

Preparation and Identification of Metal Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) With Tetradentate Ligand

تحضير وتشخيص معقدات العناصر لكل من Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) مع ليكاند رباعي المخلب

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Abstract

A new series of transformation metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II), with Schiff base (L) bisimine (4,4'-(3,3'-dimethylbiphenyl-4,4'-diyl) bis (azan-1-yl-1-ylidene) bis(methan-1-yl-1-ylidene) bis (2-methoxyphenol)) ligand, type (O₄) was prepared by condensation of (vaniline) (4-hydroxy 3- methoxybenzaldehyde) with o- Tolidine, by (2:2) metal to ligand molar ratio. The complexes were characterized by metal analysis, magnetic susceptibility, molar conductance and IR, UV-Vis, ¹H NMR spectral studies.

From the spectroscopic studies, magnetic moments, mole ratio and physical properties the suggested geometry for the prepared complexes, we suggest the octahedral Cobalt(II) and Copper(II) Complexes with ligand and the tetrahedral geometry suggested for Manganese(II), Nickel(II), Zinc(II), Cadmium(II) complexes. The results submit that the metal is connective with the ligand during the methoxy and phenolic group.

الخلاصة :-

سلسلة جديدة من معقدات العناصر الانتقالية كل من (Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Zn(II)) مع ليكاند قاعدة شيف (4,4'-(3,3'- dimethylbiphenyl -4,4'-diyl) bis (azan-1-yl-1-ylidene) bis (methan-1-yl-1-ylidene) bis (2-methoxyphenol)) مع اورثو توليدين (4-hydroxy 3- methoxybenzaldehyde) من فانيلين (2:2) ، وقد تم تشخيص كل من المعقدات المحضرة والليكاند بواسطة الطرق الطيفية (تقنية الأشعة تحت الحمراء ، الأشعة فوق البنفسجية - المرئية ، طيف الرنين النووي المغناطيسي) والحساسية المغناطيسية ، تعيين درجة الانصهار ، وتحليل الدقيق للعناصر، والتوصيلية المولارية. ومن خلال النتائج والمعطيات المتحصل عليها من التقنيات اعلاه تم الاستنتاج ان بنية ثماني السطوح لمعقد الكوبلت والنحاس وبنية رباعي السطوح لبقية المعقدات كل من المنغيز والنيكل والخراسين و الكادميوم. ذوات الصيغة العامة [Mn₂L₂], [Co₂L₂], [Ni₂L₂], [Cu₂L₂], [Zn₂L₂], [Cd₂L₂] النتائج المقترحة تبين ارتباط الفلز مع الليكاند من خلال مجاميع الفينول والميثوكسي.

1- Introduction

The preparation of metal complexes through Ligands containing among than one donor sites are Widely with interesting properties. more of these ligands, imines containing hetero atoms as donor atoms are considered as benefit due to their Possible application in Medical fields, catalytic activity and material science ⁽¹⁻⁵⁾.

Schiff base ligands are more Able to Correlation with metal ions during phenolic groups and imines group. Schiff base can readily formed stable metal complex due to strong metal binding capacity therefore Schiff base ligands are mostly employ for metal complex preparation ⁽⁶⁾.

The Schiff base and its metal complexes have more interesting activities because of their different applications in many fields: biological, analytical fields and inorganic ⁽⁷⁾. They have been considerable interesting in the pharmacological activities such as antiviral , anticarcinogenic, antifungal, antibacterial, antimicrobial and antitubercular ⁽⁸⁾ . Schiff base ligands have the ability to coordinate with various metal ions and to stabilize them in several oxidation cases ⁽⁹⁾. The Schiff

base complexes have been used as catalysis agents . These complex can be a very well homogeneous heterogeneous for catalyzing chemical reactions, it is play an important function in Agricultural Production,medical and industrial chemistry⁽¹⁰⁻¹³⁾. A great number of Salen derivatives Schiff base (N2O2) complexes have been reported so far, and their catalytic^[14-17] and biological activities^[18-21] have been studied intensively.

2-Experimental

All chemicals used in this work were obtained from Merck, Fluka and Sigma-Aldrich and were used chemically pure or analytical reagents grade .Melting points were determined by Electro thermal Stuart melting point apparatus, , England and were uncorrected. Elemental analysis measured onEuro, E.A.300, Single. Instruction manual (V.3.0 single)Babylon University.FT-IR spectra were recorded on FT-IR 8400s, shimadzu-spectrophotometer and usingKBr discs-Karbala University.H¹-NMR spectra were recorded on JNM - model \ Joal 400 MHZ usingtetramethylsilane as internal standard and DMSO-d₆ as solvent. Measurements were made atsapala organics private (India).conductivity and magnetic moment wererecorded in Bagdad University.

3- Synthesis methods.

3.1.Preparation of the ligand(H₂L)

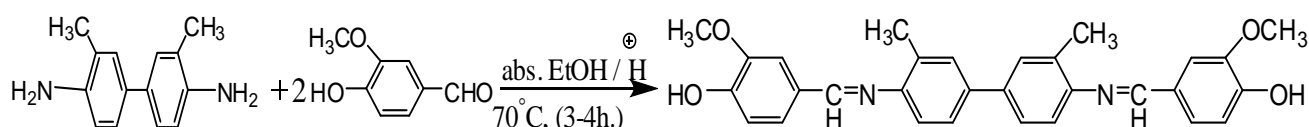
o-Tolidine (1.06g ,0.005mol) was dissolved in 20 mLethanolic solution with two drops of glacial acetic acid, after that equimolar amount 0.010 mol. of aromatic aldehyde (4-hydroxy,5-methoxybenzaldehyde) was added. The reaction mixture was refluxed with stirredfor 3-4 h. on a water bath at 70°C . TLC (Et₂O: *n*-hexane , 2:1) explained that the reaction was completed . The product was then allowed to cool down to room temperature and the colored precipitate was filtered , the product was recrystallized from ethanol.

3.2.Preparation of metal complexes

Ni(II),Cu(II) , Co(II),Mn(II),Cd(II),andZn(II)complexes were synthesis by the reaction of 2mole of corresponding metal (CuCl₂. 2H₂O,NiCl₂. 6H₂O,CoCl₂. 6H₂O, MnSO₄ .4H₂O,CdSO₄ .2H₂O, ZnSO₄ .7H₂O,) dissolved in amount of water ,with a 2mole of the ligand with constant stirring and hot ethanol solution. The mixture was refluxedfor 5 h. at 65°C.The precipitated solids were filtered ,washed with hot ethanol followed by drying at 40°Cover 6 h.

