

## **Synthesis and Characterization of Novel Macrocyclic ligand and its complexes with (Co<sup>(II)</sup>, Ni<sup>(II)</sup>, Cu<sup>(II)</sup>, Zn<sup>(II)</sup>, and Cd<sup>(II)</sup>) ions.**

Ahmad Thabet Numan, Enaàm Ismail Yousif and Mazin Saleh Breesam  
Department of chemistry, College of Education, Ibn Al-Haitham, University of Baghdad,  
P.O. 4150, Adhamiyah , Baghdad ,Iraq .

### **Abstract:**

A new Macrocyclic Schiff base ligand Bis[4-hydroxy(1,2-ethylene-dioxidebenzylidene) pheylenediamine] [H<sub>2</sub>L] and its complexes with (Co<sup>(II)</sup>, Ni<sup>(II)</sup>, Cu<sup>(II)</sup>, Zn<sup>(II)</sup> and Cd<sup>(II)</sup>) are reported . The ligand was prepared in two steps, in the first step a solution of (o-phenylene diamine) in methanol react under reflux with (2,4-dihydroxybenzylaldehyd) to give an (intermediate compound) [Bis-1,2 (2,4-dihydroxybenzylidene) pheylenediamine] which react in the second step with (1,2- dichloro ethane) giving the mentioned ligand. Then the complexes were synthesis of adding of corresponding metal salts to the solution of the ligand in methanol under reflux with 1:1 metal to ligand ratio. On the basis of, molar conductance, I.R., UV-Vis, chloride content and atomic absorption the complexes may be formulated as [M(H<sub>2</sub>L)] [M<sup>II</sup>=Co, Ni, Cu, Zn and Cd] . The data of these measurements suggest a tetrahedral geometry to Co<sup>(II)</sup>, Cu<sup>(II)</sup>, Zn<sup>(II)</sup>, and Cd<sup>(II)</sup> complexes and a square planar to Ni<sup>(II)</sup> .

### **الخلاصة :**

تضمن البحث تحضير الليكند الجديد [Bis[4-hydroxy(1,2-ethylene-dioxidebenzylidene) pheylenediamine] بخطوتين: (2,4-dihydroxybenzylaldehyd) مع (o-phenylene diamine) الخطوة الاولى مفاعلة [Bis-1,2 (2,4-dihydroxybenzylidene) pheylenediamine] وتكوين (1,2- dichloro ethane) مع [Bis-1,2 (2,4-dihydroxybenzylidene) pheylenediamine] والثانية مفاعلة [Bis[4-hydroxy(1,2-ethylene-dioxidebenzylidene) pheylenediamine] وتكوين الليكند الحلقي الجديد ثم مفاعله مع بعض العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (1:1) حيث تكونت معقدات جديدة ذوات الصيغ العامة: [M(H<sub>2</sub>L)]Cl<sub>2</sub> حيث: M<sup>(II)</sup> = Co, Ni, Cu, Zn and Cd شخصت جميع المركبات بالطرق الطيفية التالية الأشعة تحت الحمراء, الأشعة فوق البنفسجية – المرئية, مطيافية الامتصاص الذري للعناصر وتم تعيين محتوى الكلور ودرجات الانصهار , مع قياس التوصيلية المولارية الكهربائية . من النتائج أعلاه كان الشكل الفراغي المقترح لمعقد النيكل مربع مستوى بينما تتخذ معقدات الكوبلت والنحاس والكارصين والكاديوم شكل رباعي السطوح.

