Synthesis and Characterization of Novel ($Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$, $Zn^{(II)}$, and $Cd^{(II)}$) Binuclear Complexes of N, Ń – *bis* [(2, 4, 6-trihydroxy methyl)] Benzidine

A. T. Numan, M.T. Alkazweeni and E. I. Yousif
Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad

Abstract

The Synthesis of a new Schiff base ligand N , Ń – bis(2,4,6-trihydroxy methyl) benzidine [H_6L] and its complexes with $Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$, $Zn^{(II)}$,and $Cd^{(II)}$ are reported . The ligand was prepared by the reaction of 4,4-amino-biphenyl benzidine with 2,4,6-trihydroxyacetophenon monohydrate under reflux in methanol as solvent and a few drops of glacial acetic acid . Then the complexes were synthes by adding the corresponding metal salts to the solution of the ligand in methanol under reflux with 2:1 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
$[M_2 (H_4L) Cl_2.2H_2O]$ [M=Co,Ni,Cu,Zn and Cd] . The data of these measurements suggest a tetrahedral geometry to $Co^{(II)}$, $Cu^{(II)}$, $Zn^{(II)}$,and $Cd^{(II)}$ complexes and a square planar to $Ni^{(II)}$.

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 sites , 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_2O_4) (L=8,9,18,19- tetra hydro 7H,17H-dibenzol [F,O][1,5,9,13] dioxadiaza cyclohexa decine – 8,18-diol) and its complexes with $NiX_2.6H_2O$,X=Cl^- ,ClO^-_4 ,NO^-_3) salts . which were characterized by [I.R, UV-Vis, elemental analysis and conductance measurement. In 2005 Halabiand and Co-worker (13) prepared a schiff base ligand derived kind (N_2O_2) from amino – 1,2,3,6 – oxatrizain and salicylaldeyed and its transition metal complexes with (Ni $^{(II)}$, Cu $^{(II)}$, and Pd $^{(II)}$). In this paper the synthesis and characterization of a new ligand [N, Ń – bis (2,4,6-trihydroxy methyl)] benzidine] [H_6L] and its complexes with (Co$^{(II)}$, Ni$^{(II)}$, Cu$^{(II)}$, Zn$^{(II)}$,and Cd$^{(II)}$) metal ions . The ligand was prepared by reaction of [4,4-amino – biphenyl] (benzidine) with 2,4,6-trihydroxy acetophenon monohydrate .

Experimental

Reagents were purchased from Fluka and Rediel – Dehenge Chemical Co. I.R spectra were recorded as (KBr) disc using a Shimadzu 8400 s 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 (MeOH) at 25°C using a Shimadzu 160 spectrophotometer with 1.000+0.001 cm^{-1} matched quartz cells . 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°C for 10^{-3}M solutions of the samples in (MeOH) using a PW 9526 digital conductivity meter.

Synthesis of the ligand (H_6L): N, Ń – bis [(2, 4, 6-trihydroxy methyl)] benzidine

A solution of benzidine (0.4g,2mmole) in methanol (10ml) was added to 2,4,6- trihydroxyacetophenon (0.8g,4 mmole) dissolved in methanol (10ml) then (2-5) drops of glacial acetic acid was added slowly to the reaction mixture . The reaction mixture was refluxed on water bath of (78°C) for (5 hrs) with stirring, and then left for (24 h) at room temperature, giving a pale green solid [H_6L] . Yield (1.1) g, (55%), m.p. (140°C)dec.

-Synthesis of [$Co_2(H_4L)Cl_2.2H_2O$]

A solution of (H_6L) (0.1g, 0.206 mmole) in methanol (10 ml) was added to a stirred solution of $CoCl_2.6H_2O$ (0.098g, 0.411mmole) in methanol (10ml). The reaction mixture was heated under reflux for (2h).Then the mixture was filtered and the precipitate washed with an excess of methanol and dried at room temperature during (24h). A blue-green solid was obtained yield 0.12g (85%)m.p(258°C)dec.

-Synthesis of [Ni_2 (H_4L) Cl_2.2H2O]

The method used to prepare [$Ni_2(H_4L)Cl_2.2H_2O$] was analogous to the procedure given for the complex [$Co_2(H_4L)Cl_2.2H_2O$] but with $NiCl_2.6H_2O$ (0.098g, 0.412 mmole) instead of $CoCl_2.6H_2O$.The quantities of the other reagents were adjusted accordingly and an identical work – up procedure gave a yellow – green precipitate 0 .13g (92%),m.p(280°C) dec.

-Synthesis of [$Cu_2(H_4L)Cl_2.2H_2O$

A (0.070g, 0.410mmole) of $CuCl_2.2H_2O$was dissolved in (10ml) methanol. A solution of (0.1g, 0.206 mmole) of [H_6L] in (10ml) methanol was added to the above mixture. The reaction mixture was stirred at room temperature for (2hrs.), during which the color of the mixture became a pale brown . The solution was allowed for a slow evaporation a deep brown precipitate was formed, yield (0.1g) (71%),m.p(300°C)dec .