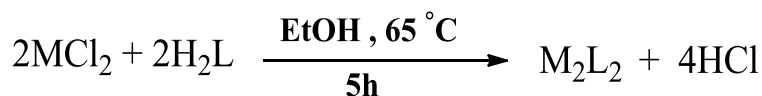
4- Results and Discussions :-

Synthesis of the ligand is explained in scheme 1.



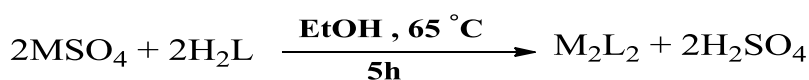
Scheme 1- Synthesis of ligand.

The Reaction of (-,Ni-, and Co chloride) withbisimineligand **H₂L** in **2:2** molar Ratio are represented in scheme 2.



Scheme 2-Reaction of (Ni,Cu- and Cochloride) with bisimine ligand.

The Reaction of (Mn-,Cd-and Zn sulphate) with bisimine ligand H_2L in 2:2 molar Ratio are represented in scheme 3.



Scheme 3. Reaction of (Cd-,Mn-and Zn sulphate) with bisimine ligand.

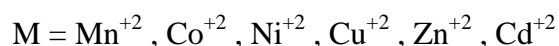
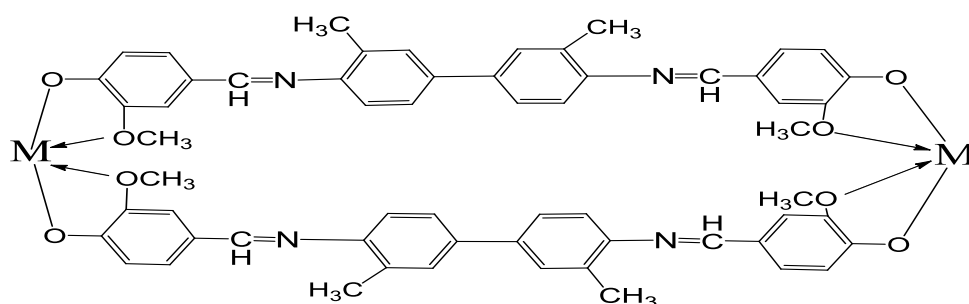


Figure 1. Structural representation of the Schiff base complexes (M_2L_2)

The complexes are insoluble in water, soluble in hot ethanol and methanol, highly soluble in DMF and DMSO, and colored solids. The physical properties of the bisimine and their complexes listed in table 1.

Table 1- The physical properties of the bisimine and its complexes

Com.	M.F.	M.Wt. g/mol	M.P. ^o C	μ_{eff} B.M	Color	Yield %
H_2L	$C_{30}H_{28}N_2O_4$	480.55	186-188	-	Yellow	86
$[Mn_2L_2]$	$C_{60}H_{52}Mn_2N_4O_8$	1176.95	192-194	diamagnetic	Light yellow	64
$[Co_2L_2]$	$C_{60}H_{52}Co_2N_4O_8$	1334.58	215-217	3.68	Dark brown	76
$[Ni_2L_2]$	$C_{60}H_{52}Ni_2N_4O_8$	1191.88	197-198	2.82	Green	69
$[Cu_2L_2]$	$C_{60}H_{52}Cu_2N_4O_8$	1353.08	219-221dec	1.69	Violet	72
$[Zn_2L_2]$	$C_{60}H_{52}Zn_2N_4O_8$	1218.62	193-195	diamagnetic	Light brown	65
$[Cd_2L_2]$	$C_{60}H_{52}Cd_2N_4O_8$	1405.99	180-182	diamagnetic	Orange	57

Infrared spectra

FT-IR spectrum, figure (2) of synthesized bisimine derivative [H₂L] illustrates good argument that the condensation reaction take place successfully by pass away the sharp and meduim bands at (3468,3410) cm⁻¹and (3373,3338) cm⁻¹which belongs to the asymmetric and symmetric stretching vibrations of the two amino (-NH₂) groups in *o*-tolidine,also pass away the sharp and strong band at 1624cm⁻¹ due to the scissoring bending vibration of (-NH₂) groups and appearing strong band at lower frequency at 1626 cm⁻¹ assigned to the stretching vibration of (C=N) group. FT-IR spectra, figures (2) - (6) of synthesized complexes showed the phenolic C-O and etheric C-O-C stretching vibrations appeared under a shift towards decreasing frequencies as shown in table 2 .This shift appearing the sharing of oxygen atom in the C-O-M bond in complexes of H₂L , azomethine groups are shifted by (1582-1593) cm⁻¹ to lower frequency.

Table 2- F.T. I.R Spectral data of imine and its complexes.

Comp.	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{H})$ aromatic ring	$\nu(\text{C}-\text{H})$ aliphatic	ν (phenolic C-O)	$\nu(\text{C}-\text{O}-\text{C})$ etheric	ν (M-O) Etheric	ν (M-O) phenolic	Others
H ₂ L	1626	3028	2885	1219	1136	-	-	$\nu(\text{O}-\text{H})$ 3421
[Mn ₂ L ₂]	1591	3133	2866	1271	1033	621	734	-
[Co ₂ L ₂]	1587	3137	2936	1253	1025	640	784	-
[Ni ₂ L ₂]	1582	3182	2940	1355	1032	614	778	-
[Cu ₂ L ₂]	1586	3284	2971	1282	1029	625	729	-
[Zn ₂ L ₂]	1592	3250	2856- 2937	1271	1031	557	615	-
[Cd ₂ L ₂]	1593	3155	2945	1271	1037	613	779	-

¹H NMR Spectra:-

The ¹H NMR spectra of the compounds were gained in DMSO- d₆ at room temperature by using TMS as an subjective standard. The chemical shift observed for the OH protons in ligand (12.1 ppm) was disappearing in the complexes. This proved the bonding of oxygen to the metal ions (C-O-M). The same conclusion was confirmed by the F.T.I.R spectra.

The appearance of a sharp singlet for the ($-\overset{\ominus}{\text{C}}=\text{N}$) proton in H₂L (8.9 ppm) obviously point that the magnetic environment is equal for all such protons, The multiplets of of aromatic ring protons showed within the range (6.9 – 8.3 ppm) and they were shiftedby chelation. In ligand and complexes, the proton of(-CH₂) at (2.3 – 2.6 ppm) was not influenced by chelation.

Table 3-¹H NMR spectra of the imine and its complexes in (δ , ppm).

