Preparation and Spectral Study of Co (II), Ni (II), Cu (II) ,Pd(II) and Pt(IV) Complexes Containing N_2 Donor Atoms

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الخلاصة

تم تحضير قاعدة شيف من نوع N_2 N,N’-bis (3,4,5-trimethoxybenzalidene) dithiooxamide (LH)) من تفاعل الأمين (الدايثايواوكسمايد) مع الألديهايد (5,4,3-ثلاثي ميثوكسي بنزالديهايد) بعملية تصعيد حوالي 12 ساعات، خمسة انواع من المعقدات حضرت باستعمال املاح الكوبلت الثنائي والنيكل الثنائي والنحاس الثنائي والبلاديوم الثنائي والبلاتين الرباعي مع الليكند المحضر. تم تحليل ودراسة الليكند المحضر بتقنيات مختلفة مثل التحليل الدقيق للعناصر والمطيافية تحت الحمراء وتقنية طيف بروتون الرنين النووي المغناطيسي وتقنية المطيافية الفوق البنفسجية-المرئية. اما المعقدات المحضرة فقد تم تحليلها ودراستها من خلال التقنيات: المطيافية تحت الحمراء وتقنية المطيافية الفوق البنفسجية-المرئية لمعرفة المجاميع الفعالة والانتقالات الالكترونية واستخدم قياس الحساسية المغناطيسية لمعرفة الخواص المغناطيسية للمعقدات. درست التوصيلية الكهربائية للمعقدات بمذيب DMSO حيث وجد ان المعقدات تكون موصلة وبصيغة 1:2. أخيرا قيست الفعالية البايولوجية لليكند ومعقداته وقد وجد أن LH, $Ni(LH)_2$, $Cu(LH)_2$ أظهرت أعظم فعاليه ضد الفطر Aspergillus niger وهونوع من أنواع الفطريات الجلديه أما المعقدات $Co\ (LH)_2$, $Pd\ (LH)_2$, $Pt\ (LH)_2$ لم يظهروا أي فعالية بايولوجية ضد هذا الفطر.

الكلمات المفتاحية

دراسة طيفية، منح نوع N_2، معقدات، الفعالية البايولوجية.

Abstract

Ligand N_2 donor (N,N’-bis (3,4,5-trimethoxybenzalidene) dithiooxamide (LH)) has been prepared from dithiooxamide with 3,4,5-trimethoxybenzaldehyde. The reaction was reflexed for 12 h. at 70 ºC. Co (II), Ni (II), Cu(II), Pd (II) and Pt (IV) complexes were synthesized via reaction between appropriate metal ion and the ligand (LH). The ligand (LH) characterized by CHNS elemental analysis, Infrared spectroscopy (FT-IR), H-NMR-spectroscopy and UV-Visible spectroscopy. The complexes characterized by Infrared spectroscopy (FT-IR), 1HNMR-spectroscopy, UV-Visible spectroscopy,magnetic susceptibility and conductivity measurements. From the analytical and spectral data, the stoichiometry has been found to be 1:2 for all the complexes. The Spectral data confirms well coordination of Schiff-bases ligand with the metal through imine nitrogen atoms of Schiff base moiety. Conductivity of complexes were measured using DMSO as a solvent where conductivities of complexes were ionic in ratio (1:2)..The ligand LH, $Ni\ (LH)_2$ and $Cu\ (LH)_2$ showed greater activity against Aspergillus niger. while the complexes $Co\ (LH)_2$, $Pd\ (LH)_2$ and $Pt\ (LH)_2$ not show any activity against this fungi.

Keywords

spectral study, N_2 donor, complexes, antifungal activity.

1. Introduction

Schiff base ligands containing N_2 donor atoms show greatest biological activity and of typical interest because of the variety of ways in which they are bonded to transition metal ions. It is known that the existence of transition metal ions bonded to biologically active compound may enhance their activities [1]. Various metal complexes with bi- and tridentate Schiff bases containing nitrogen donor atoms play an important role in biological system and represent interesting models for metalloenzymes which efficiently catalyze the reduction of dinitrogen [2]. Schiff base ligands containing N_2 donor have been widely used as ligands because they can easily attach to metal ions due to the formation of high stability of coordination compounds [3]. A series of Schiff bases and a Co(II), Ni(II) and Cu(II) complexes had been synthesized by R. B. Sumathi and M. B. Halli [4]. The ligand along with its metal complexes have been characterized on the basis of analytical data, IR, electronic, mass, ^{1}HNMR, ESR spectral data, thermal studies, magnetic susceptibility, and molar conductance measurements. Antibacterial and antifungal activities of these compounds are evaluated by minimum inhibitory concentration (MIC) method. Nura et al [5] had prepared *N,N',N"*-donor Schiff base ligand from the reaction of 2-acetylpridine as carbonyl compound with *N,N'*-dimethylethylenediamine (**L1**).The complexes with ions Cu(II), Mn(II), Ni(II) or Zn(II) have been prepared and characterized by virous analysis. The complexes showed very low cytotoxicity towards MCF-7 breast cancer cell line. They also showed moderate zone inhibition against Gram positive bacterium *Methicillin-resistant Staphylococcus aureus*, *Acinetobacter baumannii and Pseudomonas aeruginosa*. No antimicrobial activity was observed with *Klebsiella pneumonia*.

N_2 ligand (schiff base), (E)-N-(4-nitrobenzylidene)-2-(2-(4-nitrophenyl) imidazolidine- 1-yl) ethaneamine (L) and there complexes with general formula of MLX_2(where in M is Zn(II),Cd(II) and Hg(II) and X is chloride, bromide and/or iodide) had been synthesized by Morteza et al. These compounds have been prepared and characterized by physical and spectroscopic studies such as elemental analysis, molar conductance measurements, FT-IR, NMR and UV–Visible electronic spectra [6].

In the present study, the complexes of Co(II), Ni(II) Cu(II), Pd(II) and Pt(IV) with Schiff base containing N_2 donor atoms derived from 3,4,5-trimethoxybenzalidehyde and dithiooxamide have been prepared and characterized in different techniques.

2. Experimental

Chemicals and Instruments

3,4,5-trimethoxybenzalidehyde 99% (Fluka), dithiooxamide 99% (BDH), methanol(Fluka, 99%), ethanol absolute (Fluka, 99.9%), Acetone (GCC,99.9%).diethyl ether(BDH,99%), $CoCl_2$. $6H_2O$, $NiCl_2$. $6H_2O$, $CuCl_2$. $2H_2O$, $PdCl_2$. H_2O and K_2PtCl_6. $6H_2O$ (BDH,99%). While the techniques that were used in this work are: FT-IR 8000s (Shimadzu), Uv-Vis. (Shimadzu), elemental analysis (EuroEA Elemental Analyser), ^{1}HNMR, was measured by BRUKER (400 MHz) system in d6-DMSO as a solvent., melting point of compounds produced was measured by using Gallen kamp melting point, the molar conductivity for complexes was measured using WTW balance. The magnetic susceptibility of prepared complexes was measured by using magnetic susceptibility balance, Johnson Mattey.

3. Synthesis

3. 1. Synthesis of *N,N′*-bis (3,4,5-trimethoxybenzalidene) dithiooxamide (LH)

The ligand was synthesized by dissolving 10 (mmol) of dithiooxamide in 20 (mL) of a hot absolute ethanol and then 20 (mmol) of 3,4,5-trimethoxybenzaldehyde was dissolved in 20 (mL) of absolute ethanol was added, after that 2-3 drop of piperidine ($C_5H_{11}N$) was added to the mixture. The reaction was stirred and reflux or 12 (h). The precipitate was filtered and washed with cold ethanol several times and then dried at 45 (ºC) for 5 (h). The ligand was partial soluble in dichloromethane, chloroform, toluene, non-soluble in n-Hexane, and soluble in DMF. m.po = 182dec.yield = 90%. Elemental analysis CHNS: Found (calc.) %: C; 55.40 (57.00); H; 5.00 (4.50); N; 5.50 (6.50); S; 13.50 (12.60). Fig. (1) shows the structure of ligand.