### **Introduction:**

Schiff base have been widely used as bidentate ligands in the field of coordination chemistry(1-5). The Schiff base complexes are used in catalytic reaction (6) and as models for biological systems (7,8). Many Schiff base ligands with a variety of donor sets , such as (N,O) , (N,S) and (N,P) and their transition metal complexes were reported (9,10). Also Schiff base ligands are well known to have pronounced biological activities(11). These activities are attributed to the formation of stable chelates with transition metals present in human cell. In 2007 Khandar and Co-worker (12) , prepared a macrocyclic Schiff ligand kind (N<sub>2</sub>O<sub>4</sub>) (L=8,9,18,19- tetra hydro 7H,17H-dibenzol [F,O][1,5,9,13] dioxadiazacyclohexadecine – 8,18-diol) and its complexes with NiX<sub>2</sub>.6H<sub>2</sub>O , X=Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> ) salts . which were characterized by [I.R, UV-Vis, elemental analysis and conductance measurement. In 2005 Halabi and Co-worker(13) prepared a schiff base ligand derived kind (N<sub>2</sub>O<sub>2</sub>) from amino – 1,2,3,6 – oxatrizain and salicylaldehyd and its transition metal complexes with (Ni<sup>(II)</sup>, Cu<sup>(II)</sup>, and Pd<sup>(II)</sup>). In this

paper the synthesis and characterized of new Macrocyclic ligand Bis[4-hydroxy(1,2-ethylene-dioxidebenzylidene) pheylenediamine] [ $H_2L$ ] and its complexes with ( $Co^{(II)}$ ,  $Ni^{(II)}$ ,  $Cu^{(II)}$ ,  $Zn^{(II)}$ , and  $Cd^{(II)}$ ) metal ions . To prepare the ligand, the solution of o-phenylene diamine in methanol was mixed with 2,4-dihydroxybenzylaldehyd (1:2) then the resultant of reaction (intermediate compound) was added to 1,2- dichloro ethane to give the mentioned ligand.

### **Experimental:**

Reagents were purchased from Fluka and Rediel – Dehenge Chemical Co. I.R spectra were recorded as (KBr) disc using a Shimadzu 8400 FTIR spectrophotometer in the range (4000-450)  $cm^{-1}$ . Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for  $10^{-3}M$  solution in (DMSO) at  $25^{\circ}C$  using a Shimadzu 160 spectrophotometer with  $1.000\pm 0.001 cm^{-1}$  matched quartz cell . Metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu A.A 680G atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded at  $25^{\circ}C$  for  $10^{-3}M$  solutions in (DMSO) as a solvent using a PW 9526 digital conductivity meter.

### **Synthesis of the ligand ( $H_2L$ ):**

**Step (1):** Preparation of the [Bis-1,2 (2,4-dihydroxybenzylediene) pheylenediamine][ $H_4L$ ] (intermediate compound). A solution of o-phenylene diamine (0.4 g, 3.703 mmole) in methanol (5ml) was added to (2,4-dihydroxybenzaldehyde) (0.78 g, 3.703 mmole) dissolving in methanol (5ml), and then (2-4 )drops of glacial acetic acid was added slowly to the reaction mixture .The mixture was refluxed for (5hrs), and allowed to dry at room temperature for (24) hours. A orange solid was obtained. Yield (85%), (1.1) g, m.p (198) $dec^{\circ}C$ .

**Step(2):**Preparation of the ligand Bis[4-hydroxy(1,2-ethylene-dioxidebenzylidene) pheylenediamine][ $H_2L$ ].A Solution of [Bis-1,2(2,4dihydroxybenzylediene) phylenediamine] (0.4g, 1.149mmole)in methanol (5ml) with (0.06g1.149mmole) KOH in methanol was added to 1,2-dichloro ethane (0.26g, 0.11g1.149mmole) in methanol .The reaction mixture was refluxed for (5hrs) with stirring , filtered and dried at room temperature for (24) hours. A brown solid was obtained .Yield (92%), (0.39)g, m.p(165) $dec^{\circ}C$ .

### **Synthesis of ( $H_2L$ ) complexes .**

#### **1-Synthesis of [ $Co (H_2L) ] Cl_2$ (1).**

A solution of ( $H_2L$ ) (0.1g, 0.267mmole) in methanol (5ml) was added to a stirred solution of  $CoCl_2.6H_2O$  (0.06g, 0.267mmole) in methanol (5ml). The resulted mixture was heated under reflux for (2 hrs). Then the mixture was filtered and the precipitate was washed with an excess of methanol and was dried at room temperature for (24 hrs). A deep brown solid which decompose ( $275^{\circ}C$ ) was obtained. Yield (84%), (0.11g).

