

Synthesis and Characterization of New Ligand type N2O2 and its complexes with (Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) ions

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Abstract:

The [2-hydroxy -1,2-diphynel-ethanone oxime] was reacted with 1,2- dichloroethan to give the new ligand [H2L].this ligand was reacted with some metal ions (Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) in methanol as a solvent to give a series of new (1:1)complexes of the general formula [M(HL)]Cl ,(where : M= Co(II),Ni(II),Cu(II),Zn(II) and Cd(II)) are isolated All compounds have been characterized by spectroscopic methods [I.R , U.V -Vis] atomic absorption . Chloride content along with conductivity measurements. From the above data the proposed molecular structure for (Co, Cu, Ni, Zn and Cd) complexes adopting a tetrahedral structure.

الخلاصة:

تضمن البحث تحضير الليكاند الجديد -1,2-[2-(2-Hydroxyimino-1,2-diphenyl-ethoxy)-ethoxy]-1,2-diphenyl-ethanone] oxime [H2L] وذلك من مفاعلة الفا- بنزوادكسيم مع ثنائي كلورو ايثان ، ثم مفاعلة الليكاند مع بعض ايونات العناصر (Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) الميثانول وسطا للتفاعل وبنسبة (1:1) حيث تكونت سلسلة جديدة من المعقدات ذات الصيغة العامة [M(HL)]Cl حيث (Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) M). شخضت جميع المركبات بالطرق الطيفية التالية (الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية ومطيافية الامتصاص الذري للعناصر ومحتوى الكلور ودرجات الانصهار) ، مع قياس التوصيلية المولارية الكهربائية . تم اقتراح الشكل الفراغي بناءً على المعطيات التي حصلنا عليها من التحاليل وهو شكل رباعي السطوح لجميع المعقدات.

Introduction:

Oxim compounds and their complexes play a great importance in medicine, industry, and biochemistry [1]. This in turn has stimulated research into the coordination chemistry of ligands having other functions in addition to the oxime function [2]. One of the analytical application of oxime compounds their use as an were precipitants for some transition metals [3]. Oxime amine compounds play an important role in radiopharmaceuticals and related nuclear medicine [4,6]. Angle off and Co-workers [7] reported the synthesis of 1,10 – phenanthroline – 2,9 –dicarbaldehydeioxime by reacting 1,10- phenanthroline-2,9-dicarbaldehyde with hydroxylamine, this ligand and its complexes with (Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) were designed as potential agents for nucleis hydrolysis. In this paper the synthesis and characterization new [2-[2-(2-hydroxyimino-1,2-diphenyl-ethoxy)-ethoxy]-1,2-diphenyl-ethanone oxime [H2L] which derived from the reaction of [2-hydroxy -1,2-diphynel-ethanone oxime] and [1,2 dichloroethane] were reported and were also studied their metal complexes with cobalt, nickel, copper, zinc and cadmium ions.

Experimental:

Reagents were purchased form Fluka and Redial – Dehenge chemical Co. I.R spectra were record as (KBr) discs using a shimadzu 8300 FTIR spectrophotometer. Electronic spectra of the compounds were measured in the region (200–1100) nm for 10⁻³ M solution in (DMF) at 25 c using a shimadzu, 160 spectrophotometer 1cm matched quartz cell. While metal

contents of the complexes were determined by atomic absorption (A.A) technique a shimadzu AA 680 G atomic absorption spectrophotometer. The HPLC complexes were determined by using a Shimadzu in this technique 2020.injected into a column of the type (ODS – C18) using (70:30) methanol – water, isocratic system with flow rate (1ml / min) at 25 0C and wave length (nm). Electrical conductivity measurements of the complexes were recorded of 25c for 10⁻³ M solutions of the sample in (DMF) using a pw 9526 digital conductivity meter.