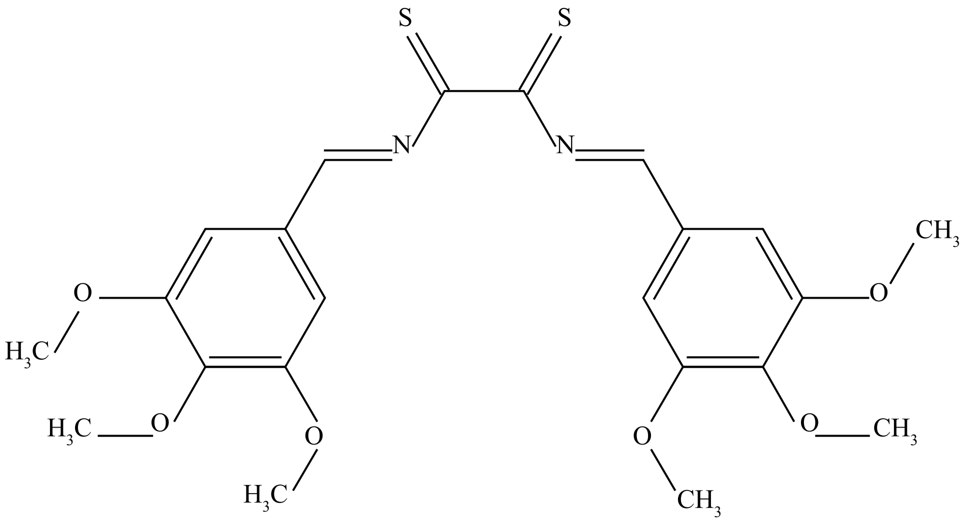


Fig. (1): The structure of ligand (LH)

3. 2. Synthesis of Co(II), Ni(II), Cu(II), Pd(II) and Pt(IV) Complexes

20 (mmol) of ligand (LH) was dissolved in 20 (mL) of methanol and 10 (mmol) of metal salt ($MCl_2.xH_2O$) was dissolved in 10 (mL) of methanol. Ligand solution and metal salt solution were mixed and reflexed for 2 (h). The final product was filtered and washed with cold methanol several times and lastly dried at 45 (ºC) for 5 (h). Physical properties of the synthesis complexes are shown in Table (1).

Table (1): Color, melting point, yield and suitable solvent for ligand and its complexes.

Compound	Color	Melting Point (dec.) °C	Yield %	Suitable Solvent
LH	DeepOrange	182	90	DMF
Co(LH)$_2$	Deep green	190	85	DMSO
Ni(LH)$_2$	orange	172	60	DMSO
Cu(LH)$_2$	Black	191	65	DMSO
Pd(LH)$_2$	Deep brown	188	60	DMF
Pt(LH)$_2$	Black green	189	70	DMF

4. Results and Discussion

4. 1. Infrared Spectroscopy

Fig.(2) shows IR peaks of LH. It is clear from the Fig. that there is a peak at 1583 (cm^{-1}) this represents the azomethine stretching band υ (H-C=N). The peak at 1186 (cm^{-1}) is due the thio carbonyl band υ (C=S). There is a peak at 1236 (cm^{-1}) which corresponds to υ (C-O-C) asymmetric stretching, while the peak at 1002 (cm^{-1}) corresponds to υ (C-O-C) symmetric. The peak at 2939 (cm^{-1}) is due the υ (CH_3) stretching, while the peak at 819 (cm^{-1}) corresponds to CH_3 (out-of-plane) bending [7]. In the IR spectra for the ligand and its complexes there is a peak band around 2830 (cm^{-1}) can be assigned to impurities (C-H stretch in aldehyde). The most significant difference in the IR spectra of the ligand and its complexes, Fig.(3-7) were the shift of H-C=N stretching frequencies of LH to higher frequencies and the change in shape of the peak due to metal - ligand coordination [8]. Furthermore, new bands have been observed between 528-665 (cm^{-1}) and 651-735 (cm^{-1}) which are due to υ (M-N) and υ (H_2O) coordination water [9]. Table 2 contains the most characteristic bands of the ligand LH and its complexes.

Table (2): Number of the most bands of FT-IR to prepadre ligand (LH) and Its complexes in (cm^{-1})W= weak, S= strong, m= medium, Stret.= Stretching, o.o.p.= Out of plane

Compound	υ H-C=N	υ C=S	Methoxy bands		υ (M-N)	Metheyl bands		H_2O (Coor)
			υC-O-C) Asymmetric	υC-O-C) Symmetric		CH_3 Stret.	CH_3 O.O.P.	
LH	$1583_{(s)}$	$1186_{(s)}$	$1236_{(w)}$	$1002_{(m)}$	-	2939	819	-
Co(LH)$_2$	$1585_{(s)}$	$1184_{(s)}$	$1236_{(w)}$	$999_{(m)}$	$528_{(w)}$	2937	763	653
Ni(LH)$_2$	$1587_{(s)}$	$1184_{(s)}$	$1232_{(w)}$	$1002_{(m)}$	$547_{(w)}$	2939	830	735
Cu(LH)$_2$	$1674_{(s)}$	$1186_{(s)}$	$1240_{(w)}$	$997_{(m)}$	$530_{(w)}$	2939	842	651
Pd(LH)$_2$	$1673_{(s)}$	$1185_{(s)}$	$1240_{(w)}$	$999_{(m)}$	$659_{(w)}$	2937	844	-
Pt(LH)$_2$	$1585_{(s)}$	$1168_{(s)}$	$1242_{(w)}$	$995_{(m)}$	$665_{(w)}$	2937	837	-

4. 2. Electronic spectra and magnetic properties

The spectrum of ligand Fig.(8) shows the first absorption band in 280 (nm) 357143 (cm^{-1}) which can be attributed to (π-π^*) transition for the aromatic nucleus. The second band appearing in 377 (nm) 26737 (cm^{-1}) is attributed to (π-π^*) transition in all molecules. The third band which appeared in 420 (nm) 238095 (cm^{-1}) was attributed to (n - π^*) transition in imino group (C=N) [10]. Fig.(9) shows absorption bands of complex $Co(LH)_2$ in visible region at 663 nm 15083 (cm^{-1}) belonging to (υ_2) ${}^4T_1g \rightarrow {}^4A_2g$ (F) and absorption bands in 520,670 (nm), 19230,14925 (cm^{-1}) respectively and from average give (υ_3) = 17630 (cm^{-1}) belonging to (υ_3) ${}^4T_1g \rightarrow {}^4T_1g$ (P) in octahedral field [11]. Using (Tanabe-Sugano) diagram for d^7,, and from υ_3/υ_2 ratio we could calculate υ_1 6703 (cm^{-1}) assigned as ${}^4T_1g \rightarrow {}^4T_2g$ (F) transition. This value refers to Δ_o [12]. The calculated value of β (0.77) indicates that the complex has covalent properties. The value ν_1 6554 (cm^{-1}) was calculated using the equation **$15B' = \upsilon_3 + \upsilon_2 - 3\upsilon_1$**. The resulting value is close to that obtained from using the Tanabe-Sugano diagram. The magnetic susceptibility of complex $Co(LH)_2$ is 2.68 (B.M) and molar conductivity measurement in DMSO was 73 (µs/cm) in type 1:2 that indicate the complex is paramagnetic and electrolyte [13], from these results, an octahedral geometry a round Co(II) can be suggested. The proposed structure of $Co(LH)_2$ is shown in Fig.(10).