#### **Synthesis of [ $Ni (H_2L) ] Cl_2$ (2), [ $Cu (H_2L) ] Cl_2$ (3) , [ $Zn (H_2L) ] Cl_2$ (4)and[ $Cd (H_2L) ] Cl_2$ (5) Complexes.**

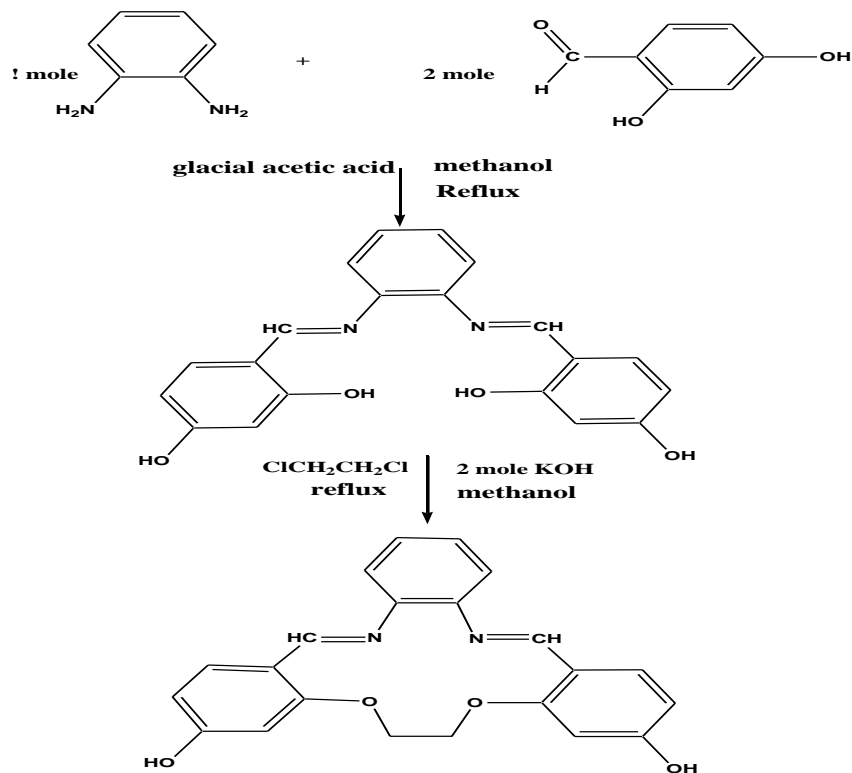
The method used to prepare these complexes was similar to that mentioned in the case preparation [ $Co (H_2L) ] Cl_2$  complex. Table (1) shows the stated weight of starting materials, % yield and some physical properties of the prepared complexes.

**Table (1) some physical properties of the complexes and their reactants quantities .**

Compound	decomposition temperature °C	Colour	Weight of metal chloride		Weight of product (g)	Yield %	chloride content	Metal ion % (Prac.) (Theo.)
			g	mmole				
[Co (H <sub>2</sub> L) Cl <sub>2</sub> ]	275	blue green	0.06	0.267	0.11	84	Nil	12.89 (11.69)
[Ni (H <sub>2</sub> L) Cl <sub>2</sub> ]	220	Yellow green	0.06	0.267	0.1	76	Nil	12.13 (11.65)
[Cu (H <sub>2</sub> L) Cl <sub>2</sub> ]	288	Yellow brown	0.04	0.267	0.12	88	Nil	13.74 (12.49)
[Zn (H <sub>2</sub> L) Cl <sub>2</sub> ]	248	Yellow White	0.03	0.267	0.13	95	Nil	11.04 (12.81)
[Cd (H <sub>2</sub> L) Cl <sub>2</sub> ]	292	Mustard	0.06	0.267	0.13	92	Nil	21.64 (20.16)