Comp.	OH	Aromatic. H	Aliphatic. H	HC=N	O—CH ₃
[H ₂ L]	12.1	6.9 - 8.3	2.3	8.9	3.8
[Co ₂ L ₂]	-	6.2 - 7.4	2.3	8.2	3.5
[Ni ₂ L ₂]	-	7.4 - 7.5	2.2 – 2.6	8.7	3.6 – 3.7
[Cu ₂ L ₂]	-	6.7 – 7.9	2.2 – 2.6	8.4	3.3
[Cd ₂ L ₂]	-	7.4 – 7.5	2.3	8.1	3.7

The electronic spectra:-

The electronic spectral data of the imine and its complexes are outlined in Table 4. the spectrum of the imine H₂L exhibit 2 major peaks: at (320-355, and 370.0) nm. The first peaks were assigned to benzene ring and imino group (π-π*) transitions. The first band of (Mn₂L₂, Co₂L₂, Ni₂L₂, Cu₂L₂, Zn₂L₂ and Cd₂L₂) were shifted to a shorter wavelength at(315, 325, 323, 328,330 ,318)nm ,respectively. along with an augmentation in its intensity.

The second band in the spectrum of H₂L (380 nm) attributed to (n - π*)transition. The second band of (Mn₂ L₂, Co₂L₂, Ni₂L₂, Cu₂L₂, Zn₂L₂ and Cd₂L₂) were shifted to a longer wavelength at(410, 515, 460, 490, 360, 400)nm, respectively. with an increase in its intensity. This shift may be belong to the donation of the lone pairs of the oxygen atom of the ligand H₂L to the metal ion (o → M).⁽²²⁾

Table 4. The electronic spectral data of the imine and its compounds.

compound	λ _{max} nm	λ _{max} cm ⁻¹	ε L / mol.cm
H ₂ L	320-355	31250-28169	3300
H ₂ L	370	27027	2400
[Mn ₂ L ₂]	315	31746	4900
[Mn ₂ L ₂]	410	24390	3600
[Co ₂ L ₂]	325	30769	3100
[Co ₂ L ₂]	515	19417	322
[Ni ₂ L ₂]	323	30959	3050
[Ni ₂ L ₂]	460	21739	340
[Cu ₂ L ₂]	328	30487	3100
[Cu ₂ L ₂]	490	20408	350
[Zn ₂ L ₂]	330	30303	3700
[Zn ₂ L ₂]	360	27777	3400
[Cd ₂ L ₂]	318	31446	3550
[Cd ₂ L ₂]	400	25000	3460

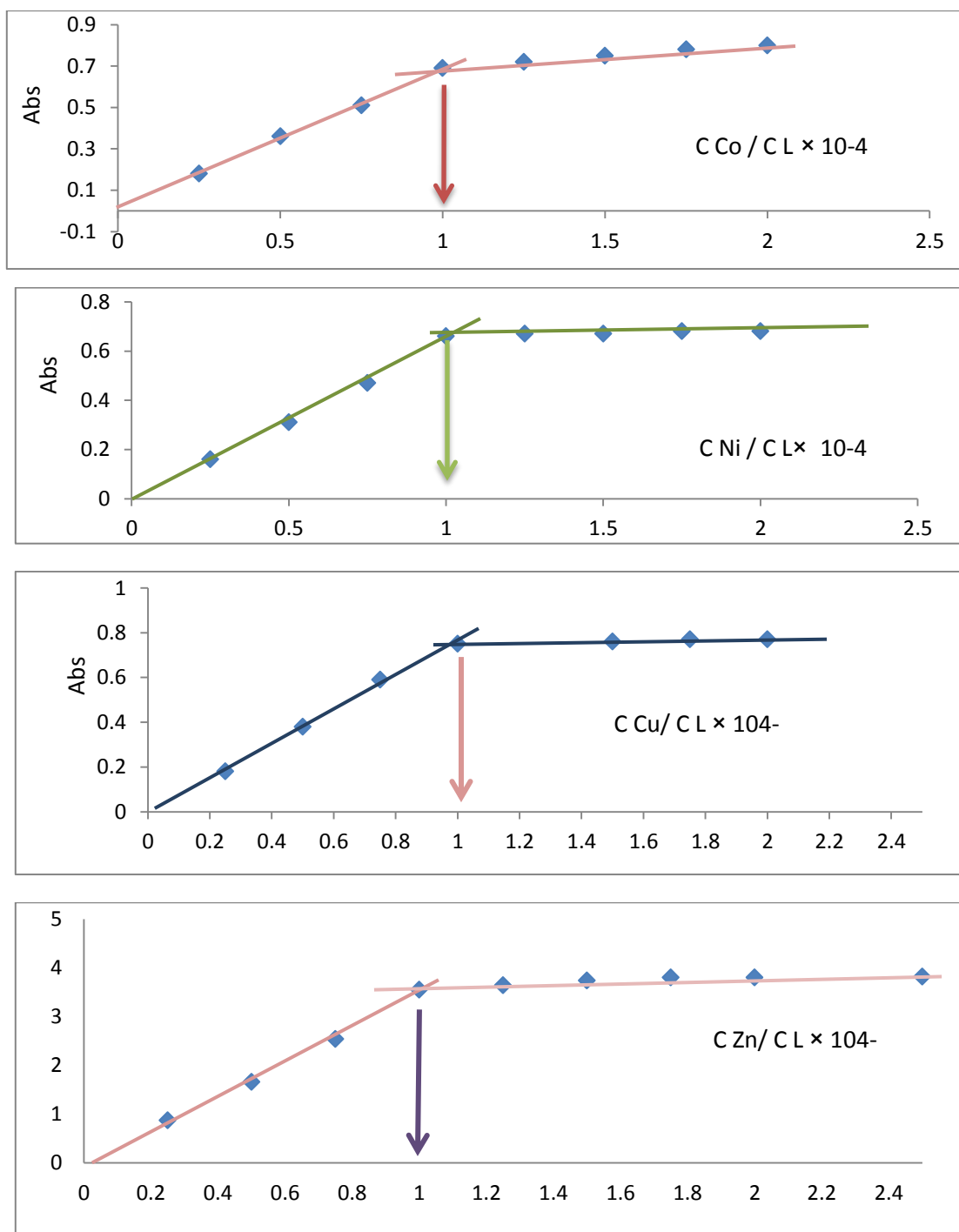
Table 5-Micro Analytic (CHN) data.