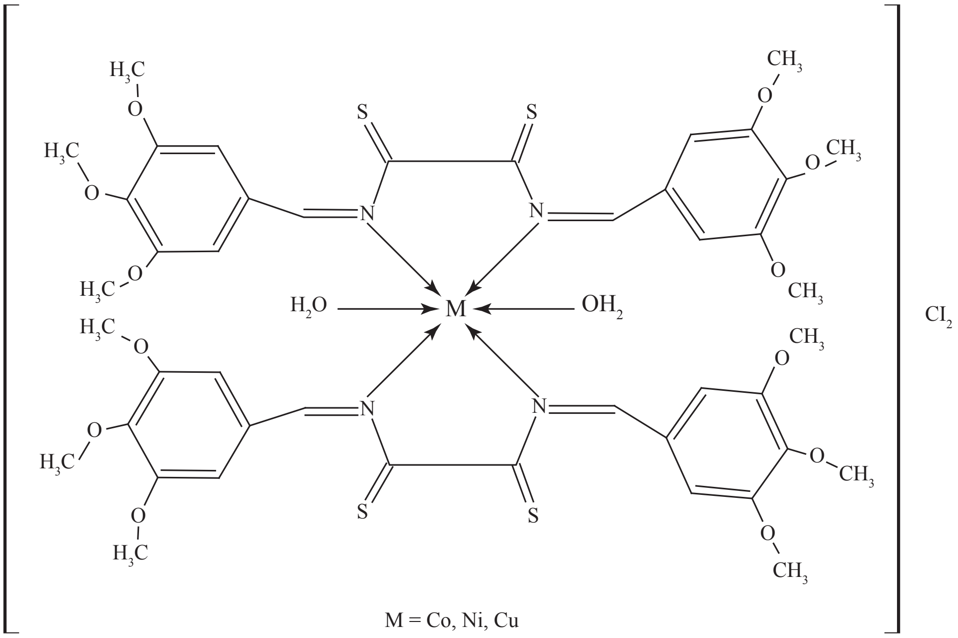


Fig. (10): The proposed structure of Co^{2}+, Ni^{2}+ and Cu^{2}+complexes

Spectrum of $Ni(LH)_2$ complex is shown in Fig.(11). In this figure, two absorption bands in visible region at 508,445 (nm), 19665,22446 (cm^{-1}) respectively belonging to transitions (υ_2) ${}^3A_2g \rightarrow {}^3T_1g$(F), ($\upsilon_3$)${}^3A_2g \rightarrow {}^3T1g$(P) respectively in octahedral field [14]. From the value $\upsilon_3 \backslash \upsilon_2$ and energy level diagram (Tanabe-Sugano) for d^8 ions in an octahedral field can calculate the value of υ_1 8522 (cm^{-1}) that belongs to transition ${}^3A_2g \rightarrow {}^3T_2g$(F) that's equal for Δ_o. This value is characteristic of octahedral field about nickel (II) complexes [15]. The calculated value of β (0.86) indicates that the complex has covalent properties. The magnetic susceptibility (μ=3.394 B.M) and conductivity measurement in DMSO was 84 (μs/cm) that indicate the complex was (electrolyte) [13]. According to these data and those obtained from I.R spectra, an octahedral geometry around Ni(II) can be suggested as illustrated in Fig.(10).

$Cu(LH)_2$ complex Fig.(12) has band near 527 (nm) 18957 (cm^{-1}) and band at 445 (nm) 22471 (cm^{1}). This band belongs to transitions $^2B_1g\rightarrow{}^2A_1g$, $^2B_1g\rightarrow{}^2B_2g$ respectively that appears the coordinate octahedral distorted around copper (II) ion. The magnetic susceptibility (μ=1.65856 B.M) and conductivity measurement in DMSO were 86 (μs/cm) that indicate the complex was (electrolyte) [13]. According to these data and those obtained from I.R spectra, an octahedral geometry around Cu(II) can be suggested as illustrated in Fig.(10). The spectrum of $Pd(LH)_2$ complex Fig.(13) shows absorption band in 534 (nm) 18726 (cm^{-1}) belonging to $^1A_1g\rightarrow{}^1B_1g$ transition and another in 568 (nm) 17605 (cm^{-1}) belonging to $^1A_1g\rightarrow{}^1Eg$ transition. Therefore this complex was square planar [16]. The magnetic susceptibility (μ=0 B.M) and conductivity measurement in DMSO were 74 (μs/cm) that indicate the complex was (electrolyte) [13]. According to these data and those obtained from I.R spectra, a square planar geometry around Pd(II) can be suggested as illustrated in Fig.(14).

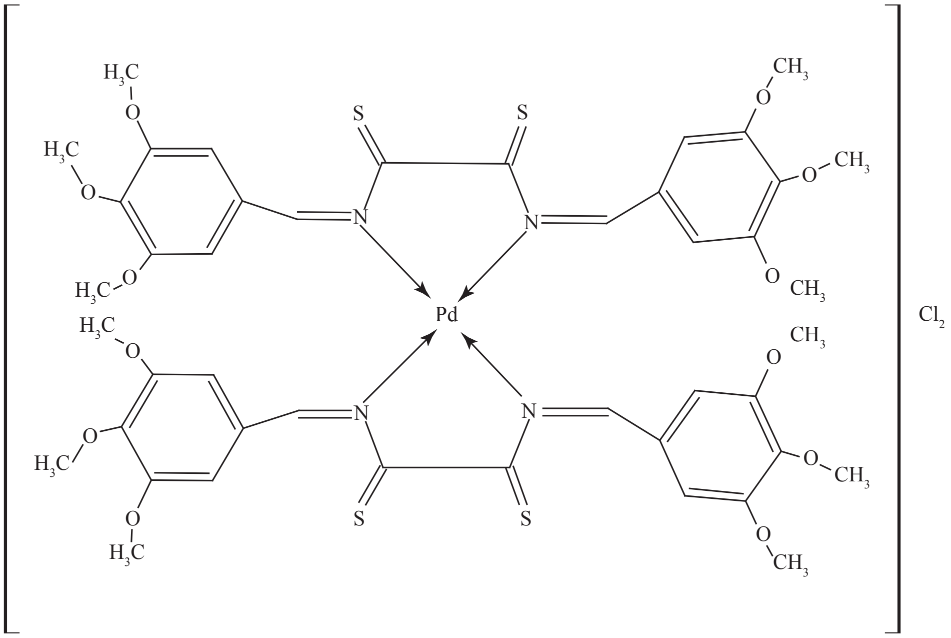


Fig.(14). The proposed structure of $Pd(LH)_2$ complex

Fig.(15) shows the spectrum of Pt (IV) complex that shows three bands in 443,486,513 (nm), 22573,20576,19493 (cm^{-1}) respectively belonging to transitions in octahedral field [16]. (υ_1) $^1A_1g\ (t_2g)^6\rightarrow{}^3T_1g\ (t_2g)^5\ (eg)^1$, ($\upsilon_2$) $^1A_1g\ (t_2g)^6\rightarrow{}^3T_2g\ (t_2g)^5\ (eg)^1$ and (υ_3) $^1A_1g\ (t_2g)^6\rightarrow{}^1T_1g\ (t_2g)^5\ (eg)^1$. The magnetic susceptibility (μ=0 B.M) and conductivity measurement in DMSO were 88 (μs/cm) that indicate the complex was (electrolyte) [13]. According to these data and those obtained from I.R spectra, an octahedral geometry around Pt(IV) can be suggested as illustrated in Fig.(16).