-Synthesis of [Zn_2 (H_4L) $Cl_2.2H_2O$

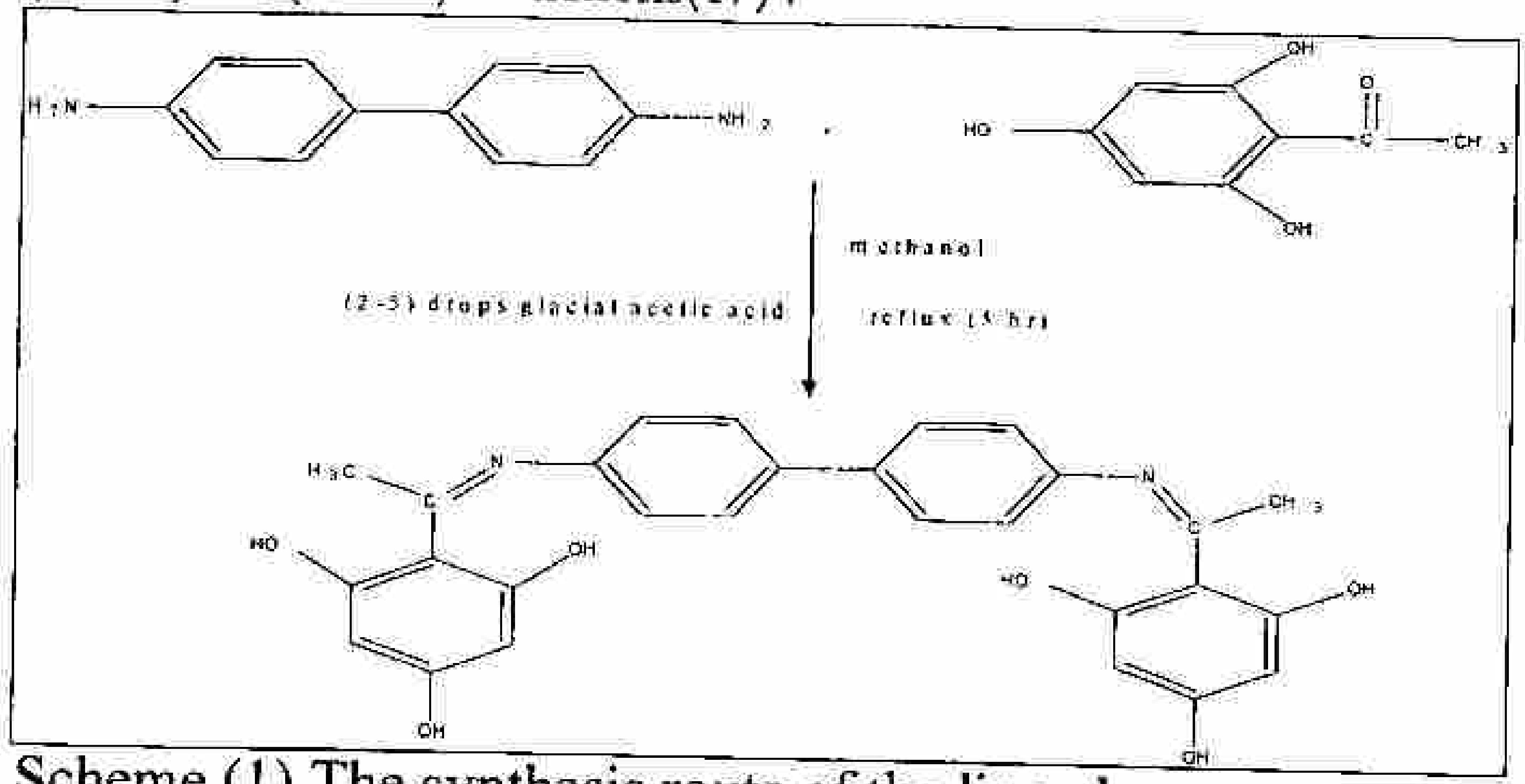
A similar procedure to that described for the complex [$Cu_2(H_4L)Cl_2.2H_2O$] but with $ZnCl_2.2H_2O$ (0.056g,0.410 mmole) in place of $CuCl_2.2H_2O$ with (0.1g,0.206 mmole) [H_6L] was followed to give a yellow – white precipitate , which was washed with (2ml) methanol to yield (0.11g) (78%) m.p(265°C) dec.

-Synthesis of [Cd_2 (H_4L) $Cl_2.2H_2O$]

In (50ml) round bottom flask (0.094g, 0.411 mmole) of $CdCl_2$. $2H_2O$ was suspended in (10ml) methanol. A solution of (0.1g, 0.206 mmole) of [H_6L] in (10ml) methanol was added to the above mixture. Then the reaction was allowed to reflux for (2h). The mustard precipitate crystals which formed upon standing were collected , washed with (2ml) ether, and dried to give (0.14g) (87%) of the title compound , m.p(272°C)dec.

Results and Discussion

The [H_6L] pro-ligand was prepared according to the general method shown in Scheme (1).The(I.R) spectrum for [H_6L] Fig (2-1) , display five bands at (3531)cm^{-1} , (3468)cm^{-1} , (3383)cm^{-1} , (3364) cm^{-1} and (3292) cm^{-1} due to the υ(O-H) stretching of the phenolic hydroxyl groups and hydrated water (14,15) .The band at (1631) cm^{-1} is attributed to the υ(C=N) stretching frequency for the imine group (16) .The sharp bands at (1285) and (1169cm^{-1}) are attributed to υ (C-O) and υ(C-N) stretching respectively . While (U.V-Vis) spectrum. Fig (3-1) exhibits a high intense absorption peak at (250 nm) (40000 cm^{-1}) (ε_{max} = 2110 molar $^{-1}$.cm^{-1})which assigned to overlap of ($\pi \rightarrow \pi^*$)and (n $\rightarrow \pi^*$)transitions(17) .



