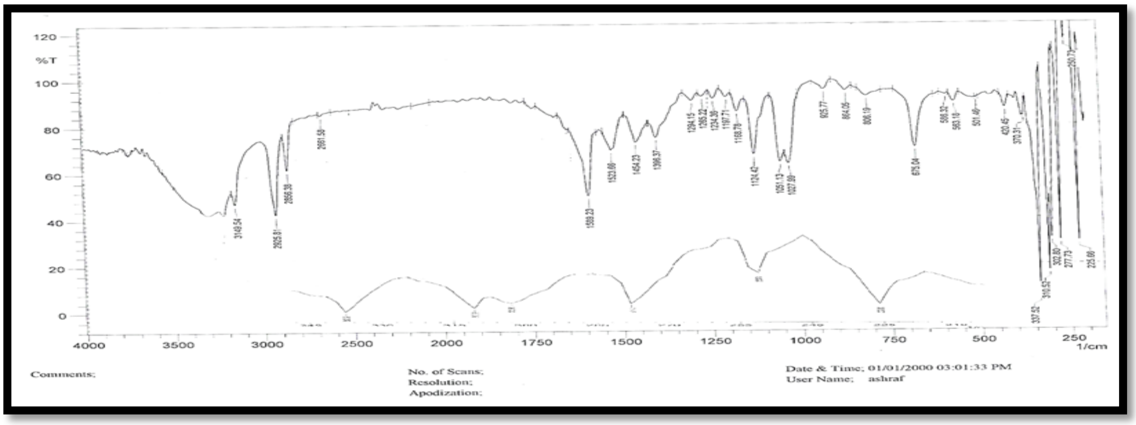


Figure (2): FTIR spectrum of $NiLCl_2$

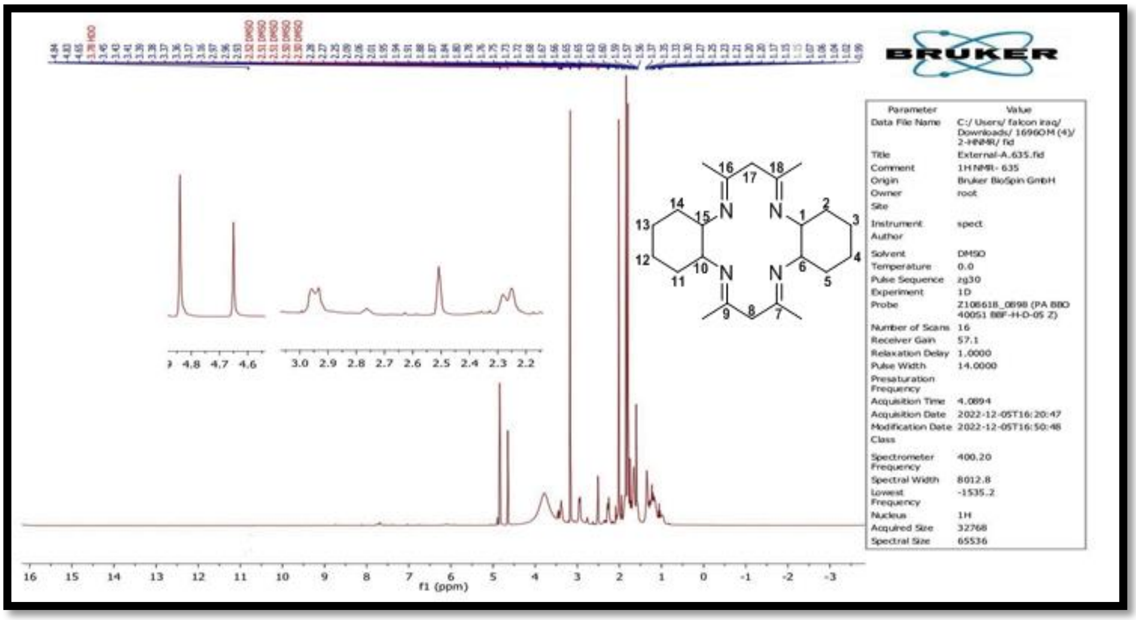
Table (2): FT-IR data of (L) (cm^{-1}) and its complexes