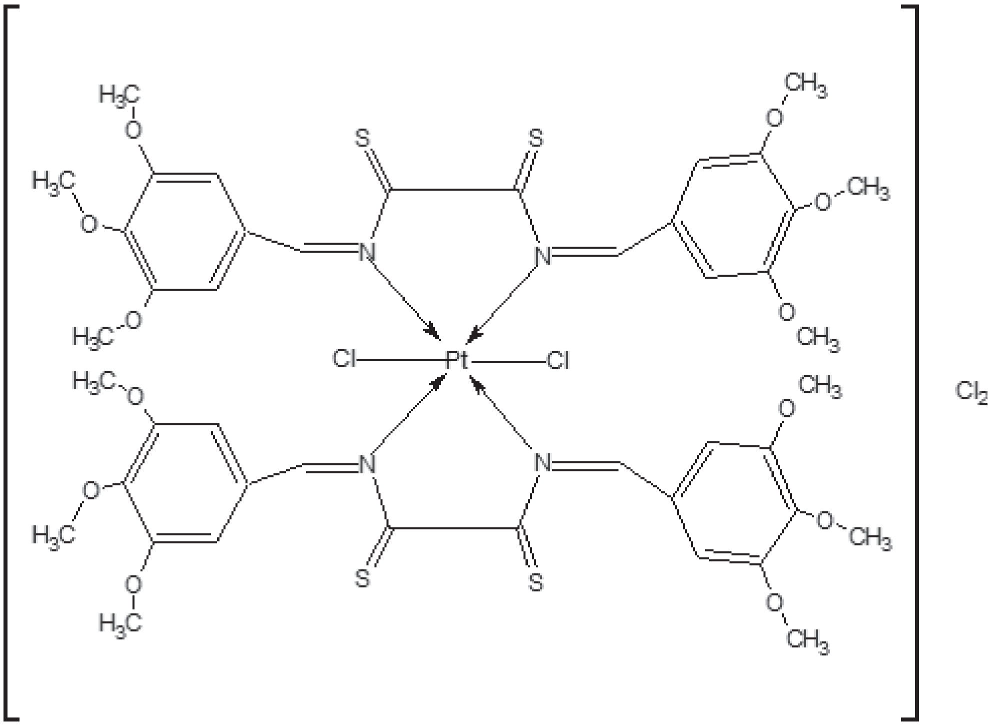
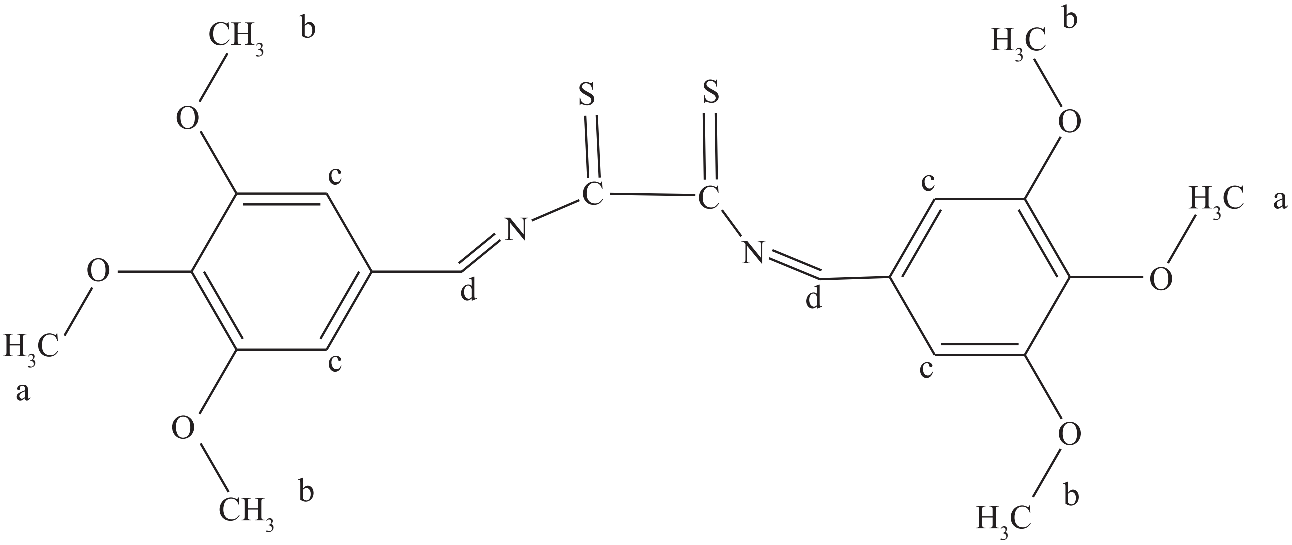


Fig. 16 The proposed structure of $Pt(LH)_2$ complex

4. 3. ^{1}H NMR Spectroscopy of Ligand LH.

1HNMR spectrum Fig.(17) of ligand (LH) showed the following signals at δ (ppm): 2.485 (S,DMSO), 3.330 (S, H_2O in DMSO), 3.607-3.771 (6H,3×Ha), 3.752-3.776 (12H,4×Hb), 6.81-7.01 (4H,4×Hc), 8.08-8.33ppm for imine protons (2×Hd) [17,18].



^{1}HNMR spectrum Fig.(18) of complex (Co(LH)$_2$) appeared in the following signals at δ (ppm): 2.479-2.508 (DMSO), 3.544-3.579 (H_2O in DMSO), 3.608-3.697 (m,9H,3×CH_3, methoxy groups), 6.730-7.216 (m,4H,aromatic), 7.95-8.193 for azomethine protons [19,20]. The signals of azomethine protons were shifted to the high field and this gives good evidence for formation of complex (Co(LH)$_2$).

5. Antifungal activity

The antifungal activity of ligand LH and their complexes have been tested for the in vitro growth inhibitory activity against the *Aspergillus niger* (this fungi effect to the dermatophytes) by using the disc diffusion method. The fungi was cultured in Potato dextrose agar medium and used as inoculums for this study. The studied compounds were dissolved in DMSO to final concentration of 10 (mg/mL) and soaked in filter paper discs of 6mm diameter. These discs were placed on the already seeded plates and incubated at 25-28 (°C) for 10 (days) [21]. The results show the inhibition of growth of the fungi. The compounds LH, Ni(LH)$_2$ and Cu(LH)$_2$ showed greater activity against *Aspergillus niger*, while the compound Co(LH)$_2$, Pd(LH)$_2$ and Pt(LH)$_2$ not show any activity against this fungi.

6. Conclusion

The elemental analysis technique was used to identify the ligand that was synthesized. In addition, 1HNMR spectroscopy, Uv-Visible spectroscopy and Infrared spectroscopy were used to identify the structure of the compounds that were produced. Nature of structure LH gave octahedral complexes with ions Co(II), Ni(II) and Cu(II). Magnetic Susceptibility Measurements of Complexes determine, were the magnetic moment of Co(LH)$_2$ Complex was 2.68 (B.M), this value agrees with octahedral low spin of cobalt complexes, the magnetic moment value, Pd(LH)$_2$ and Pt(LH)$_2$. Complexes were very low, this appeared diamagnetic properties, the magnetic moment of Ni(LH)$_2$. Complex was 3.394 (B.M), this agrees with octahedral structure, Magnetic moment value for CuLH Complex was 1.7 (B.M) this agreement with distorted octahedral of Cu(II) complexes.

Acknowledgments

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Fig.s of spectra

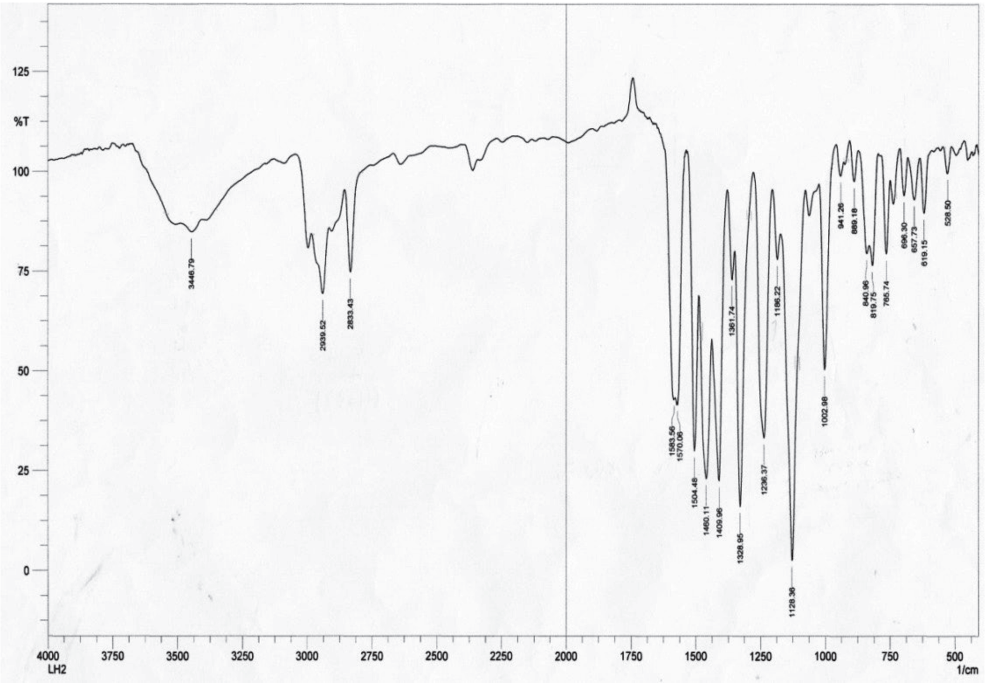

Fig.(2): FT-IR spectrum of Ligand (LH)