Scheme (1) The synthesis route of the ligand

The complexes were prepared by the reaction of [H_6L] with Co $^{(II)}$, Ni $^{(II)}$, Cu $^{(II)}$, Zn $^{(II)}$, and Cd $^{(II)}$ in methanol solution under reflux. These complexes are stable in this solution. The analytical and physical data listed in table (1). The higher decomposition points of complexes in comparision 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 spectral are shown in table (2). The shifting of C=N band to lower frequencies in the complexes is due to the increase 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 631-536 cm^{-1} and 598-438 cm^{-1} are due to υ(M-N) and υ(M-O)stretching respectively and suggest that the oxygen atom in addition to the nitrogen are involved in coordination with the metal ion(21-23). Fig(2-2 ,2-3 , 2-4 ,2-5 and 2-6) represent the I.R spectra for the complexes .The molar conductance data of the complexes in methanol (10^{-3} M) corresponding to non electrolyte nature (24) table (3) . (U.V-Vis.) spectra of complexes display absorption bands at the range (243-380) nm, which assigned to the ligand field and charge transfer transition(25) . Besides that other bands appear. In the Co^{II} complex (fig 3-2) the band at 620 nm is attributed to d-d electronic transition of type ($^4T_2 \leftarrow {}^4A_2$). The band present in Ni ^{II} complex at 754nm corresponds to ($^1A_{2g} \leftarrow {}^1A_{1g}$)(26). In the Cu ^{II} complex the band at 394 nm may be assigned to ($^2E \leftarrow {}^2B_2$). The absence of d-d transition in the Zn ^{II} complex is due to its d ^{10} electronic configuration. The positions of the bands in (U.V-Vis.) spectra suggest a tetrahedral structure to Co ^{II}, Cu ^{II}, Zn^{II} ,Cd ^{II} and a square planar to Ni ^{II}.

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Table: (1) Analytical and physical data of the ligand and it's complexes

Complexes formation	colour	M.P.^{0}C	Yield%	Chloride content	Atomic absorption
$[C_{28}H_{24}N_2O_6]$ $[H_6L]$	Pale green	140 dec	55	–	–
$[Co_2(C_{28}H_{22}N_2O_6)Cl_2.2H_2O]$	blue green	258 dec	85	9.63 (10.03)	17.12 (16.67)
$[Ni_2(C_{28}H_{22}N_2O_6)Cl_2.2H_2O]$	Yellow green	280 dec	92	9.77 (10.03)	16.21 (16.62)
$[Cu_2(C_{28}H_{22}N_2O_6)Cl_2.2H_2O]$	Deep Brown	300 dec	71	8.22 (9.90)	16.98 (17.75)
$[Zn_2(C_{28}H_{22}N_2O_6)Cl_2.2H_2O]$	Yellow White	265 dec	78	8.28 (9.85)	17.16 (18.16)
$[Cd_2(C_{28}H_{22}N_2O_6)Cl_2.2H_2O]$	Mustard	272 dec	87	9.11 (9.90)	27.23 (27.62)

(Calc):Calculated

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

Compound	υ(O-H)phenol υ (O-H)(H2O)	υ(C-O)	υ (C=N)	(C-N)	M-O M-N	Additional peaks
$[C_{28}H_{24}N_2O_6]$ $[H_6L]$	3531 3468 3384 3364 3292	1285	1632	1169	- -	υ (C=C)ring 1475 CH3 1364
$[Co_2(C_{28}H_{22}N_2O_6]Cl_2.2H_2O]$	3564 3267	1259	1614	1053	528 631	υ (C=C) ring 1416 υ (C-H) aroma 3040
$[Ni_2(C_{28}H_{22}N_2O_6]Cl_2.2H_2O]$	3563 3301 3247	1244	1616	1087	523 615	υ (C=C)ring 1412 υ(C-H)alph 2924 υ(C-H) aroma 3164
$[Cu_2(C_{28}H_{22}N_2O_6]Cl_2.2H_2O]$	3299 3224 3116	1231	1610	1084	438 538	υ (C=C) ring 1497 υ (C –H) aroma 3065
$[Zn_2(C_{28}H_{22}N_2O_6]Cl_2.2H_2O]$	3267 3220 3191	1227	1614	1034	528 562	υ (C=C) ring 1414 υ (C –H) aroma 3040
$[Cd_2(C_{28}H_{22}N_2O_6]Cl_2.2H_2O]$	3301 3238 3124	1238	1616	1047	527 580	υ (C=C) ring 1416 υ (C –H) aroma 3040

Table (3) : Electronic spectral data , and conductance measurement for the ligand[H_6L] and it's complexes

Compound	λ nm	Wave number Cm^{-1}	ϵ_{max} Molar Cm^{-1}	Assignment	Am ($\Omega^{1}.cm^{2}.Mole^{-1}$)	Propose structure
[H_6L]	250	40000	2110	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	
[$Co_2(H_4L)Cl_2.2H_2O$]	243	41152	2158	$^4T_2 \leftarrow {}^4A_2$	13	tetrahedral
	382	26178	557			
	620	16129	1			
[$Ni_2(H_4L)Cl_2.2H_2O$]	244	40983	2126	$^1A_2g \leftarrow {}^1A_{1g}$	2.76	Square planar
	380	26315	1436			
	754	13262	58			
[$Cu_2(H_4L)Cl_2.2H_2O$]	257	38910	1286	$^2E \leftarrow {}^2B_2$	1.25	tetrahedral
	343	29154	818			
	394	25380	673			
[$Zn_2(H_4L)Cl_2.2H_2O$]	244	40983	2156	Ligand field	5.3	tetrahedral
	380	26315	58	charge transfer		
[$Cd_2(H_4L)Cl_2.2H_2O$]	250	40000	1927	Ligand field	2.2	tetrahedral
	320	31250	555	Charge transfer		