**Results and discussion**

The [H<sub>2</sub>L] pro-ligand was prepared according to the general method shown in Scheme (1).The(I.R) spectrum for [H<sub>2</sub>L] Fig (2-1) , display band at (3203)cm<sup>-1</sup> due to the ν(O-H) stretching of the hydroxyl groups phenol (14,15). The band at (1693) cm<sup>-1</sup> is attributed to the ν(H-C=N) stretching frequency for the imine group(16). The band at (1203) cm<sup>-1</sup> is attributed to ν (C-O-C) stretching vibration. (U.V-Vis) spectrum of the ligand Fig (3) showed three high intense absorption peaks at (275 nm ), (36363cm<sup>-1</sup>) ( ε<sub>max</sub> = 1549 molar<sup>-1</sup>.cm<sup>-1</sup>), (345 nm ( 28985 cm<sup>-1</sup>) (ε<sub>max</sub> = 1441 molar<sup>-1</sup>.cm<sup>-1</sup>) and (397) nm ( 25188cm<sup>-1</sup>) (ε<sub>max</sub> 1434 molar<sup>-1</sup>.cm<sup>-1</sup>) which assigned to overlap of (π →π\*), (n →π\*) and (n →π\*) transitions(17).

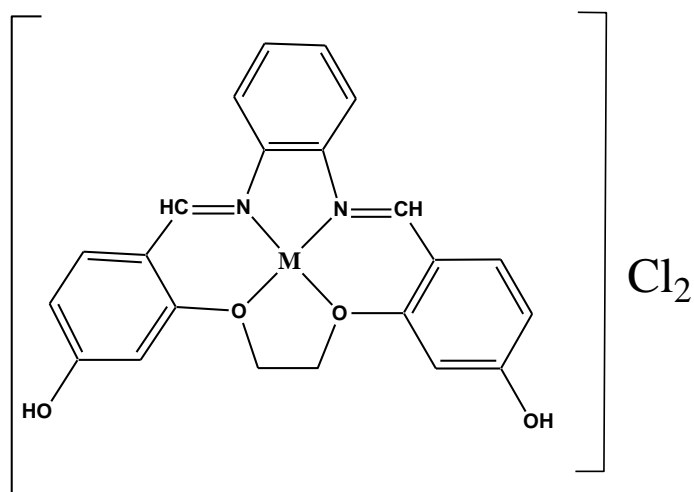


Scheme (1) The synthesis route of the ligand

The complexes were prepared by the reaction of ligand [H<sub>2</sub>L] with Co<sup>(II)</sup>, Ni<sup>(II)</sup>, Cu<sup>(II)</sup>, Zn<sup>(II)</sup>, and Cd<sup>(II)</sup> in methanol solution under reflux. These complexes are stable in this solution. The analytical and physical data listed in table (1). The higher decomposition point of complexes in comparison with free ligand suggests the thermal stability of complexes which increases with increasing of electronegativity of metal in the period (Co, Ni, and Cu) and in the group (Zn, Cd)(18). The I.R spectra are shown in table (2). The shifting of  $\nu$  (H-C=N) band to lower frequency in the complexes is due to the of bond order , as a result of delocalization of metal ion electron density to the ligand(19,20), indicating the coordination through the nitrogen atom . The appearance of the bands at 642-545 cm<sup>-1</sup> and 465-410 cm<sup>-1</sup> are due to  $\nu$ (M-N) and  $\nu$ (M-O) stretching respectively (21-23). Fig( 2-1) and (2-2) represent the I.R spectra for the complexes . The molar conductance data of the complexes in DMSO (10<sup>-3</sup>M) found in the range(72-81)  $\Lambda$ m ( $\Omega^1$ .cm<sup>2</sup>.Mole<sup>-1</sup>) (Table -3) which indicates that the complexes are electrolyte(1:2) ratio (24) (table 3) . (U.V-Vis.) spectra of complexes display absorption bands at the range (259-383) nm, which assigned to the ligand field and charge transfer transition (25). In the Co<sup>II</sup> complex the band at 625 nm is attributed to d-d electronic transition of type (<sup>4</sup>T<sub>1(p)</sub> ← <sup>4</sup>A<sub>2</sub>). The band present in Ni<sup>II</sup> complex at 754nm corresponding to (<sup>1</sup>A<sub>2g</sub> ← <sup>1</sup>A<sub>1g</sub>) (fig.3-1)(26). In the Cu<sup>II</sup> complex the band at 825 nm may be assigned to (<sup>2</sup>T<sub>2</sub> ← <sup>2</sup>E). The absence of d-d transition in the complexes (4) and (5) are due to the configuration (d<sup>10</sup>) structure for the metal ions . The positions of the bands in (U.V-Vis.) spectra suggest a tetrahedral structure to Co<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and a square planar to Ni<sup>II</sup>. The analysis of the (A.A) and chloride content results for the complexes ([Co(H<sub>2</sub>L)]Cl<sub>2</sub>, [Ni(H<sub>2</sub>L)]Cl<sub>2</sub>, [Cu (H<sub>2</sub>L)]Cl<sub>2</sub>, [Zn (H<sub>2</sub>L)]Cl<sub>2</sub> and [Cd (H<sub>2</sub>L)]Cl<sub>2</sub>), table (1) are in a good agreement with the calculated values.