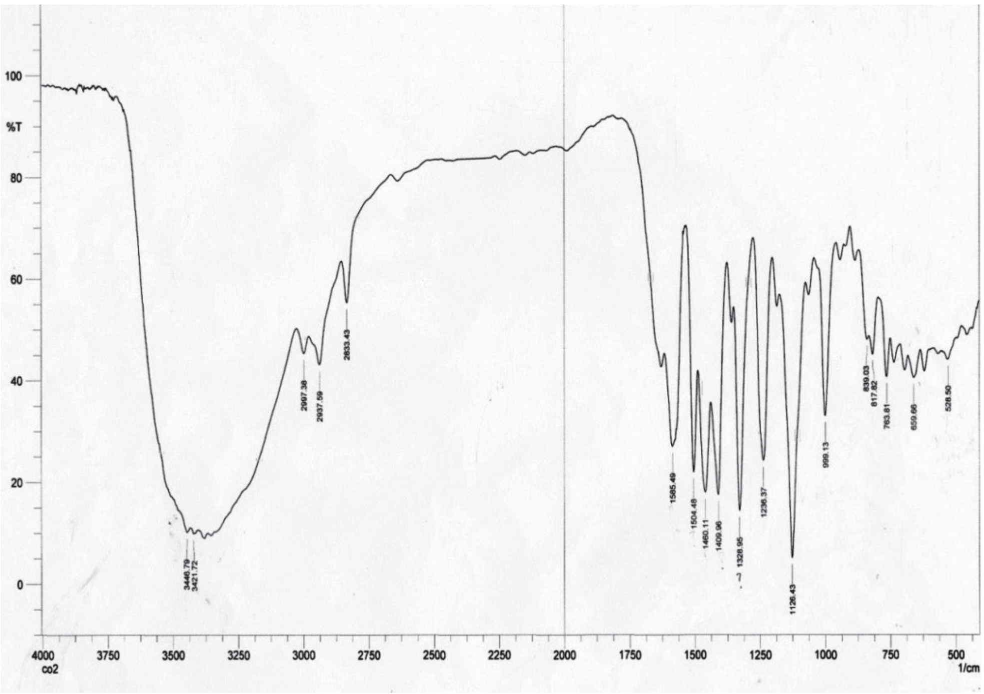

Fig.(3): FT-IR spectrum of Co(LH)$_2$

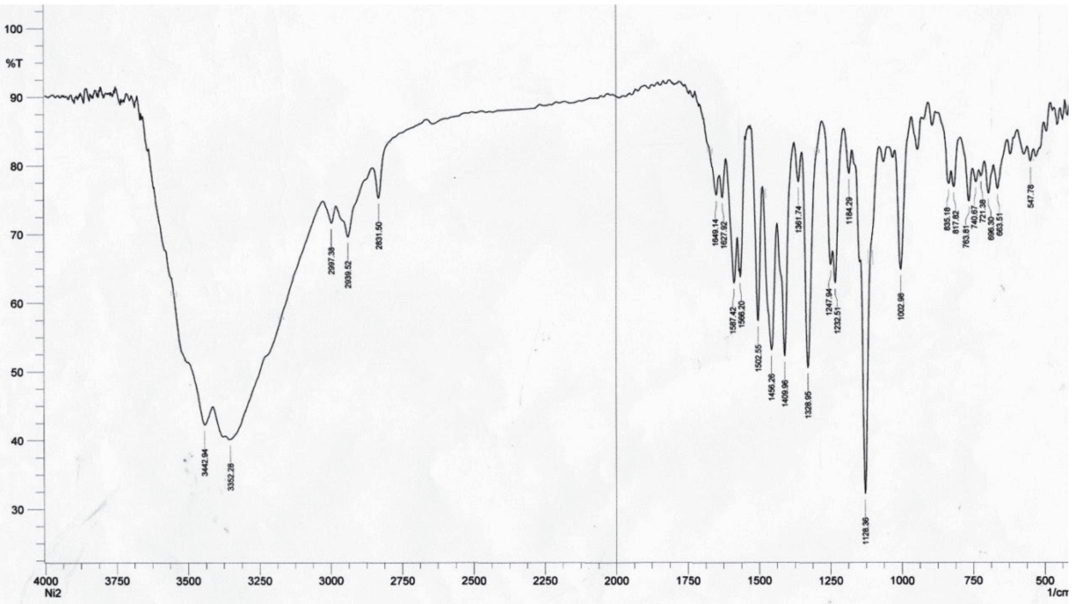

Fig.(4): FT-IR spectrum of $Ni(LH)_2$

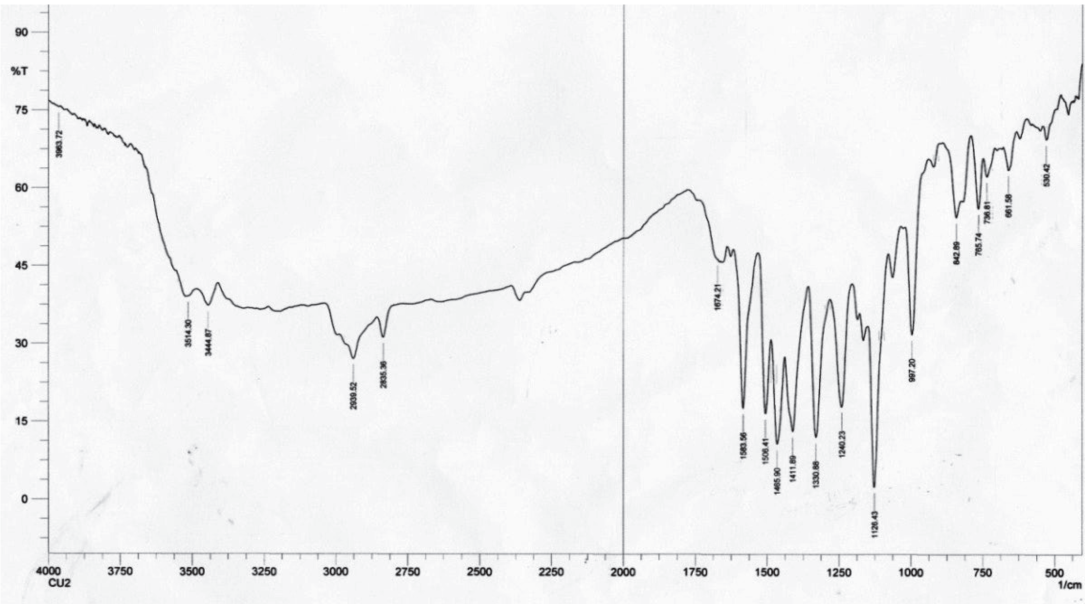

Fig.(5): FT-IR spectrum of $Cu(LH)_2$