Synthesis of ligand (H2L):

A solution of [1,2- dichloroethan] 0.25 g, (2.5 mmol) was added slowly to a mixture of [2-hydroxy -1,2-diphynel-ethanone oxime 1.14g, (5.0 mmol) dissolved in methanol 5mL with KOH. The mixture was refluxed for 4hrs, and then stirred at room temperature for 1hrs. Solid was collected by filtration , and dried under vacuum for 24hr , to give [H2L] as Yellow solid , yield 1.5g , 62% m.p (131 – 133c) .

Synthesis of complexes:

CoCl2 .6H2O (0.074gm, 0.31 mmol) was suspended in 5mL methanol. To this suspension a mixture of 0.15g, (0.31 mmol) of [H2L] in 5mL methanol was added and allowed to reflux for 2hrs. A green precipitate formed, recrystallization washed with 1mL Benzene to give 0.1157g, (65%) m.p (148 – 150 0C) .Synthesis of [Ni (HL)]Cl (2), [Cu(HL)]Cl (3), [Zn (HL)]Cl (4) and [Cd (HL)]Cl

Complexes:-

The method used to prepare these complexes was similar to that mentioned in preparation of [Co (HL)]Cl complex. Table (1) 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.

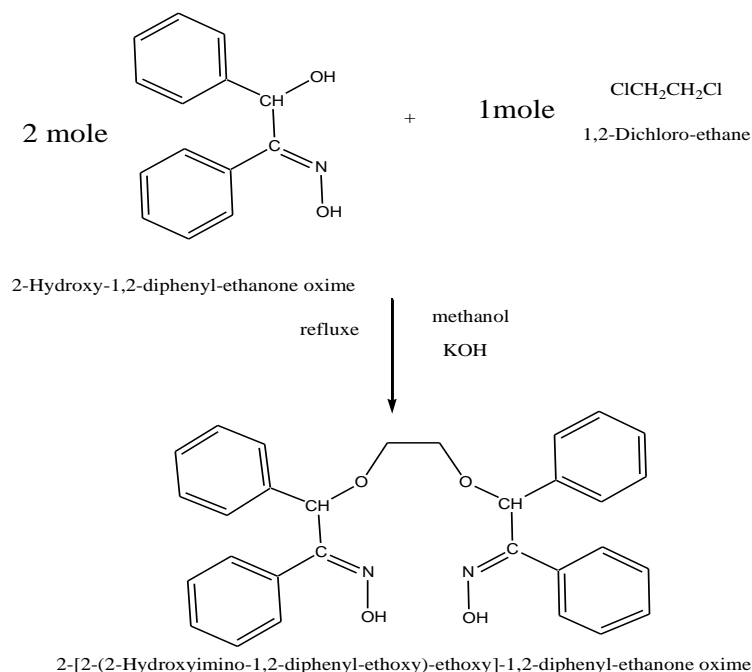
Compound	m.p 0C dec.	Color	Weight of metal		Weight of product (g)	Yield %	Metal content (calc.) %	Chloride content
			g	mmole				
[Co(HL)]Cl	250	blue- green	0.074	0.31	0.1157	60	9.66 (9.67)	Nil
[Ni(HL)]Cl	235	green	0.064	0.31	0.115	60	9.54 (9.64)	Nil
[Cu(HL)]Cl	242	green	0.053	0.31	0.137	72	12.4 (10.35)	Nil
[Zn(HL)]Cl	258	White - yello w	0.042	0.31	0.126	70	12.62 (10.62)	Nil
[Cd (HL)]Cl	260	Yello w	0.062	0.31	0.13	69	18.02 (16.96)	Nil

(calc.)=calculate, (dec.)=decomposed

Result and Discussion:

The [H2L] pro–ligand was prepared according to the general method shown in scheme (1). The (I.R) spectrum for (H2L) ligand Fig. (2), displayed one band at 1490 cm⁻¹ due to the (C=N) stretching for the oxime groups respectively (7). The band at 1193 cm⁻¹ due to the (C-O-C) ether. The band at 3251 cm⁻¹ is attributed to the (O–H) stretching of oxime group.