compound	C%		H%		N%	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
H ₂ L	75.98	75.96	15.89	15.85	5.84	5.80
[Mn ₂ L ₂]	67.59	67.56	4.95	4.91	5.37	5.35
[Co ₂ L ₂]	67.07	67.04	4.89	4.87	5.34	5.31
[Ni ₂ L ₂]	67.12	67.07	4.92	4.89	5.26	5.21
[Cu ₂ L ₂]	66.51	66.47	4.86	4.82	5.18	5.16
[Zn ₂ L ₂]	66.28	66.25	4.84	4.82	5.16	5.14
[Cd ₂ L ₂]	60.98	60.95	4.46	4.43	4.75	4.74

Table 6- Molar Conductivity Measurements in DMSO-d₆

compound	Conductivity $\text{cohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$
[Mn ₂ L ₂]	71.3
[Co ₂ L ₂]	5.7
[Ni ₂ L ₂]	75.2
[Cu ₂ L ₂]	3.4
[Zn ₂ L ₂]	74.5
[Cd ₂ L ₂]	72.5

Figure 2. The ligand with M = Co⁺², Ni⁺², Cu⁺², Zn⁺² 2:2 molar Ratio



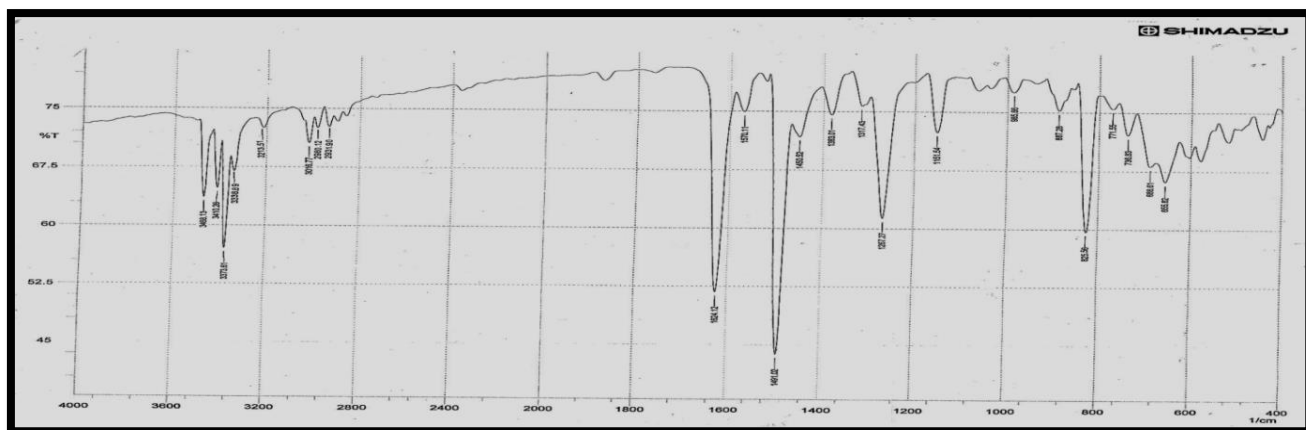


Figure 1:- F.T.I.R spectrum of *O*- Tolidine

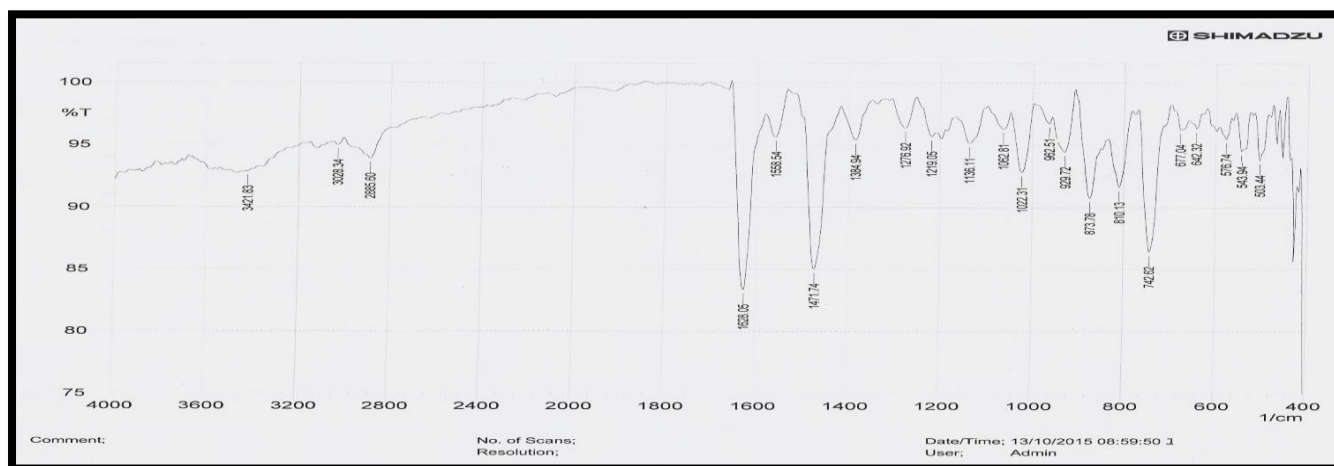


Figure2:- F.T.I.R spectrum of compound [H₂L]

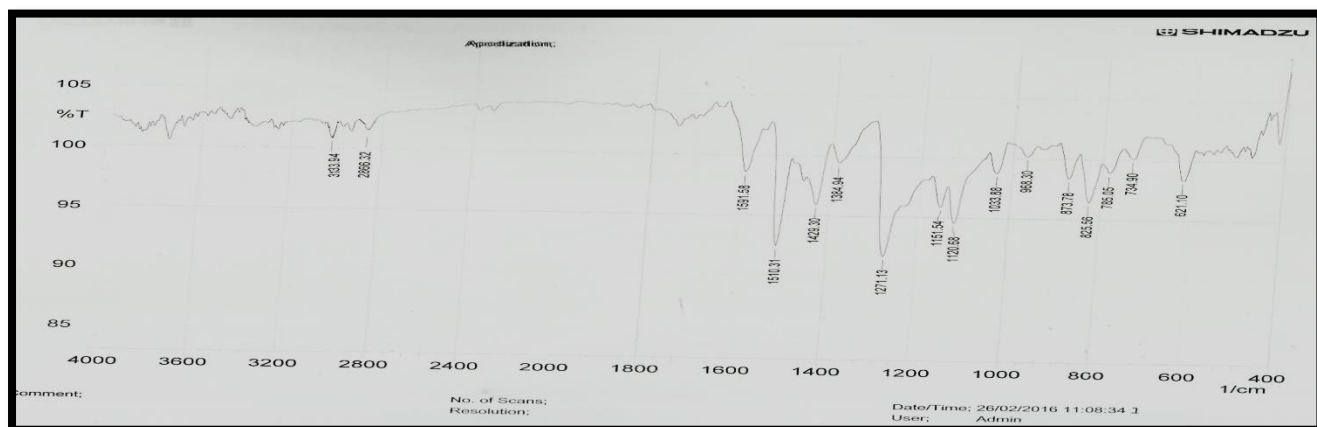


Figure3:- F.T.I.R. spectrum of compound [Mn₂L₂]