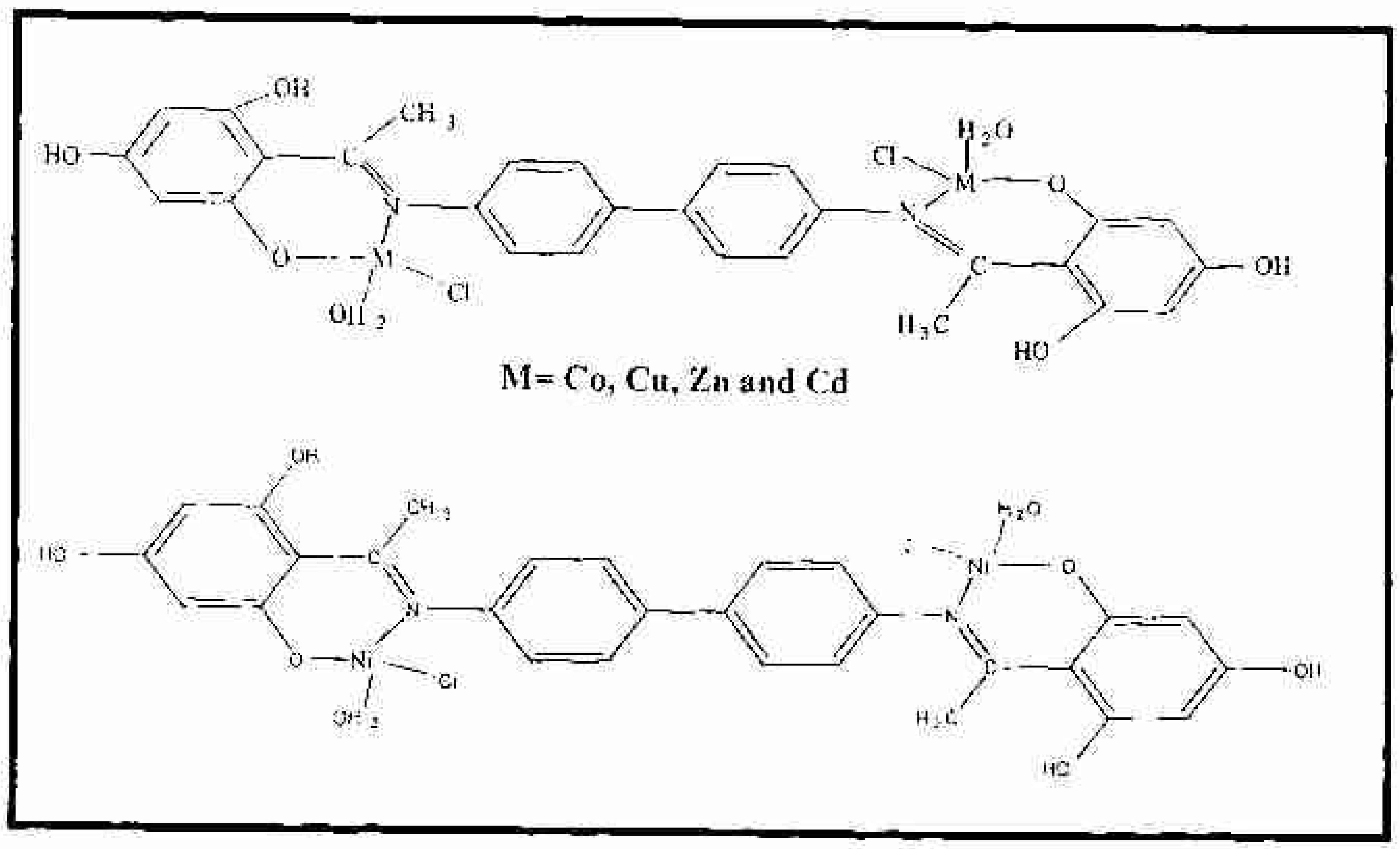


Fig. (1)The suggested structure for the complexes

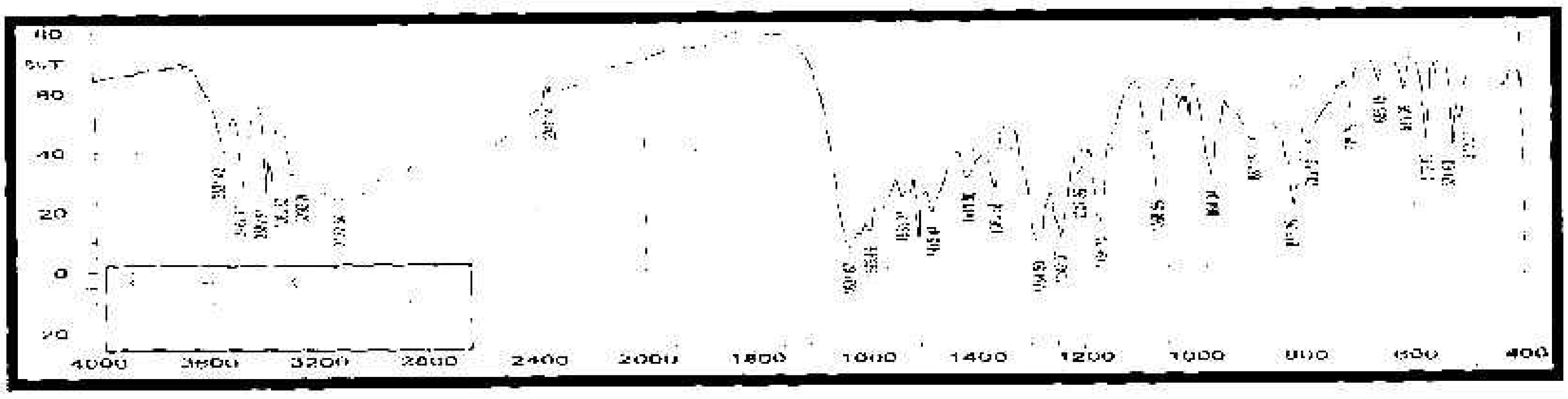


Fig (2-1) .The I.R. Spectrum of the ligand [H_6L]