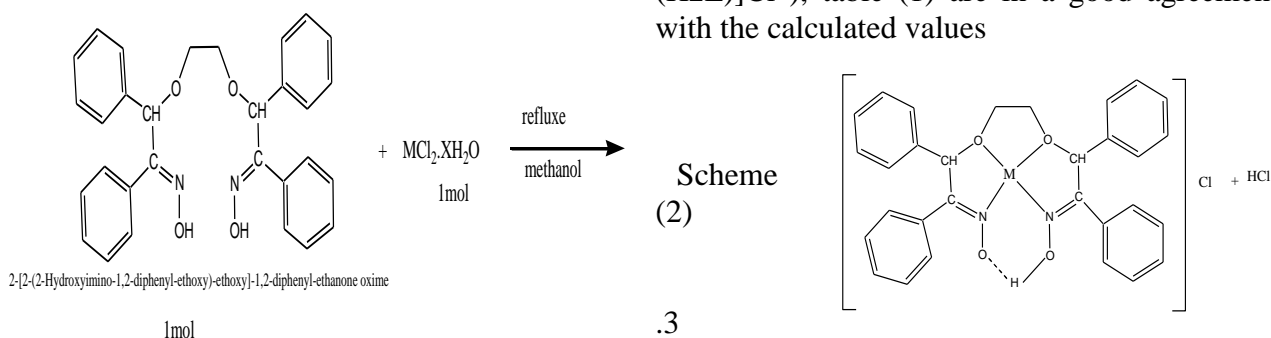
The strong bands at 1014 and 987 cm^{-1} are attributed to (N-O) stretching. While (U.V-Vis) spectrum. Fig (3), the spectra show three a high intense absorption peaks at (272) nm (36764 cm^{-1}) ($\epsilon_{\text{max}} = 1106 \text{ molar}^{-1} \cdot \text{cm}^{-1}$), (348) nm (28735 cm^{-1}) ($\epsilon_{\text{max}} = 374 \text{ molar}^{-1} \cdot \text{cm}^{-1}$) and (468) nm (21367 cm^{-1}) ($\epsilon_{\text{max}} = 114 \text{ molar}^{-1} \cdot \text{cm}^{-1}$) which assigned to overlap of ($\pi \rightarrow \pi^*$), ($n \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions(8).



Scheme (1) The synthesis route of the ligand

The synthesis of the complexes was carried out by the reaction of [H₂L] ligand with [MCl₂.H₂O] [where M= (CoII, NiII, CuII, ZnII and CdII) in methanol under reflux. These complexes are stable in solution and electrolytes with (1:1) (Table-3). The analytical and physical data Table (1) and spectral data Table (2) and Table (3) are compatible with suggested structures Fig (1). The (I.R) Spectral data of the complexes are presented in Table (2). The bands at 3380 cm^{-1} , 3421 cm^{-1} , 3242 cm^{-1} , 3224 cm^{-1} and 3249 cm^{-1} were assigned to the ν (O---H---O) hydrogen bonding stretching vibration (9). In general the (I.R) spectra of the complexes show one band at 1508 cm^{-1} which assigned to the ν (C=N) stretches for the oxime groups respectively. The oxime groups are shifted to higher frequencies 1490 cm^{-1} , as a result of the reduced band order (10). This can be indicative of nitrogen oxime (with hydroxyl group) coordination to metal ion (11). The strong ν (N-O) stretching bands at 1014 and 970 cm^{-1} for the free ligand are shifted markedly to higher frequencies. This is presumably due to the complexation with the metal ions (12). For these complexes the two (N-O) bands are unequal. These results are in good agreement with those reported by Bigatto and co-workers (13). The band ν (O-H) stretching of the oxime group in the free ligand at 3251 cm^{-1} disappeared in the complexes spectra due to the formation hydrogen bonding. The bands at (607–572) cm^{-1} and (493 – 445) cm^{-1} range were assigned to ν (M-N) and ν (M-O) stretching respectively. Indicating that the oxime nitrogen's and oxygen were involved in coordination with metal ion (14-16). The (U.V-Vis) spectra for the complexes (1), (2), (3), (4) and (5) are shown in Fig. (3a and 3b). The absorption data for complexes are given in Table (3). In general, the spectra show two intense peaks in the U.V region at (300,360), (300,341), (299,343), (285,365) and (298,378) nm for complexes (1), (2), (3), (4) and (5). These peaks were assigned to ligand field and charge transfer transitions