**References:**

- 1.
2. Sousa .C; Freire.C;and Decostro.B, ,Molecules, 8 , 894, 2002.
3. Singh.V.K; sinho.R;. Kant.R and sinha.B.K, Asian J. chem.. 10, 532,1998.
4. Yildirm.L.T, Atakd.O,Crystal. Res. Technol. 37, 1352 , 2002.
5. Pui.A, Croatica Chemica Acta, 75,165, 2002.
6. Garnovski.A.D , Nivorozhkin.A.L, Coord. Chem. Rev,126,1, 1993.
7. Hamiltan.D.E; Drago.R.S and Zombeck.A, 1987 J.AM. Chem . Soc. 159:374
8. Chen.D, Martel.A.E,Inory. Chem., 26, 1026 , 1987.
9. Costamagna.J; Vargas.J; Latorre.R ; Alvarado.A and G. mena, Coord. Chem.. Rev., 119,67, 1992.
10. Caseuato.V; Gerriero.P ; Tampurini.S and vigato.J.P.A, Inor., Chemic. Acta.,119,75, 1986.
11. Freybry.D.P ; Mockler.G.M and E.sinn, J. Chem. Soc. Daltontrans, 5,445, 1976.
12. Raoand.S, MittraS.A, J. Indian , Chem .Soc.,55,420, 1978.
13. Khandar.A.A and S.A.Hosseini – Yazdi, Polyhedron 26,P.33-38,2007.
14. EI-Halabi.M .N and Awadallah.M, Jouranal of the Islamic university of Gaza,(series of Natural studies and Engineering ) 13,No.2,P 85-90, 2005.
15. Nakamoto. K . “Inferared Spectra of Inorganic and coordination Compounds”. Willey,New York1963.
16. Lane, L. W.and Taylor, L.T.J,Coord.Chem., 2,295,1973.
17. Socrates.G, “Infrared Characteristic Group Frequencies” Ed . Wiley – Interscience Publication, 1980.
18. Kemp.W, “ Organic Spectroscopy ” 2<sup>nd</sup> .Ed., 144, 1987.
19. Huheey.L.E; Keiter.E and.Keiter.R.I, “Inorganic chemistry: principles of structure and reactivity” Harper Collins College, 1993.
20. Hadziand.D, Premru.L, Spectrochim . Acta ., 23A,35,1967 .
21. Abdul- Rahman.A.A,Ph D . Thesis , collage Abn Al - Haetham University of Baghdad, 2002 .
22. Nakamoto .K,“Infrared Spectra of Inorganic and Coordination Compounds ” 4<sup>th</sup>.Ed.,J.Wiely and Sons , New York, 1996 .
23. Ferraro.J,“Low Frquency Vibrations of Inorganic and Coordination Compounds ” Ed.Plenum,New York , 1971.
24. Nanjappan.P ;Ramalingam.K ; Jurisson.S ;Pirro.j ; Diroxo.R; Narra .R.K; Newotinik.D.Pand Nunn.A.D, Abstracts of papers , Ninth International Symposium on Radiopharmaceutical Chem, 1992 .
25. Geary.W.J,Coord .Rev., 7,81,1961.
26. Green Wood.N.N and A. Earnshow, “Chemistry of the Elements ” , Ed. J. Wiley and Sons Inc. New York, 1998.
27. Lever.A.B.L, “Inorganic Electronic Spectroscopy ” Ed. New York , 1968.