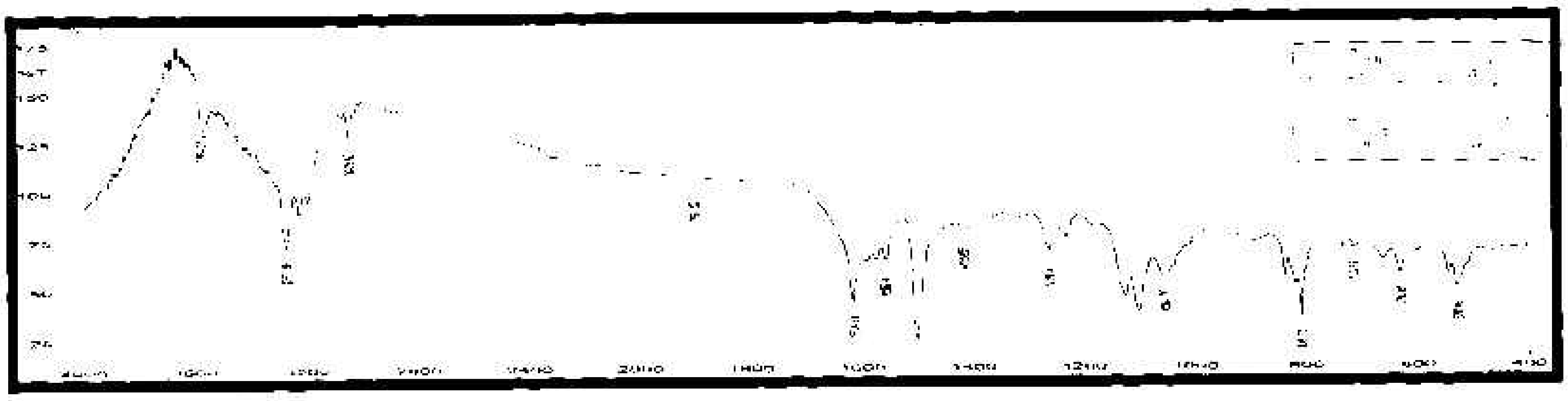


Fig (2-2) .The I.R. Spectrum of [Co_2 (H_4L) Cl_2 . $2H_2O$]

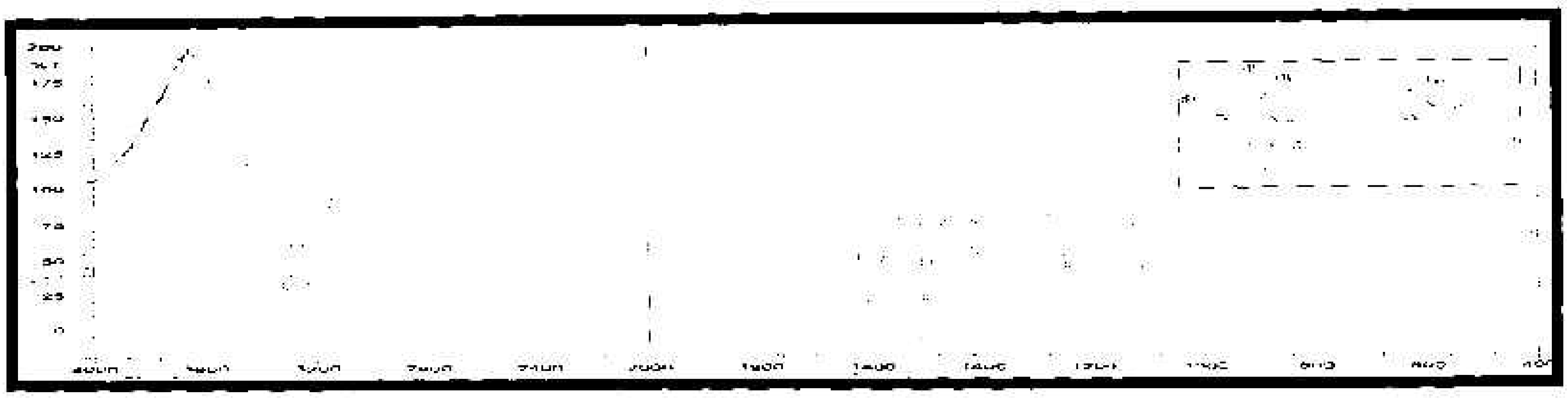
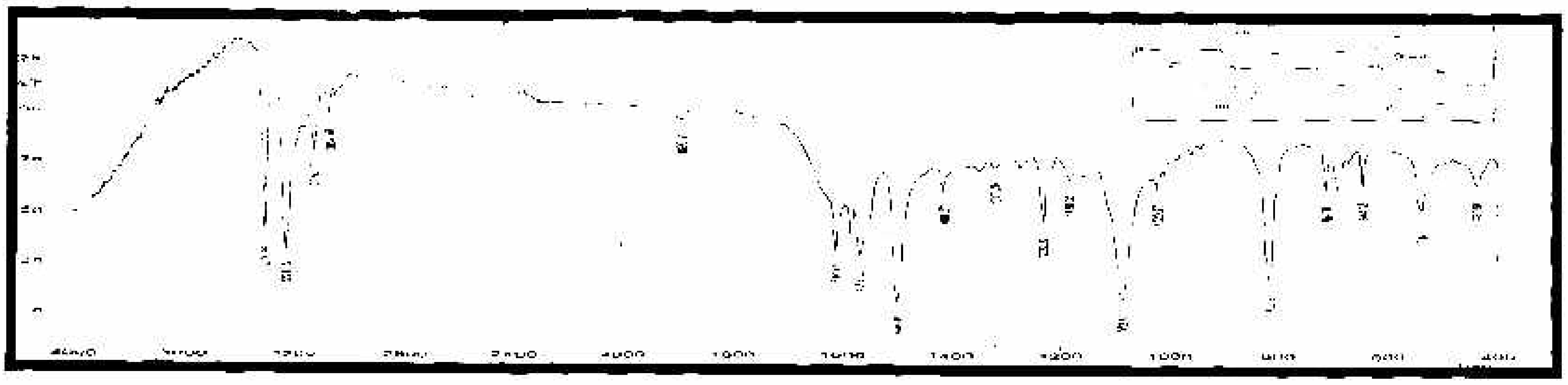