(17). Besides that other bands appear. Complex (1) exhibited two peaks at (608) nm and (677) nm. They can be attributed to (d-d) transition type (4A₂ → 4T₁ (p)) and (4A₂ → 4T₁ (F)) respectively. The observed weak peak in spectrum of complex (2) is at (403) nm was assigned to (d-d) transition type (3T₁ → 3T₁ (p)). The spectra of complexes (3) exhibited weak peak at (437) nm respectively (18). They can be attributed to (d-d) transition type (2E → 2B₂). The absence of (d-d) transition in the complexes (4) and (5) are due to (d₁₀) structure for the metal ions. These U.V-Vis data suggest a tetrahedral configuration around the metal ion for the five studied complexes Fig (1). The molar conductance of the complexes in (DMF) lie in the (37.5– 80 s. cm⁻¹ mole⁻¹) range Table (3) indicating the complexes are electrolytic with (1:1) ratio (19). The micro analysis of the (A.A) and chloride content results for the complexes ([Co (H₂L)]Cl, [Ni (H₂L)]Cl, [Cu (H₂L)]Cl, [Zn (H₂L)]Cl [and [Cd (H₂L)]Cl), table (1) are in a good agreement with the calculated values



The synthesis route of the Complex

Comp ound	ν (O - H) Oxi me	ν (O- H- O) hydr ogen	ν (C - H) ν (C - H) alipha rom	ν (C = N) Oxi me	ν (O - C - O) ether	ν (N - O)	ν (M - N)	ν (M - O)
H ₂ L	325 1	----	2930 3030	1490	1193	897 1014	----	----
Co(H L)Cl	----	3380	3025 3052	1623	1191	919 1095	578	460
Ni(HL)Cl	----	3421	2025 3058	1623	1176	910 1097	590	445
Cu(H L)Cl	----	3242	2923 3058	1577	1178	918 1085	572	493
Zn(H L)Cl	----	3224	2921 3058	1600	1190	916 1099	580	480
Cd(H L)Cl	----	3249	2925 3040	1508	1070	923 1070	607	475

Table (2) I.R spectral data of the ligand and its complexes

Compound	λ nm	Wave number Cm-1	ϵ_{max} Molar Cm-1	Assignme nt	HPLC Retentio n Time (min)	Am (s.cm 2.mlo)	Rati o
[H2L]	272 348 468	36764 28735 21367	1106 374 114	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$	-----	-----	----- --
[Co(HL)]Cl	300 360 609 676	33333 27777 16420 14792	2304 873 145 181	Ligand field C.T 4A2 \rightarrow 4T1 (p) 4A2 \rightarrow 4T1 (F)	11.462	71.5	1:2
[Ni(HL)]Cl	300 341 403	33333 29325 24813	1520 1870 1784	Ligand field C.T 3T1 \rightarrow 3T1 (p)	5.894	76.9	1:2
[Cu(HL)]Cl	299 367 437	3344 27247 22883	1115 790 826	Ligand field C.T 2E \rightarrow 2B2	-----	80.0	1:2
[Zn(HL)]Cl	285 365	35971 24785	1725 1874	Ligand field C.T	-----	73.8	1:2
[Cd(HL)]Cl	298 378	32874 2987	1546 1475	Ligand field C.T	-----	74.7	1:2

Table (3) Electronic spectral data and conductance measurement of ligand and its complexes