$M^{(II)} = Co, Ni, Cu, Zn \text{ and } Cd$

**Figure (1) the suggested structure for the complexes**

**Table (2) I.R spectral data of the ligand and it's complexes**

Compound	$\nu(\text{O-H})$ phenol	$\nu(\text{H-C-N})$	$\nu(\text{C-O-C})$	$\nu(\text{C-N})$	M-O M-N	Additional peaks
[H <sub>2</sub> L]	3203	1693	1203	1116	- -	$\nu(\text{C=C})$ ring 1510
[Co Cl <sub>2</sub> (H <sub>2</sub> L)]	3409	1631	1188	1126	435 640	$\nu(\text{C=C})$ ring 1508 $\nu(\text{C-H})$ alph 2962
[Ni Cl <sub>2</sub> (H <sub>2</sub> L)]	3397	1628	1195	1122	415 642	$\nu(\text{C=C})$ ring 1503 $\nu(\text{C-H})$ alph 2955
[Cu Cl <sub>2</sub> (H <sub>2</sub> L)]	3404	1625	1191	1124	459 624	$\nu(\text{C=C})$ ring 1500 $\nu(\text{C-H})$ alph 2965
[Zn Cl <sub>2</sub> (H <sub>2</sub> L)]	3385	1620	1199	1128	465 635	$\nu(\text{C=C})$ ring 1505 $\nu(\text{C-H})$ alph 2948
[Cd Cl <sub>2</sub> (H <sub>2</sub> L)]	3377	1626	1197	1120	410 545	$\nu(\text{C=C})$ ring 1506 $\nu(\text{C-H})$ alph 2952

**Table (3) : Electronic spectral data , and conductance measurement for the ligand[H<sub>2</sub>L] and it's complexes**

Compound	$\lambda$ nm	Wave number $\text{Cm}^{-1}$	$\epsilon_{\text{max}}$ Molar $\text{Cm}^{-1}$	Assignment	$\Delta m$ ( $\Omega^1 \cdot \text{cm}^2 \cdot \text{Mole}^{-1}$ )	Propose structure
[H <sub>2</sub> L]	275	36363	1549	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
	345	28985	1441			
	397	25188	1434			
[Co (H <sub>2</sub> L)] Cl <sub>2</sub>	297	33670	216	charge transfer ${}^4T_{1(p)} \leftarrow {}^4A_2$	72	tetrahedral
	343	29154	154			
	382	26178	874			
	625	16000	54			
[Ni (H <sub>2</sub> L)] Cl <sub>2</sub>	267	37453	1468	charge transfer ${}^1A_{2g} \leftarrow {}^1A_{1g}$	78	Square planar
	343	29154	2012			
	406	24630	1339			
	754	13262	58			
[Cu (H <sub>2</sub> L)] Cl <sub>2</sub>	259	38610	240	charge transfer ${}^2T_2 \leftarrow {}^2E_g$	69	tetrahedral
	376	26595	497			
	825	121212	94			
[Zn (H <sub>2</sub> L)] Cl <sub>2</sub>	290	34482	502	charge transfer	81	tetrahedral
	344	29069	2499			
[Cd (H <sub>2</sub> L)] Cl <sub>2</sub>	283	35461	465	Charge transfer	75	tetrahedral
	383	26109	730			