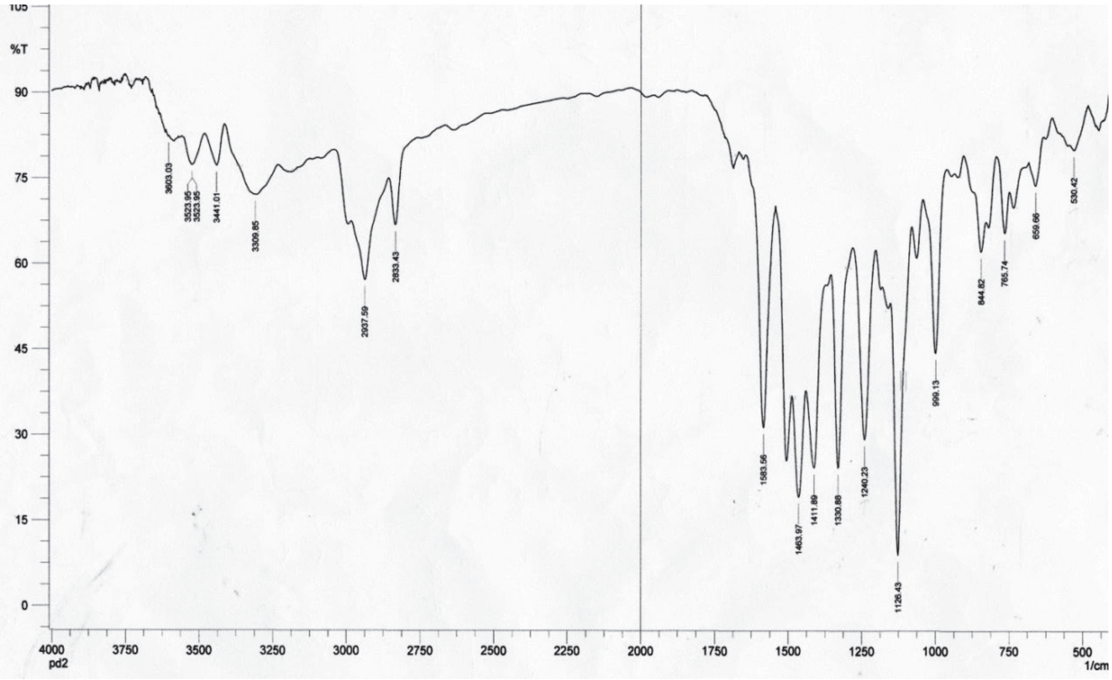

Fig.(6): FT-IR spectrum of $Pd(LH)_2$

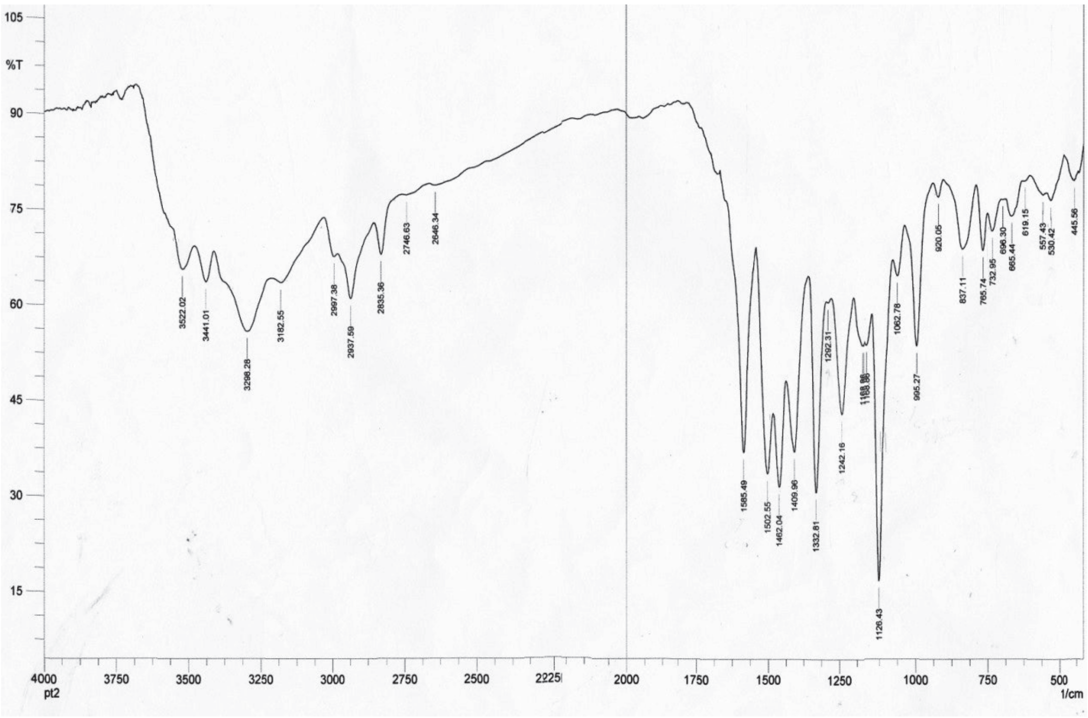

Fig.(7): FT-IR spectrum of $Pt(LH)_2$

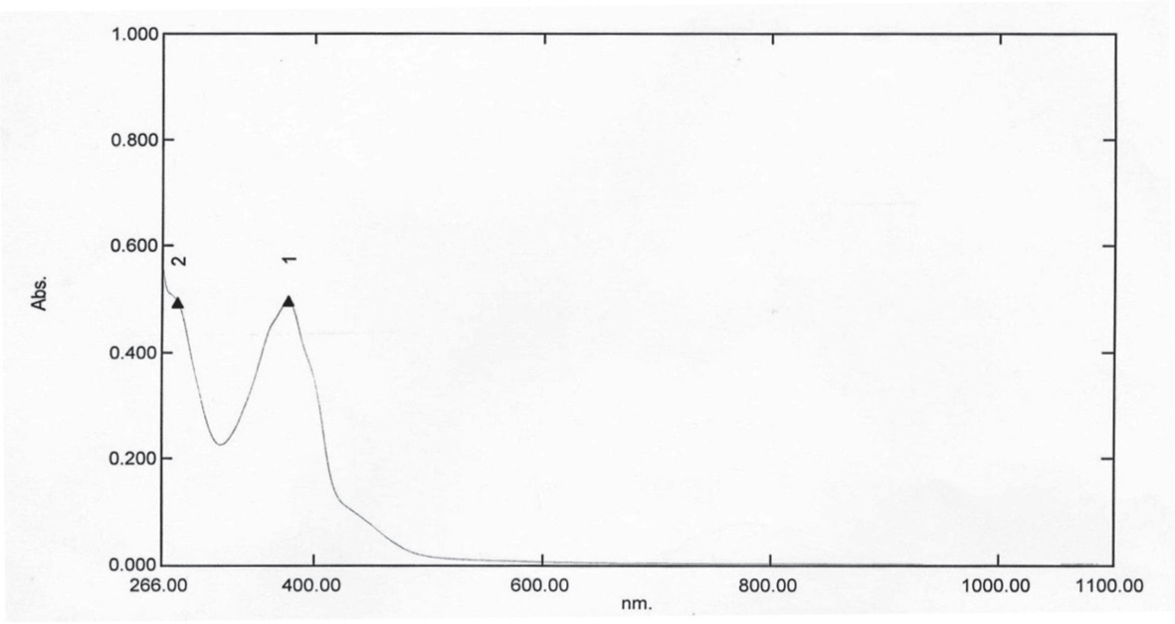

Fig.(8): UV-Vis- spectrum of Ligand(LH)