No.	Empirical formula	υ(C-H) alipha	υ(C=N)	υ(M-N)	υ(M-Cl)
1	$[C_{22}H_{36}N_4Cl_2]$ L	2933 2858	1575	–	–
2	$[NiC_{22}H_{36}N_4Cl_2]$	2925 2856	1589	420	310
3	$[MnC_{22}H_{36}N_4Cl_2]$	2925 2856	1585	491	343
4	$[CuC_{22}H_{36}N_4Cl_2]$	2931 2856	1602	420	310
5	$[CoC_{22}H_{36}N_4Cl_2]$	2945 2880	1606	462	297
6	$[HgC_{22}H_{36}N_4Cl_2]$	2931 2858	1604	420	297

3.4. ^{1}H and ^{13}C NMR spectra

The **^{1}H-NMR** spectra of compound **L** is listed in the experimental section, it is showing the similar multiple signals corresponding for the (H1, H6, H10 and H15) proton of the cyclo hexane at δ = 4.65-4.84 ppm [28]. The singlet signals at δ = 3.16-3.45 ppm was attributed to the (H8 and H17) protons [29]. The protons CH_3 groups were observed as singlet within the chemical shifts range δ =2.28-1.91 ppm. The multiple signals at δ =1.88-1.72 ppm were ascribed to the cyclo hexane protons (H2, H5, H11 and H14). The **^{1}H-NMR** spectra are also shown that cyclo hexane protons

(H3, H4, H12 and H13) were observed signals at the chemical shift δ = 1.68-1.02 ppm, **Figure (3)** [30, 31].



Parameter	Value
Data File Name	C:/ Users/ falcon iraq/ Downloads/ 1696OM (4)/ 2-HNMR/ fid
Title	External-A.635.fid
Comment	1H NMR- 635
Origin	Bruker BioSpin GmbH
Owner	root
Site	
Instrument	spect
Author	
Solvent	DMSO
Temperature	0.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z108618_0898 (PA BBO 40051 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	57.1
Relaxation Delay	1.0000
Pulse Width	14.0000
Presaturation Frequency	
Acquisition Time	4.0894
Acquisition Date	2022-12-05T16:20:47
Modification Date	2022-12-05T16:50:48
Class	
Spectrometer Frequency	400.20
Spectral Width	8012.8
Lowest Frequency	-1535.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Figure (3): ^{1}H-NMR spectrum of L

The ^{13}**C-NMR** spectral data, are listed in the experimental section. The ^{13}**C-NMR** spectra for compounds **L_2** is given in (**Figures 4.7** and **4.8**). The signal shows in the region of δ =162.94 ppm, is characteristic for the (C=N) group [30, 32]. The signals at the chemical shifts δ =57.03-60.42 ppm were assigned to the (C1, C6, C10 and C15) carbons in the cyclo hexane [30, 33]. The (C8 and C17) groups are appear in the region δ =52.42-49.02 ppm. Similarly, the ^{13}**C-NMR** signal for (C2, C5, C11 and C14) carbons were found at δ =33.01-29.03 ppm. The (C3, C4, C12 and C13) carbons signals were observed at δ =25.96-22.79 ppm. The peak at δ =18.80 ppm could be assigned to the methyl carbon of the alkyl group (CH_3), **Figure (4), Table (3).** [34].