* C.T = (Charge transfer)
M=Co, Cu, Ni, Zn, and Cd

Figure (1) The suggested structure for the complexes

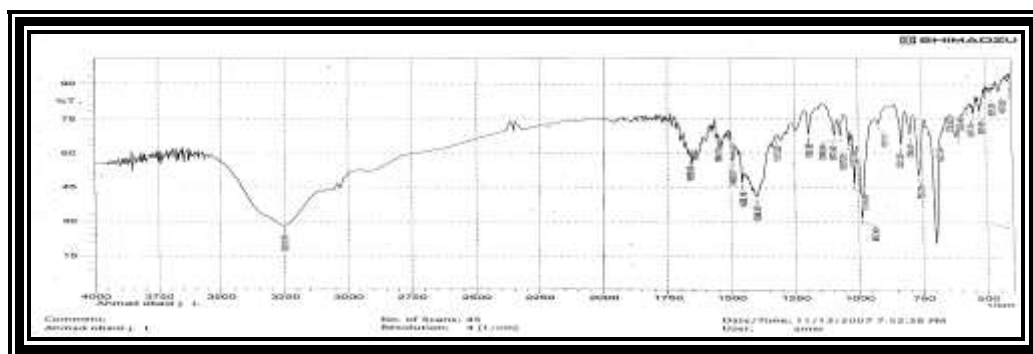


Fig. (2)The (I.R) spectra of the ligand (H2L)