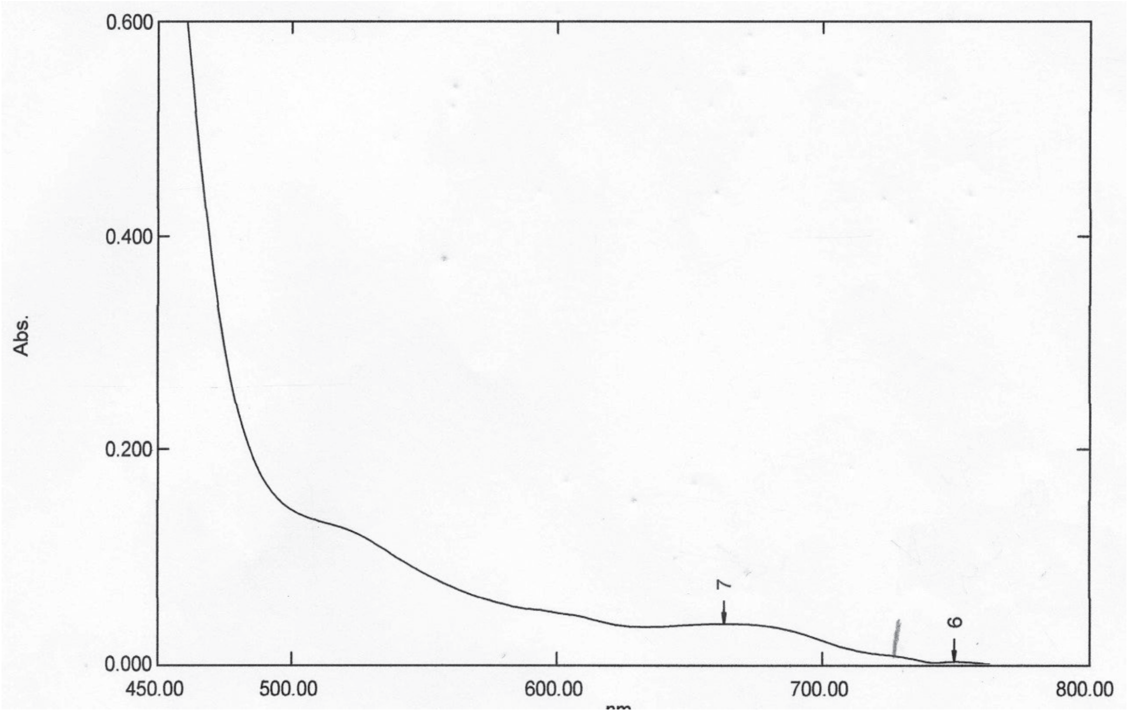

Fig.(9): UV-Vis- spectrum of Co$(LH)_2$

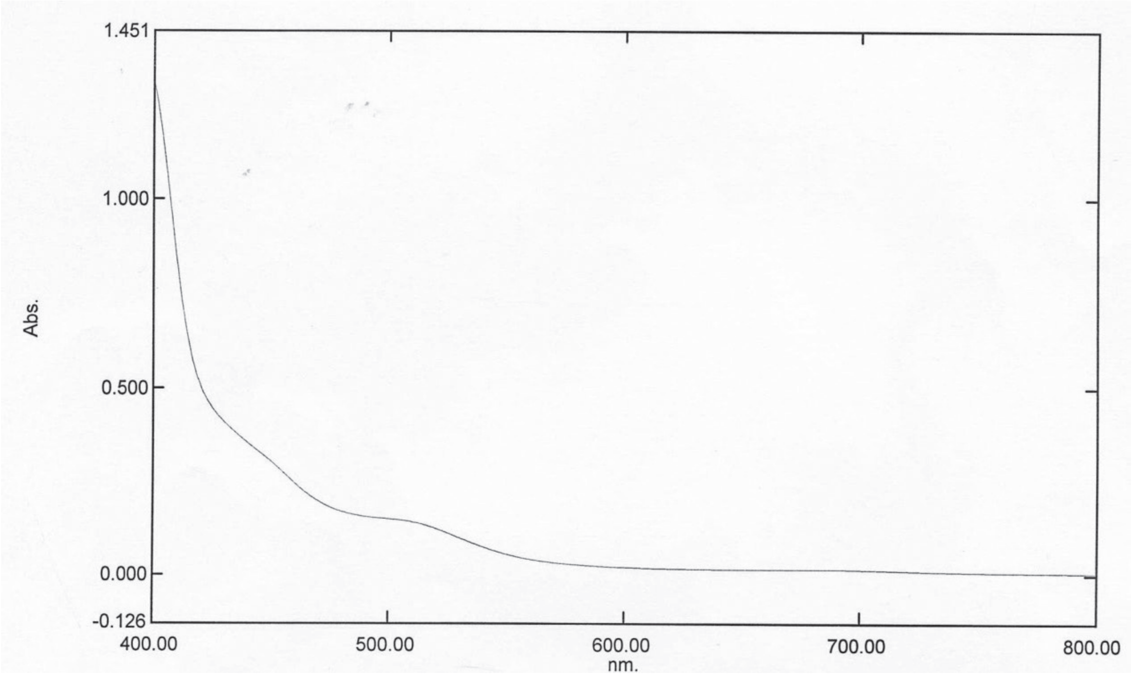

Fig.(11): UV-Vis- spectrum of $Ni(LH)_2$

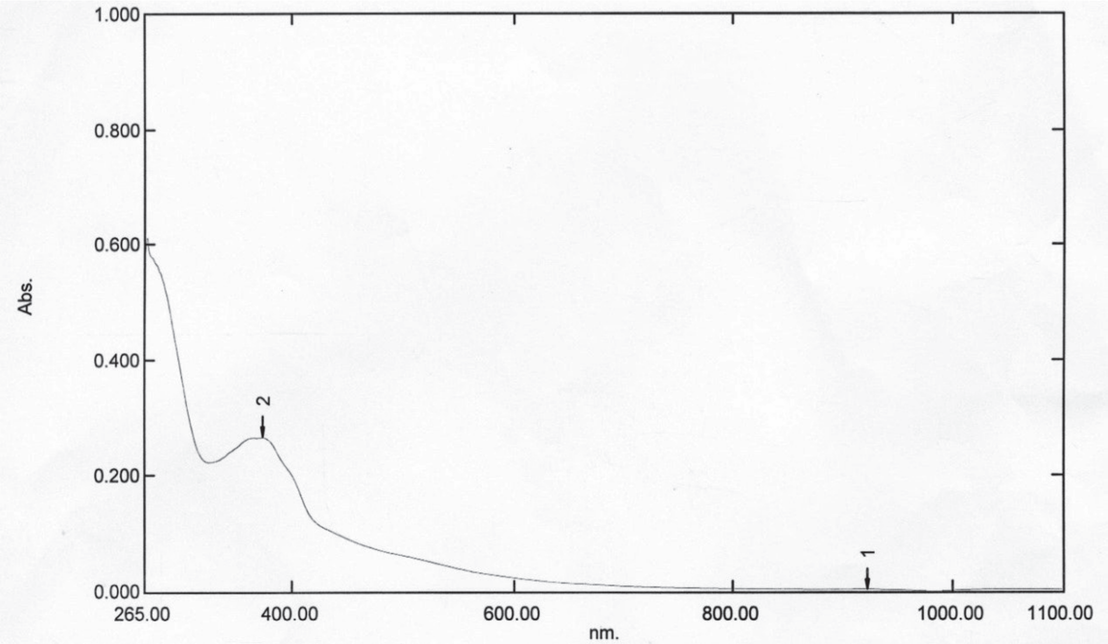

Fig.(12): UV-Vis- spectrum of $Cu(LH)_2$

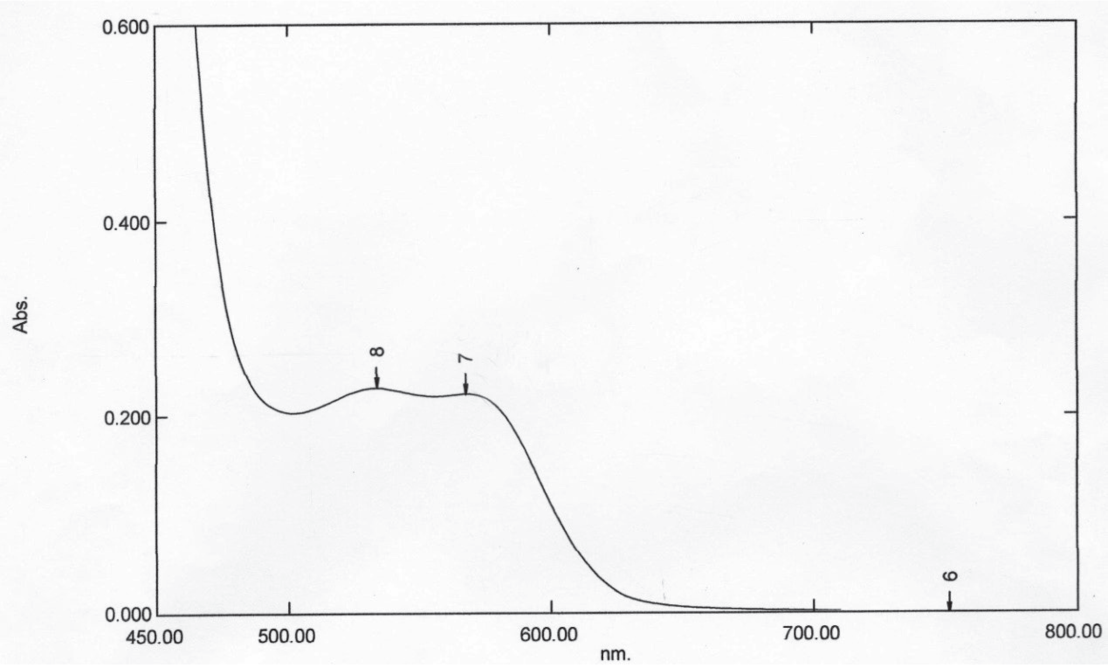

Fig.(13): UV-Vis- spectrum of $Pd(LH)_2$