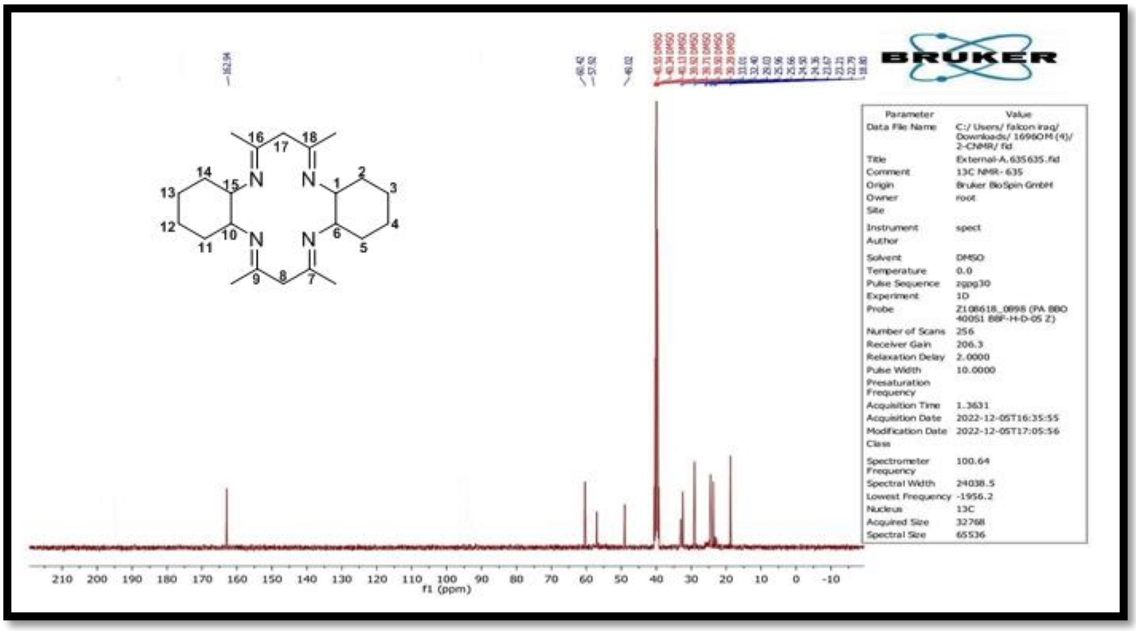


Figure (4): ^{13}C-NMR spectrum of L

Table (3): ^{1}H-NMR data for (L) measured in DMSO-d^{6} and chemical shift in ppm

Com.	**Protons kind**	**δ (ppm)**	**Carbons kind**	**δ (ppm)**
L	H1, H6, H10 and H15	4.65-4.84	C=N	162.94
	H8 and H17	3.16-3.45	C1, C6, C10 and C15	57.03-60.42
	CH_3 group	2.28-1.91	C8 and C17	52.42-49.02
	H2, H5, H11 and H14	1.88-1.72	C2, C5, C11 and C14	33.01-29.03
	H3, H4, H12 and H13	1.68-1.02	C3, C4, C12 and C13	25.96-22.79
	DMSO	2.51,	CH_3 group	18.80
	HDO	3.78	DMSO solvent	40.0

3.5 Electronic spectra

3.5.1. Ligand (L)

The highest absorption intense was found at (35714) cm $^{-1}$ which is due to transitions (π→π*) and at (30769) cm $^{-1}$ which is due to transitions (n→π*) in the electronic spectrum of the (L) , in Table (4), Figure.(5) data are recorded.