Fig (2-3) .The I.R. Spectrum of [Ni_2 (H_4L) Cl_2 . $2H_2O$]



Fig(2-4) .The I.R. Spectrum of [Cu_2 (H_4L) Cl_2 .2H2O]

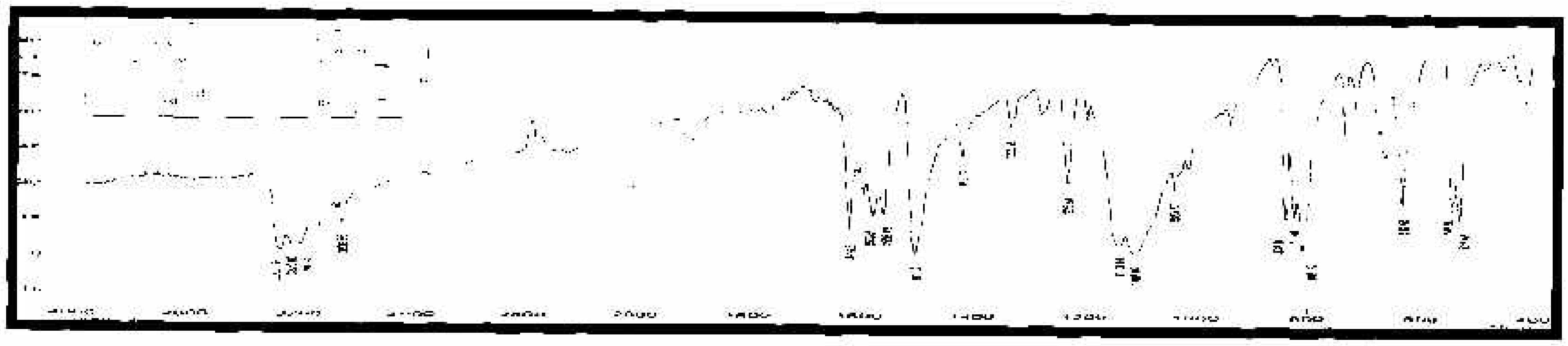
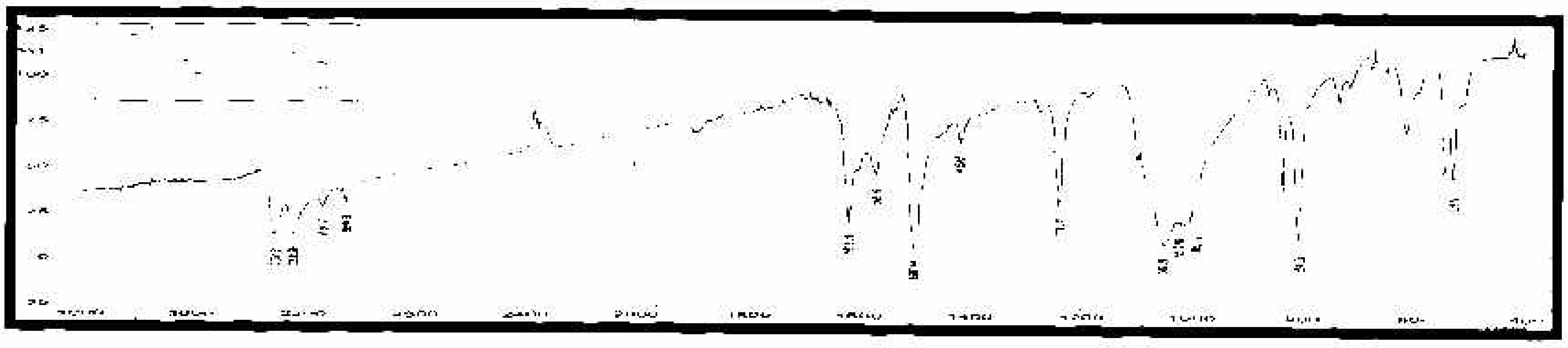


Fig (2-5) .The I.R. Spectrum of [Zn_2 (H_4L) Cl_2 . $2H_2O$]



Fig(2-6) .The I.R. Spectrum of [Cd_2 (H_4L) Cl_2 . $2H_2O$]