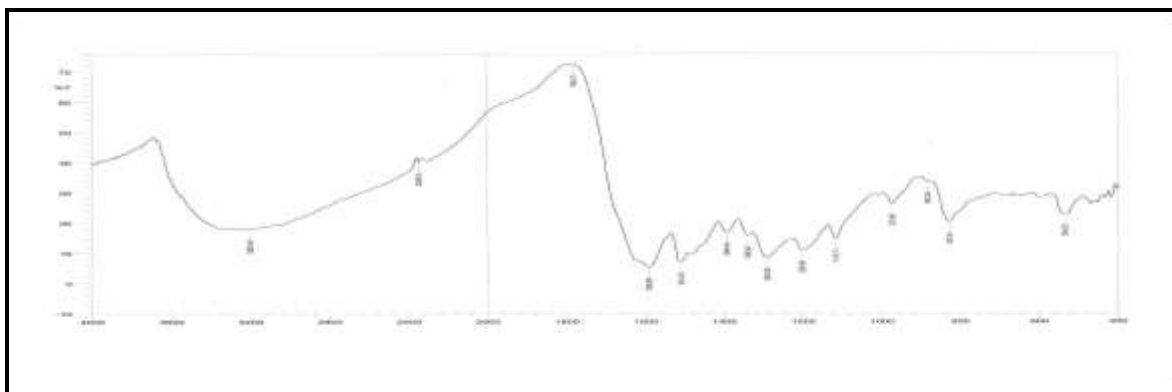


Fig (2) .The I.R. Spectrum of the ligand [H<sub>2</sub>L]