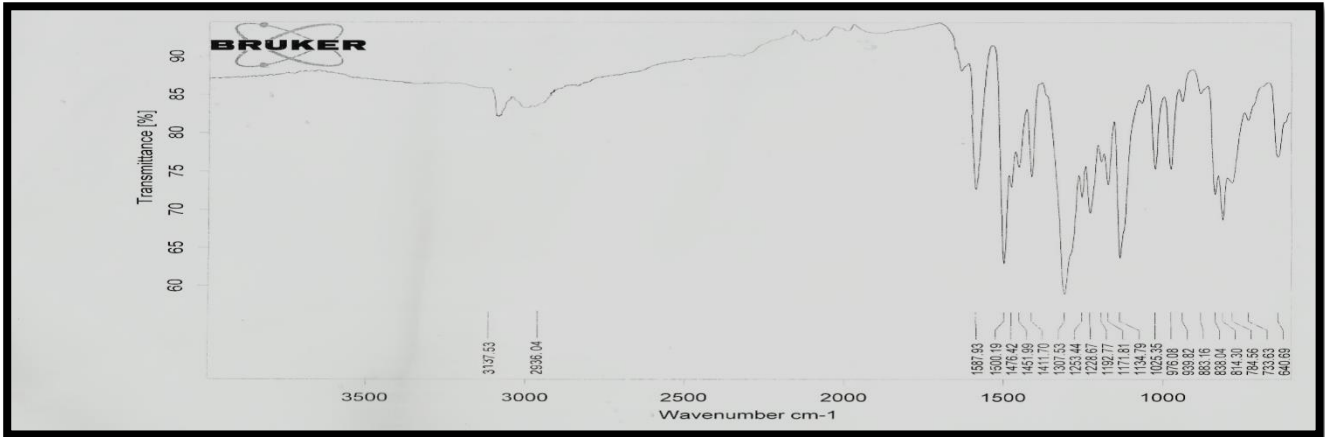


Figure4:- F.T.I.R spectrum of compound $[Co_2L_2]$

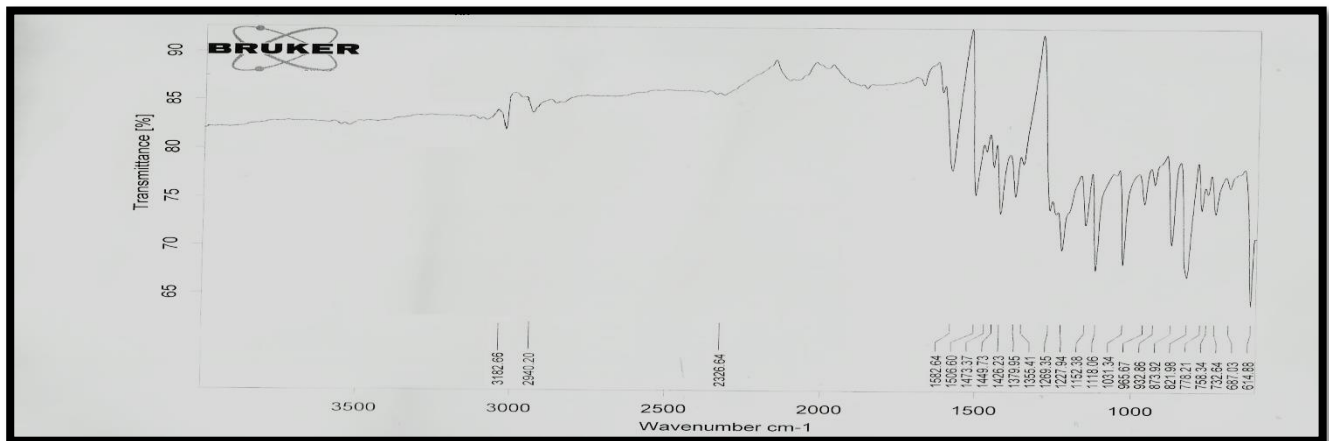


Figure5:-F.T.I.R spectrum of compound $[Ni_2L_2]$

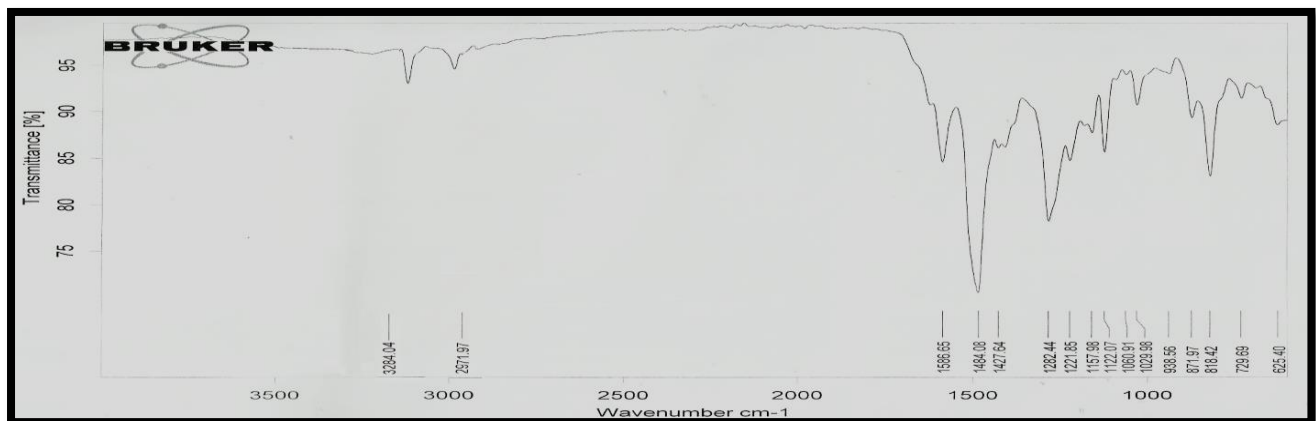


Figure6:-F.T.I.R spectrum of compound $[Cu_2L_2]$