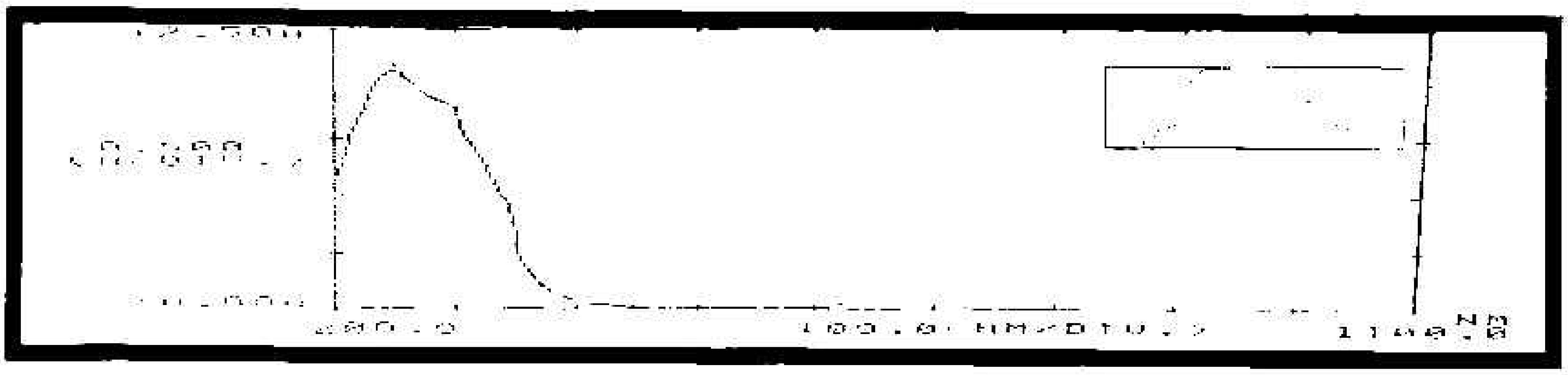


Fig (3-1) .The U.V Spectrum of the ligand $[H_6L]$

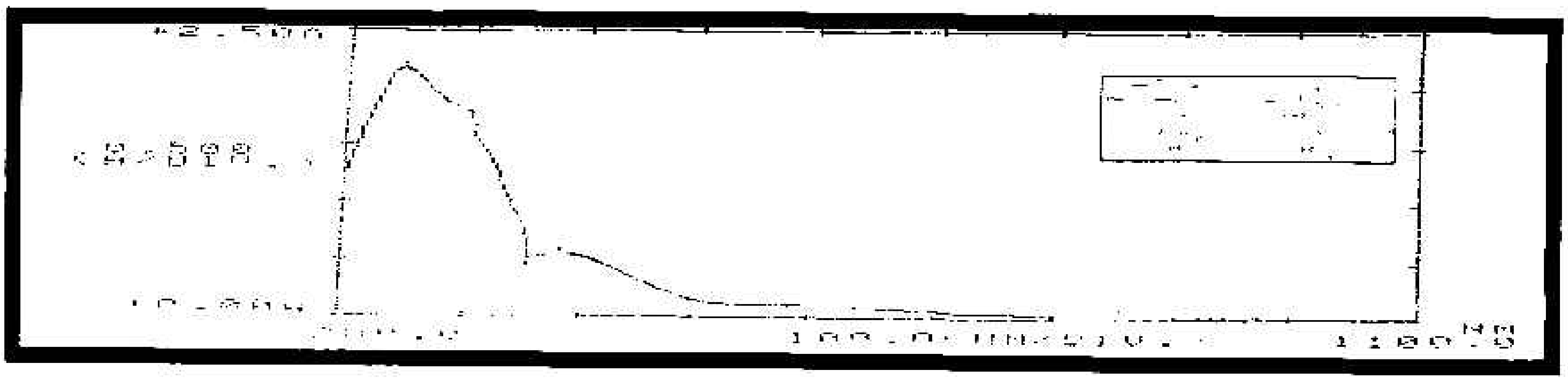


Fig (3-2) .The U.V Spectrum of $[Co_2(H_4L)Cl_2 . 2H_2O]$ complex

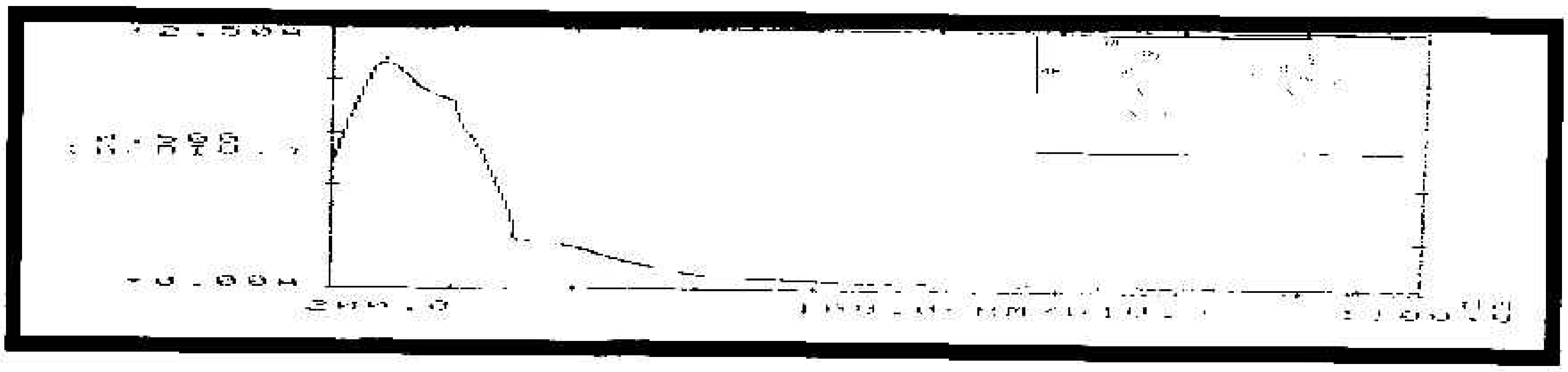
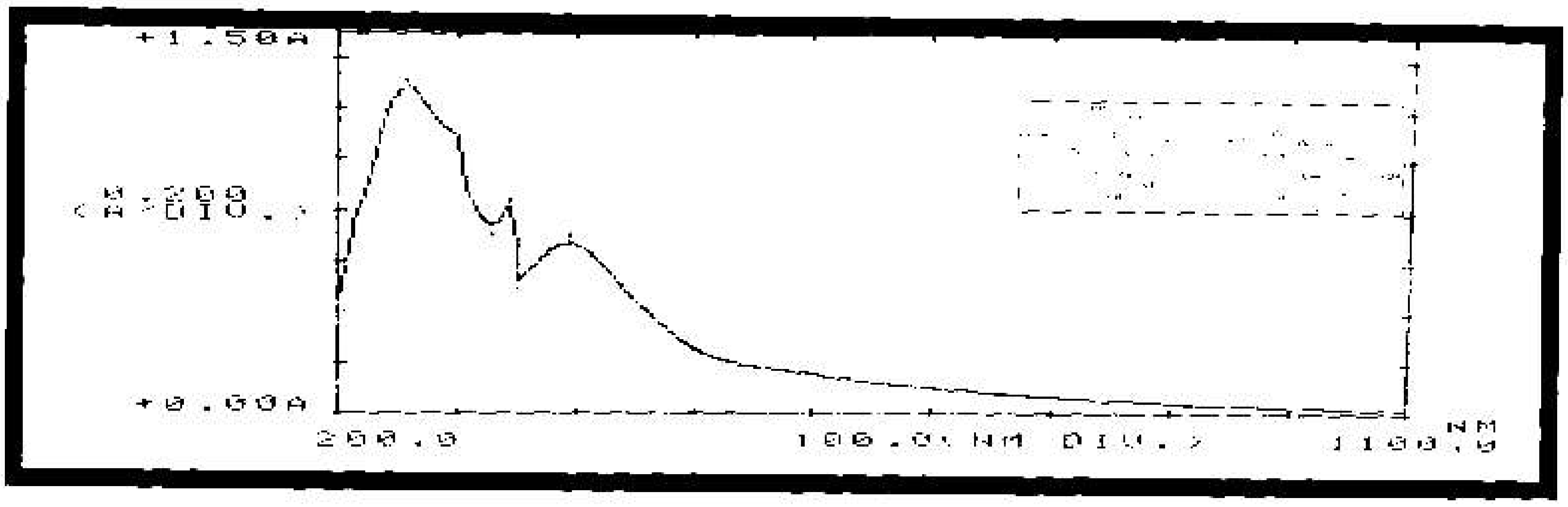
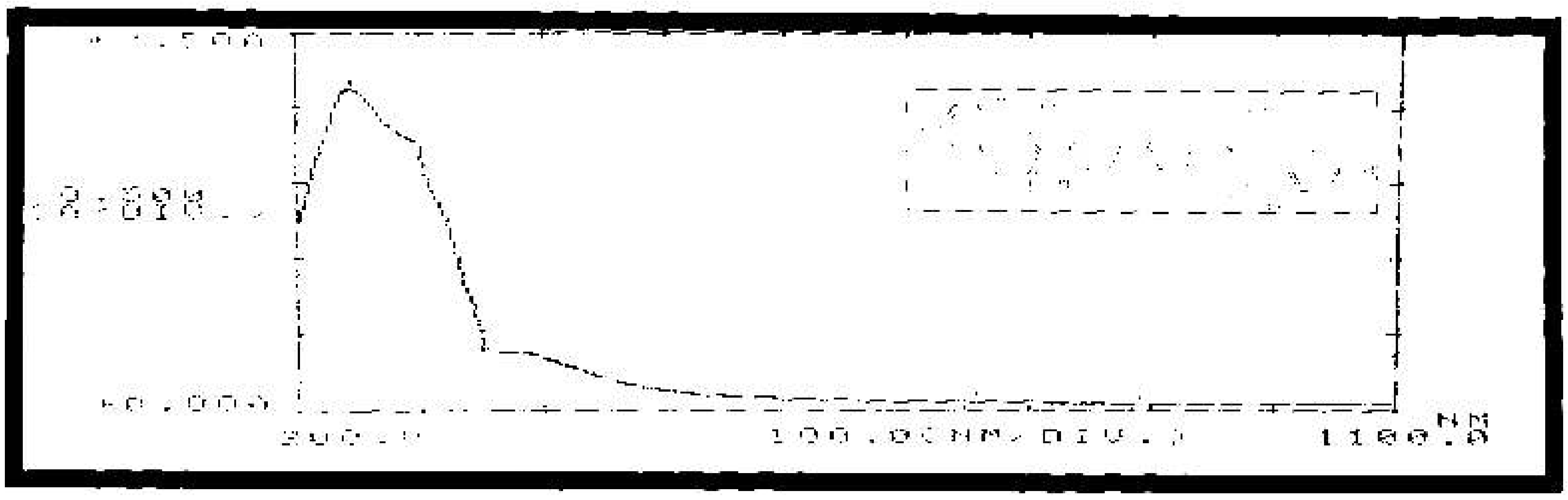


Fig (3-3) .The U.V Spectrum of $[Ni_2(H_4L)Cl_2 . 2H_2O]$ complex



Fig(3-4) .The U.V Spectrum of [Cu_2 (H_4L) Cl_2 . $2H_2O$] complex



Fig(3-5) .The U.V Spectrum of [Zn_2 (H_4L) Cl_2 . $2H_2O$] complex

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد21 (3) 2008

تحضير وتشخيص معقدات ثنائية النواة لليكاند N, Ń – bis [(2,4,6 – trihydroxymethyly)] benzidine [H_6L] مع بعض العناصر الفلزية (Co (11) , Ni (11) , Cu (11) , Zn (11) ,and Cd (11))

أحمد ثابت نعمان، محسن القز ويني وإنعام إسماعيل يوسف
قسم الكيمياء ، كلية التربية ابن الهيثم ، جامعة بغداد

الخلاصة

تضمن البحث تحضير الليكند الجديد N, Ń – bis [(2, 4, 6 – trihydroxymethyl)] benzidine [H_6L]. وذلك من مفاعلة (4,4-amino-biphenyl benzidine) مع (2,4,6-trihydroxyacetophenon)(monohydrate) ثم مفاعلة الليكاند مع بعض العناصر الفلزية باستعمال الميثانول وسطا للتفاعل وبنسبة (2:1) بوجود حامض الخليك الثلجي اذ تكونت معقدات جديدة ذوات الصيغ العامة :

[M_2 (H_4L) $Cl_2.2H_2O$]

اذ:

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

شخصت جميع المركبات بالطرائق الطيفية الأتية (الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية ومطيافية الامتصاص الذري للعناصر ومحتوى الكلور ودرجات الانصهار) ، مع قياس التوصيلية المولارية الكهربائية . من النتائج أعلاه كان الشكل الفراغي المقترح لمعقد النيكل مربعا" مستوى، بينما تتخذ معقدات الكوبلت والنحاس والخارصين والكادميوم شكل رباعي السطوح.