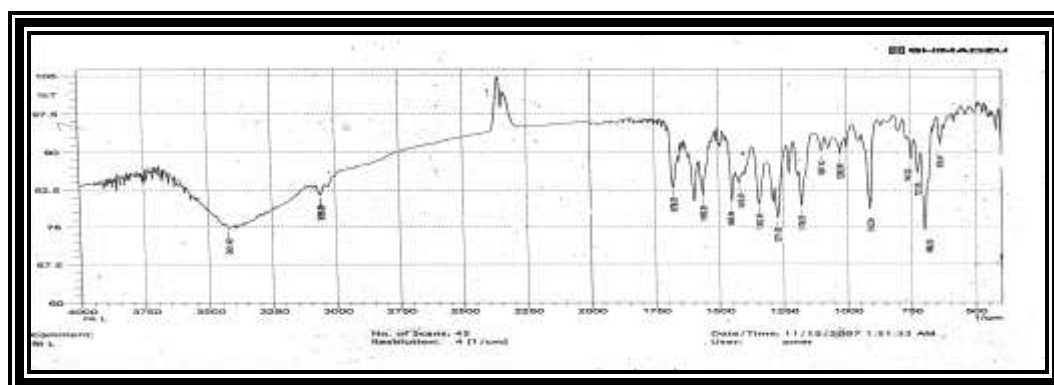


Fig . (2a)The (I.R) spectra of the complex [Ni (HL)] Cl

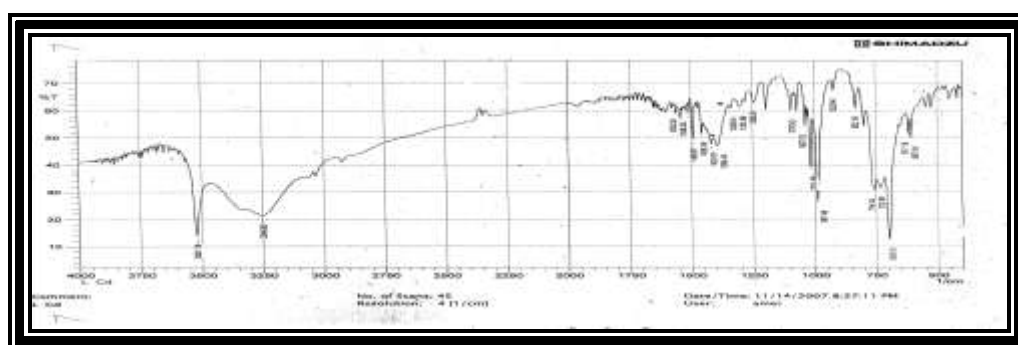


Fig. (2b)The (I.R) spectra o f The complex [Cu (HL)]Cl

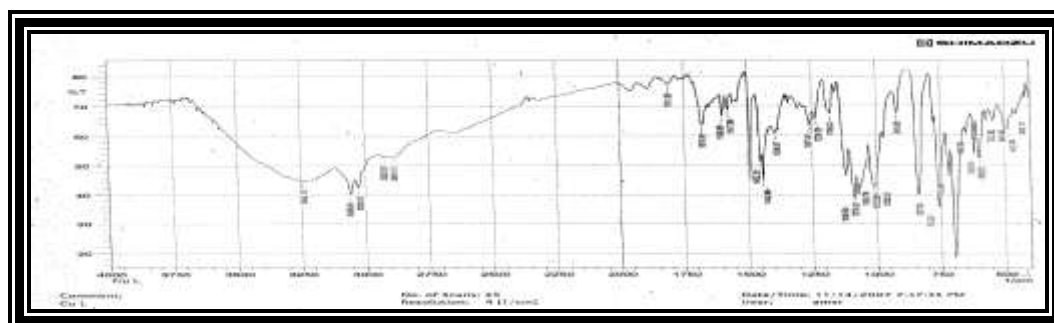


Fig. (2c)The (I.R) spectra o f The complex [Zn (HL)]Cl

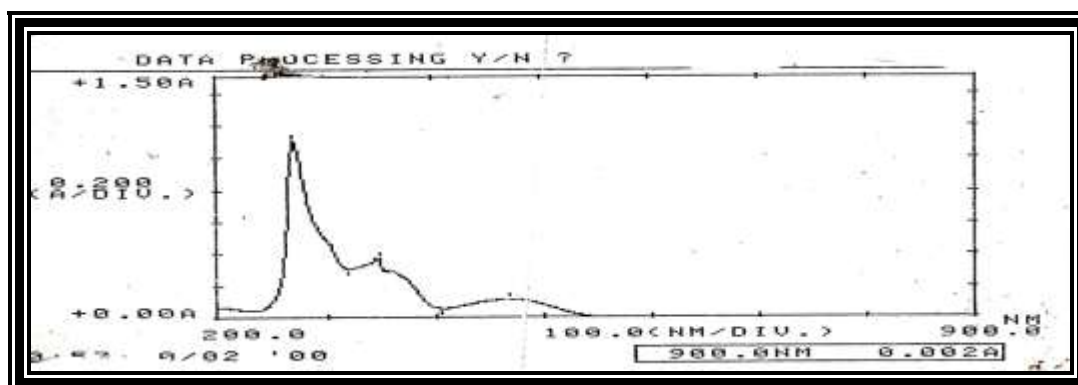


Fig. (3)The (UV - Vis) spectra of the ligand (H2L)