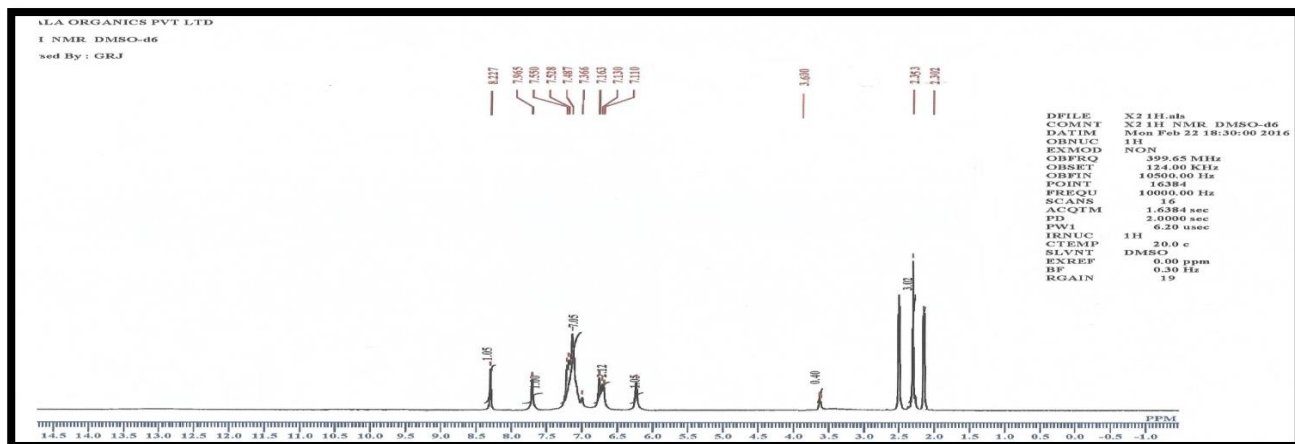


Figure 10:- ¹H NMR spectrum of compound [Co₂L₂]

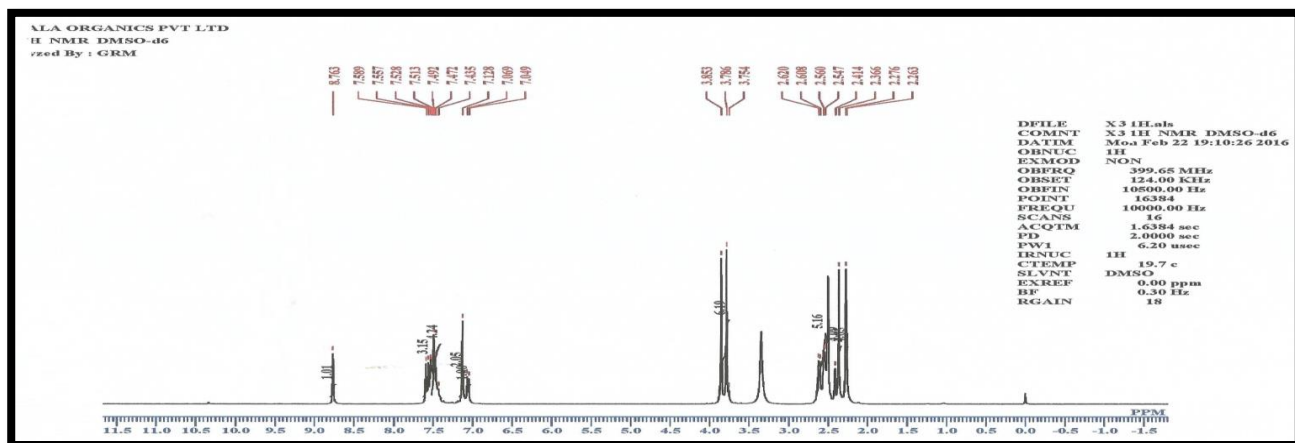


Figure 11:- ¹H NMR spectrum of compound [Ni₂L₂]

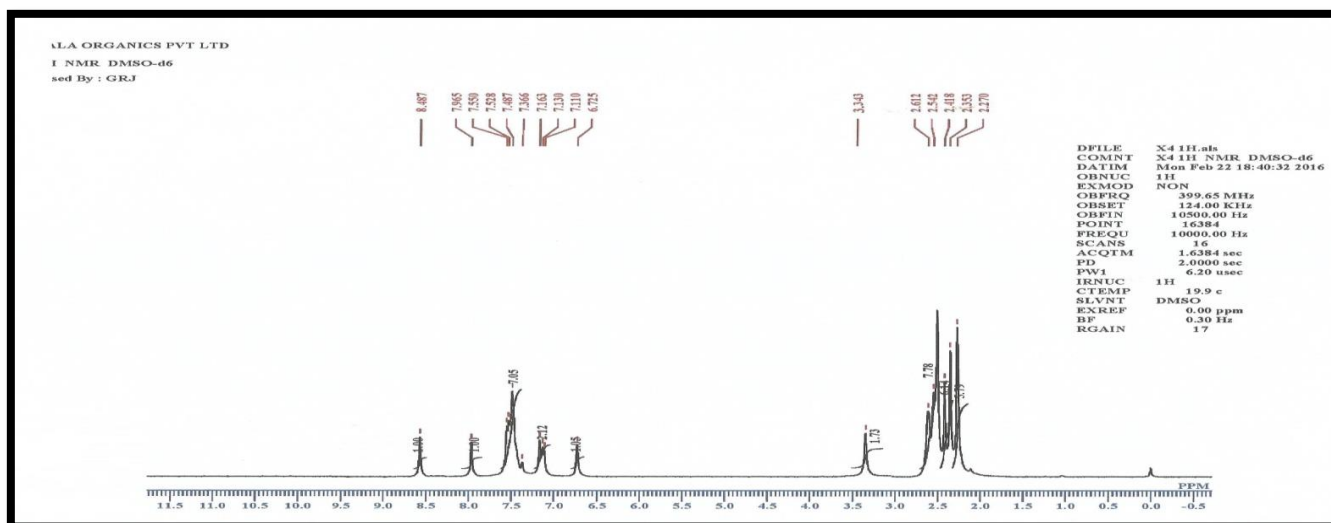


Figure 12:- ¹H NMR spectrum of compound [Cu₂L₂]