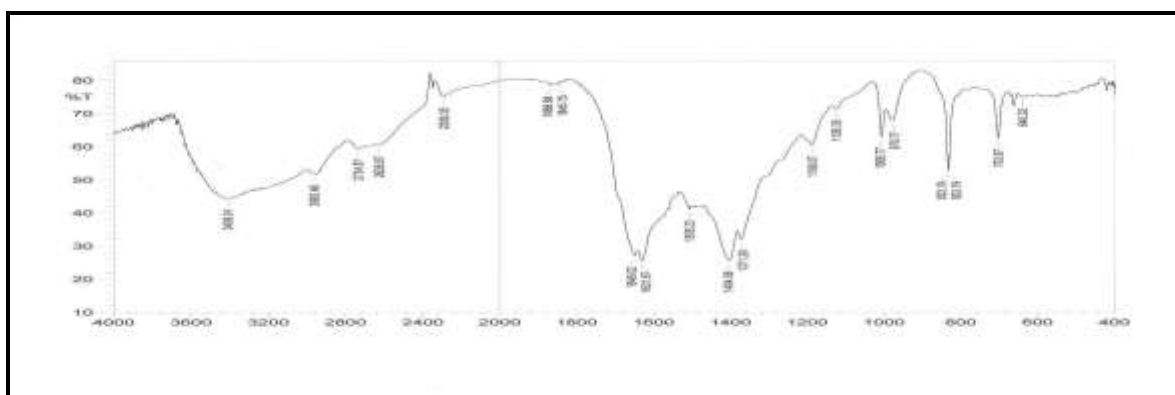


Fig (2-1) .The I.R. Spectrum of the [Co (H<sub>2</sub>L)] Cl<sub>2</sub>

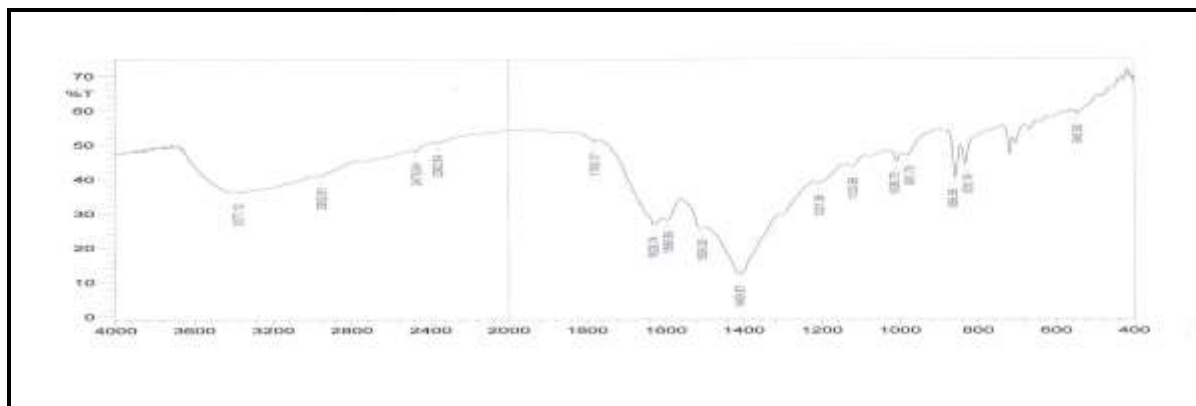


Fig (2-2) .The I.R. Spectrum of the [Cd (H<sub>2</sub>L)] Cl<sub>2</sub>



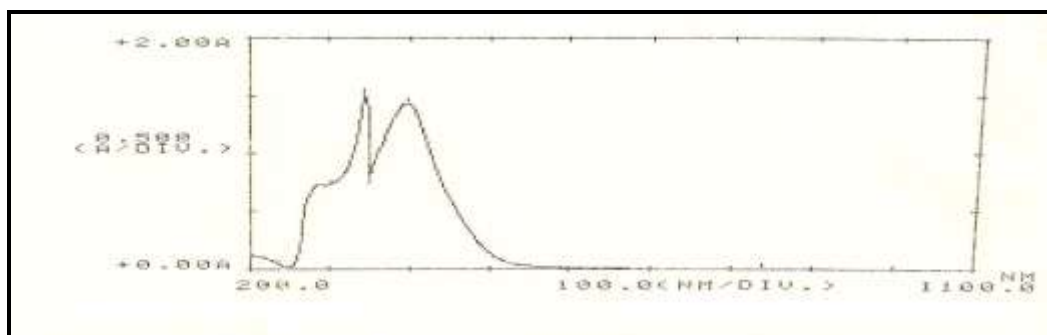


Fig (3) .The U.V Spectrum of the ligand [H<sub>2</sub>L]

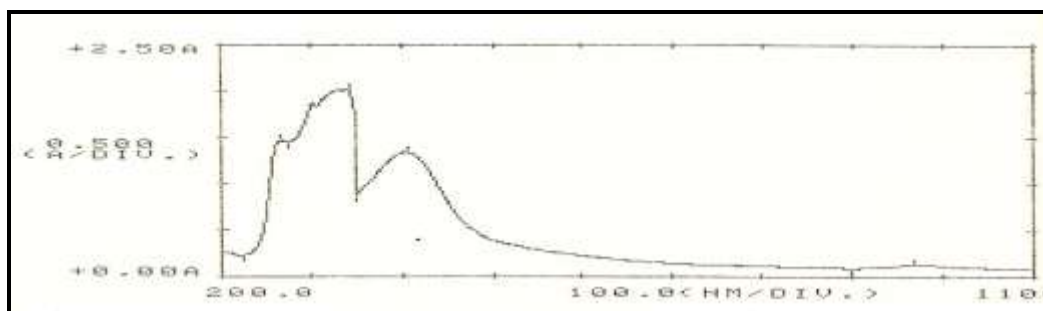


Fig (3-1) .The U.V Spectrum of the [Ni (H<sub>2</sub>L)] Cl<sub>2</sub>

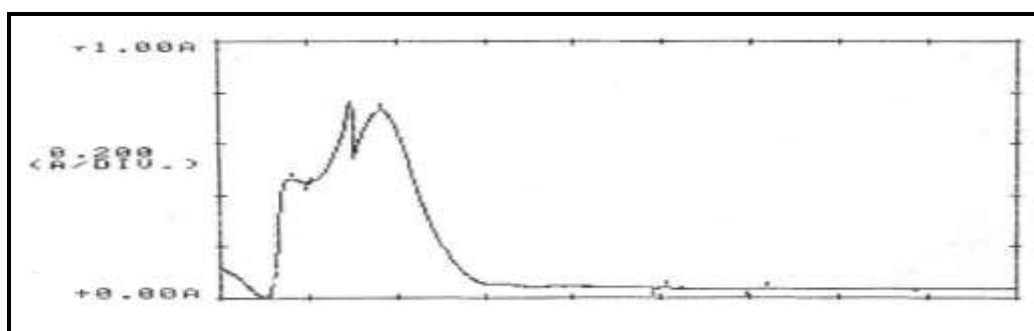


Fig (3-2) .The U.V Spectrum of the [Cd (H<sub>2</sub>L)] Cl<sub>2</sub>