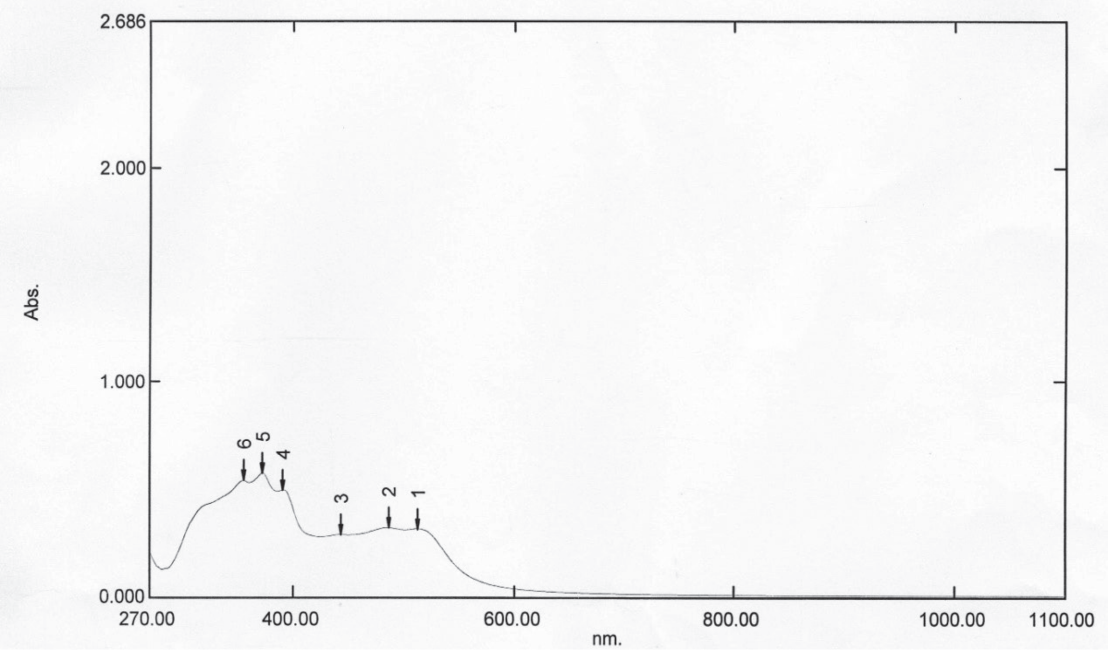

Fig.(15): UV-Vis- spectrum of $Pt(LH)_2$

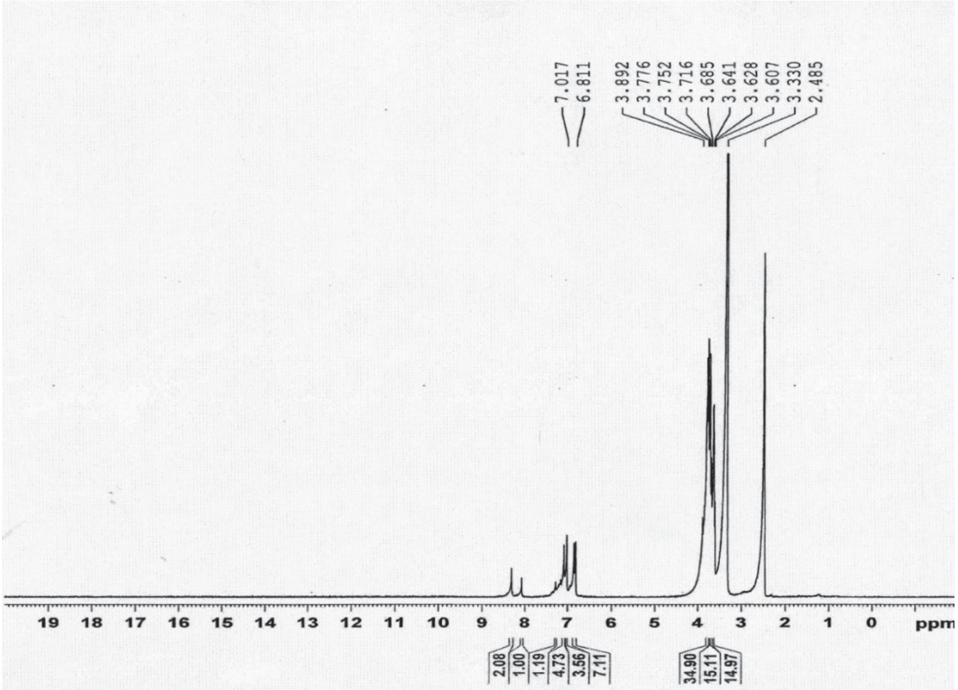

Fig.(17): ^{1}H NMR-Spectrum of ligand(LH)

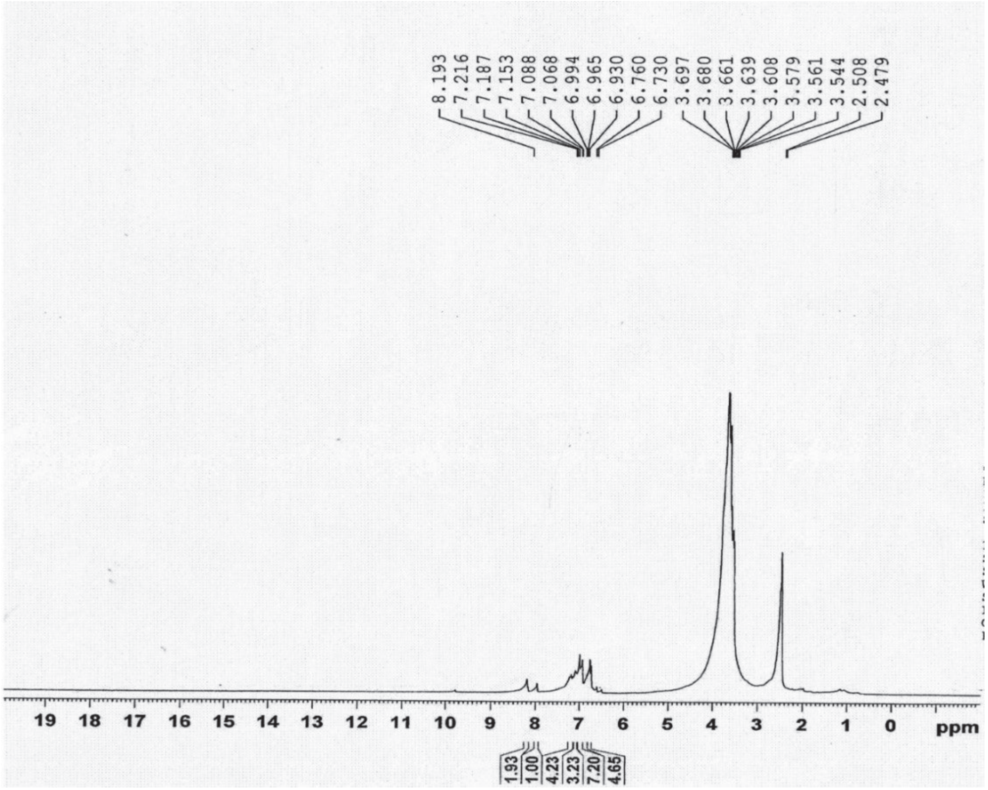

Fig.(18): ^{1}H NMR Spectrum of Co(LH)$_2$.

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