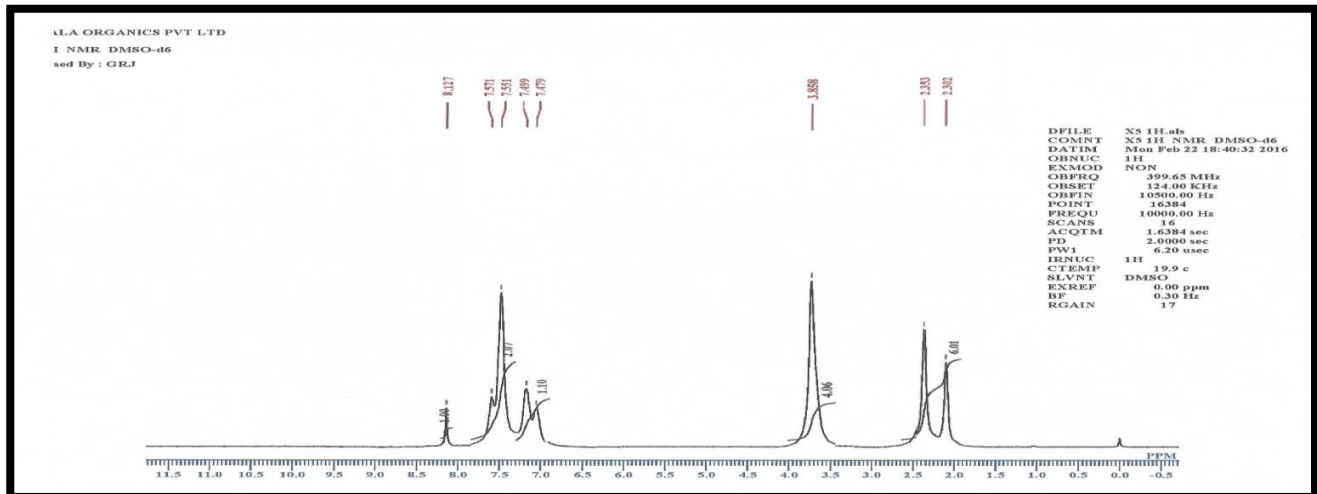


Figure 13:- ^1H NMR spectrum of compound $[\text{Cd}_2\text{L}_2]$

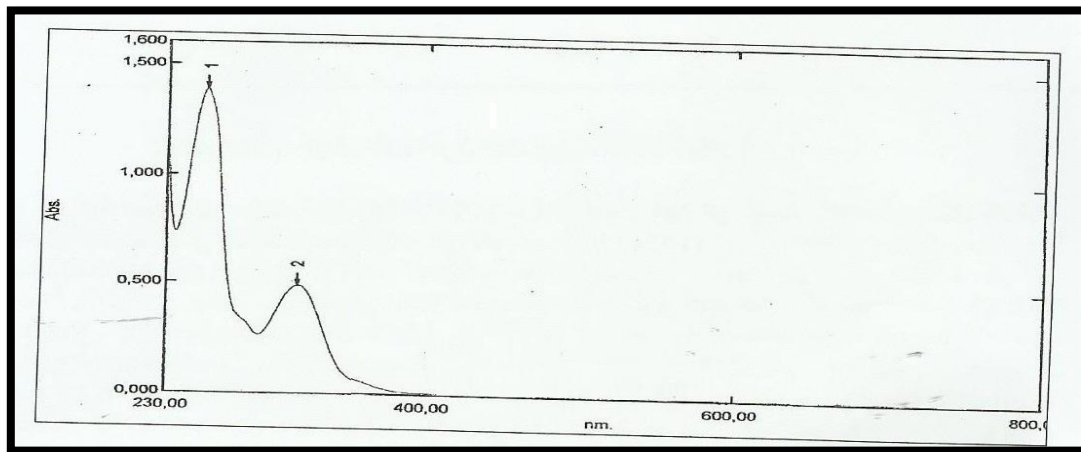


Figure 14:- UV –Vis spectrum of ligand (H_2L)

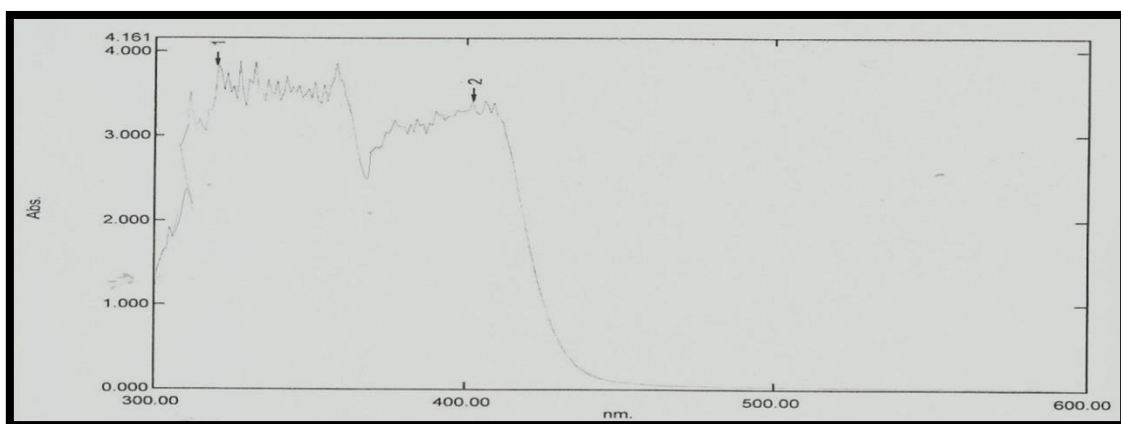


Figure 15:- UV –Vis spectrum of Complexes $[\text{Zn}_2\text{L}_2]$ 5

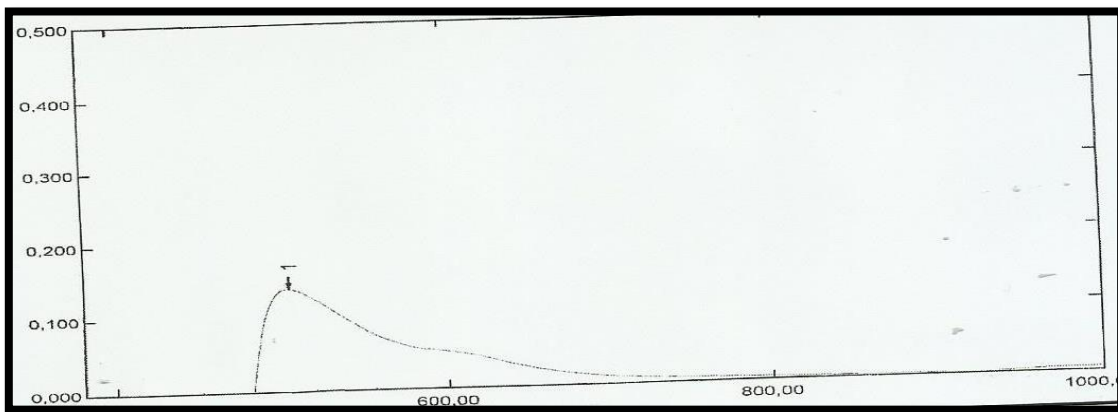


Figure16:- UV –Vis spectrum of Complexes[Co₂L₂]