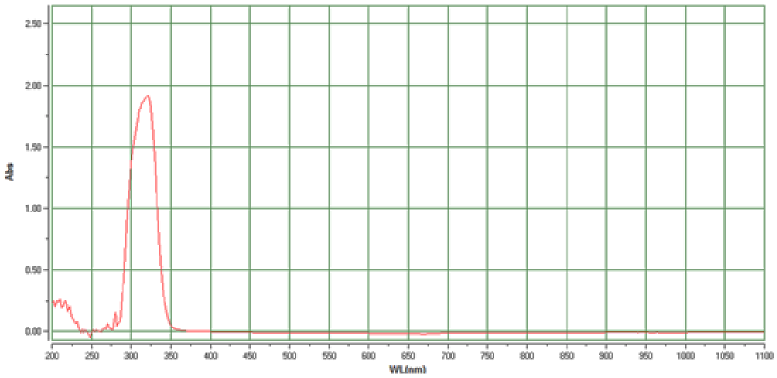


Figure (5): Electronic spectrum of L

3.5.2. Ligands (L) Complexes

The electronic spectrum of the manganese complex showed bands at (38022, 30303, 15822 and 10101) cm^{-1} due to L.F, C.T, $^{6}A_{1}g \rightarrow {}^{4}T_{1}g_{(G)}$ and $^{6}A_{1}g \rightarrow {}^{4}T_{2}g_{(D)}$ transitions respectively, suggesting that it had octahedral geometry. On the basis of the bands in the cobalt complex at (30864, 22222, 17543 and 10152) cm^{-1}, which is back to L.F, C.T mix $^{4}T_{1}g_{(F)} \rightarrow {}^{4}T_{1}g_{(P)}$, $^{4}T_{1}g_{(F)} \rightarrow {}^{4}A_{2}g$ and $^{4}T_{1}g_{(F)} \rightarrow {}^{4}T_{2}g_{(F)}$ transitions respectively, the octahedral geometry of the complex was proposed. Regarding the nickel complex, the electron spectra appear absorption bands may be assigned to L.F, C.T mix $^{3}A_{2}g \rightarrow {}^{3}T_{1}g_{(P)}$, $^{3}A_{2}g \rightarrow {}^{3}T_{1}g_{(F)}$ $^{3}A_{2}g \rightarrow {}^{3}T_{2}g_{(F)}$ transition which exhibit in (37735, 30487, 14925 and 10050) cm^{-1} respectively. A characterization of these bands indicates that the complex has octahedral geometry. Confirming the octahedral geometry of the copper complex is the appearance of the bands at (37735, 31250 and 11210) cm^{-1} is returns to L.F and $^{2}T_{2g} \rightarrow {}^{2}E_{g}$ transitions. On the basis of the bands in the Mercury complex at (30769 and 27777) cm^{-1}, which is back to L.F and C.T transitions respectively, the octahedral geometry of the complex was proposed. In Table (4), UV data was displayed. In Figure(6) the spectra of the (L) and its complexes were displayed [35, 36].

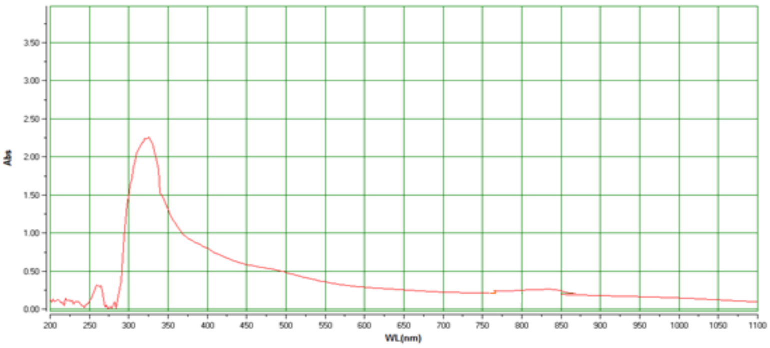


Figure (6): Electronic spectrum of [$CuLCl_2$] complex

3.5. Magnetic moments and Conductivity measurements

In Table (4), the values of measured magnetic susceptibility and the effective magnetic moment (μeff) for Mn (II), Co(II), Ni(II), and Cu(II) complexes are displayed. These complexes exhibit μeff (5.90, 5.28, 3.08 and 1.78) B.M respectively of L these normal values are consistent with octahedral complexes. The non-electrolytes nature of all metal complexes was confirmed by molecular conductivity measurements [36].

Table (4): UV-Vis data of L and its complexes.