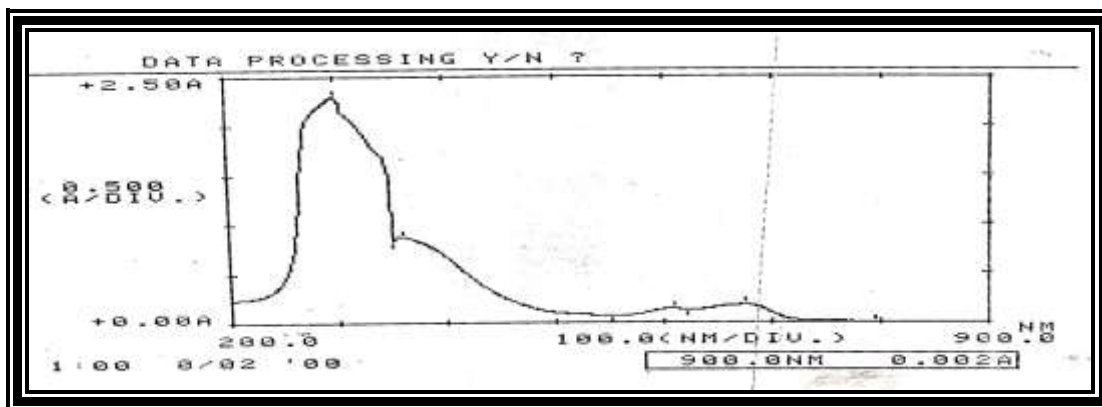


Fig. (3a)The (UV - Vis) spectra of The complex [Co(HL)]Cl

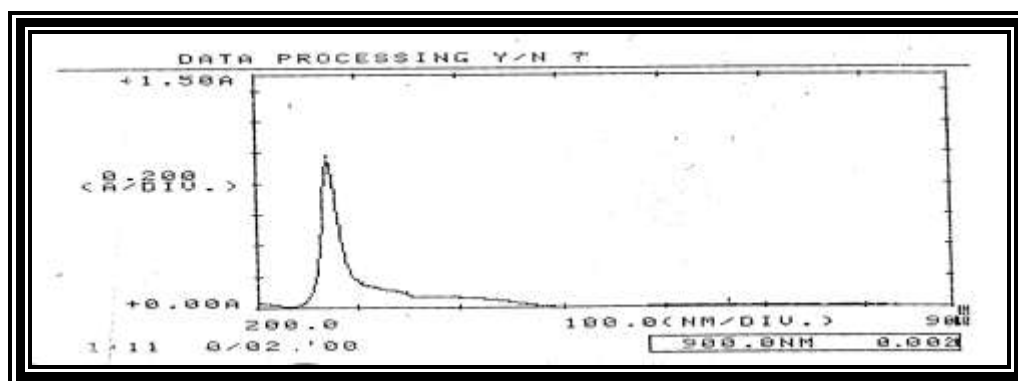


Fig. (3b)The (UV - Vis) spectra of The complex [Cd (HL)]Cl

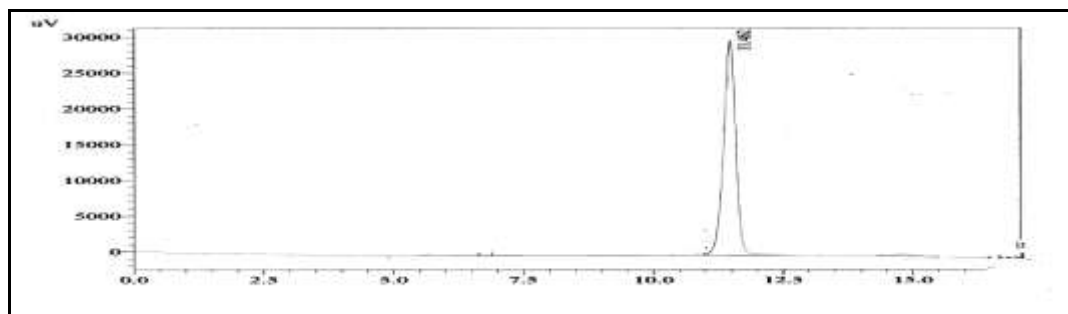


Fig (4a) .The HPLC chromatogram of the [Co (HL)] Cl

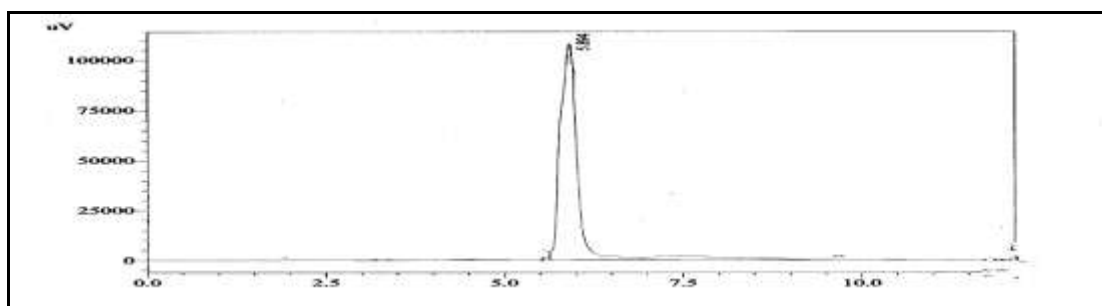


Fig (4b) .The HPLC chromatogram of the [Ni (HL)] Cl

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