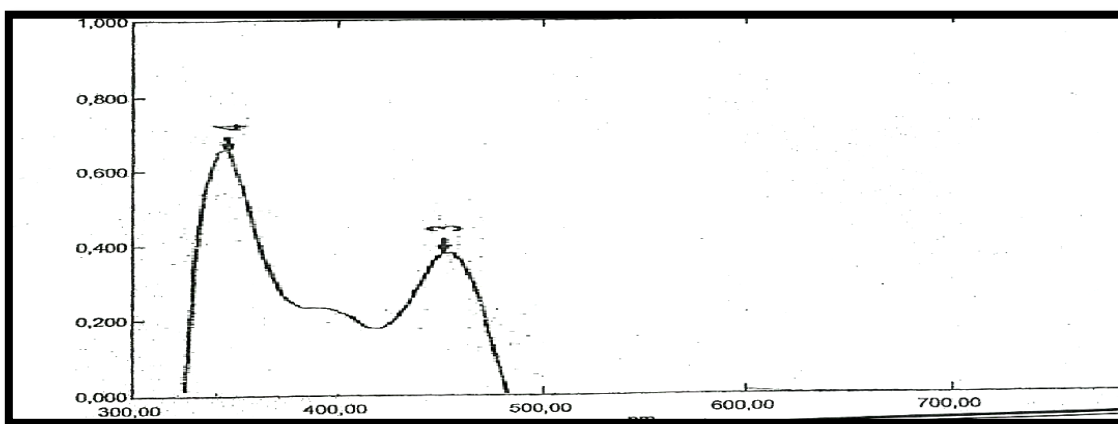


Figure 17:- UV –Vis spectrum of Complexes[Ni₂L₂]

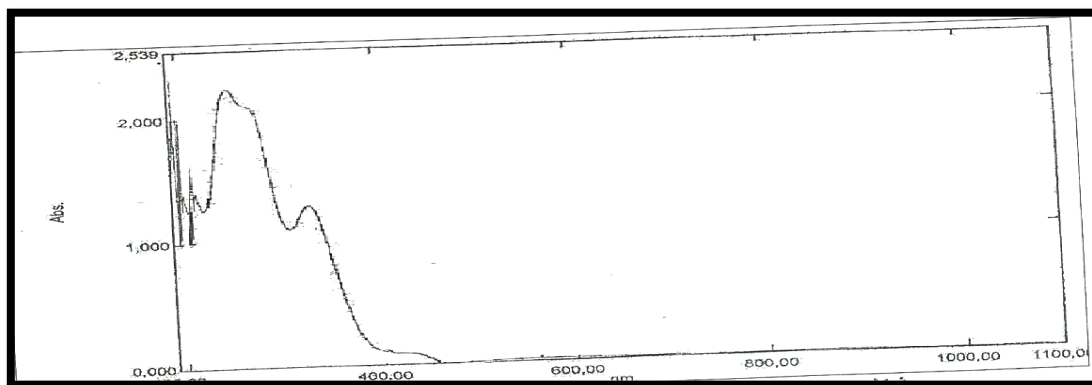


Figure18:- UV –Vis spectrum of Complexes[Cu₂L₂]

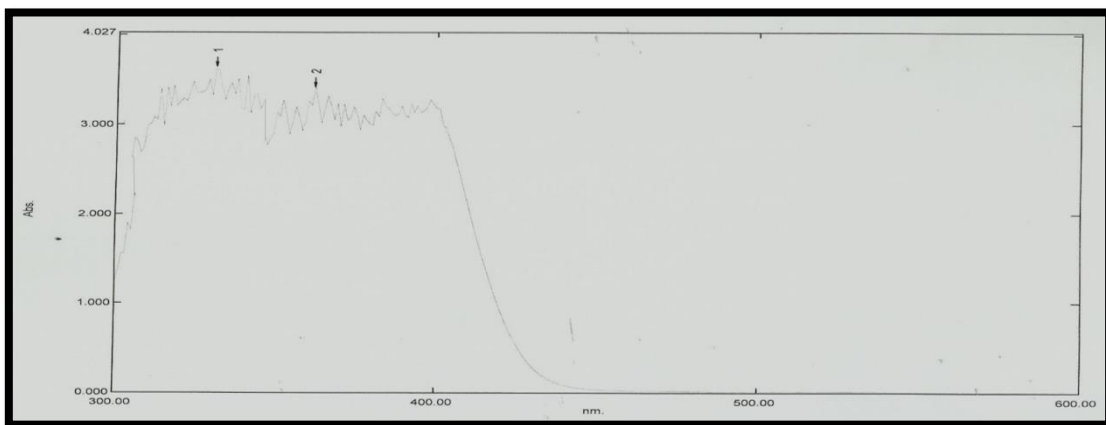


Figure19:- UV –Vis spectrum of Complexes $[Zn_2L_2]$

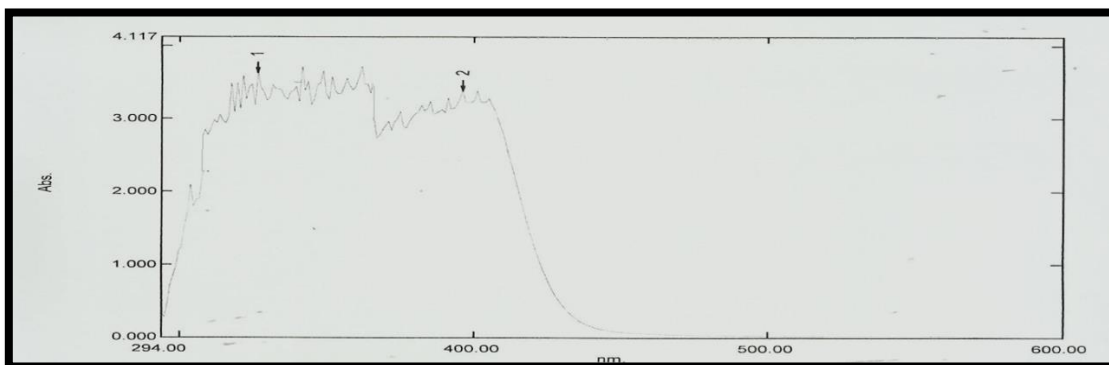


Figure20:- UV –Vis spectrum of Complexes $[Cd_2L_2]$

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