Com.	Wave number		A	ε_{max} molar^{-1} cm^{-1}	Transitions	μ_{eff} B.M.	Conducts Ohm^{-1}cm^{2}mol^{-1}
	nm	cm^{-1}					
[$C_{22}H_{36}N_4Cl_2$] L	280 325	35714 30769	0.25 1.90	250 1900	$\pi - \pi^*$ $n - \pi^*$	------	-------
[$NiC_{22}H_{36}N_4Cl_2$]	265 328 670 995	37735 30487 14925 10050	0.20 2.28 0.033 0.019	200 2280 33 19	L.F C.T mix $^3A_2g \rightarrow {}^3T_1g_{(P)}$ $^3A_2g \rightarrow {}^3T_1g_{(F)}$ $^3A_2g \rightarrow {}^3T_2g_{(F)}$	3.08	19
[$MnC_{22}H_{36}N_4Cl_2$]	263 330 632 990	38022 30303 15822 10101	0.25 2.30 0.030 0.020	250 2300 30 20	L.F C.T $^6A_1g \rightarrow {}^4T_1g_{(G)}$ $^6A_1g \rightarrow {}^4T_2g_{(D)}$	5.90	7
[$CuC_{22}H_{36}N_4Cl_2$]	265 320 892	37735 31250 11210	0.25 0.34 0.017	250 340 17	L.F C.T $^2Eg \rightarrow {}^2T_2g$	1.78	21
[$CoC_{22}H_{36}N_4Cl_2$]	324 450 570 985	30864 22222 17543 10152	2.60 0.034 0.025 0.013	2600 34 25 13	L.F C.T mix $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$ $^4T_1g_{(F)} \rightarrow {}^4A_2g$ $^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$	5.28	13
[$HgC_{22}H_{36}N_4Cl_2$]	325 360	30769 27777	0.30 2.35	300 2350	L.F C.T	0.00	8

3.6. Thermogravimetric

The Co-complex was prepared subjected to thermal analysis using a STAPT-1000 Linseis company1 Germany [37]. In an atmosphere of argon gas, this measurement was done within temperature range (20-1000)°C and heating rate 10°C/min. Where it was recorded all results are derived from the TG curves for these compounds examined in Table (5), Figure.(7).

Table (5): Temperature values for analysis along with corresponding weight loss values.

Compounds	Stage	TGA		
		TG range(°C)	% Estimated mass loss (mg) (calculated)	Fragmentation
			Mass loss	
$C_{22}H_{36}Cl_2CoN_2$	1	50-250	1.391 (1.389)	- 17C , 5H$_2$, Cl$_2$, 2N$_2$
	2	251-900	1.358 (1.354)	- 14C , 13H$_2$

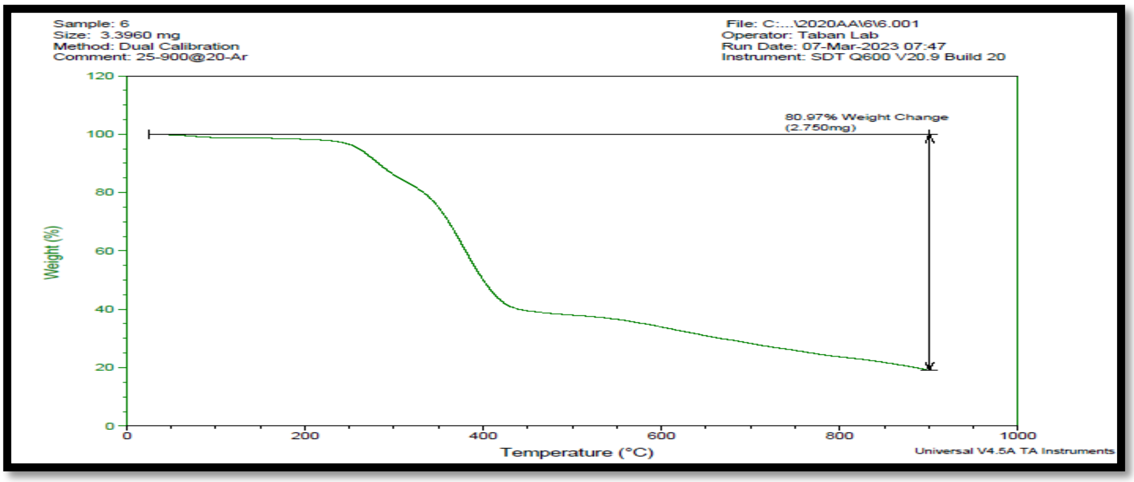


Figure (7): Thermal study of (L)

4. Conclusions

In the present study, synthesis and characterization of seven complexes of ligand (L) obtained by reaction 1,2-diamino cyclo hexane with the benzyl using transition metal ions such as Mn(II), Ni(II), Co(II), Cu(II) and Hg(II) . The ligand (L) being tetra dentate and potent donors were found be (C=N) groups, Where all complexes have octahedral shapes. Thermal analysis of cobalt complex was carried out in two steps by fission into several small aggregates.

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