

## Synthesis and Characterization of New Ligand type (N<sub>2</sub>) and it's polymeric Complexes with (Co<sup>(II)</sup>, Ni<sup>(II)</sup>, Cu<sup>(II)</sup>, and Pd<sup>(II)</sup>) ions

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### Abstract

The reaction of acrylamide with diacetylmonoxime was realized under reflux in methanol to give the new bidentate ligand [N-acryloyl-2-3-butaylidine mono-imine mono-oxime] [HL]. This ligand was used as monomer to react with some metal ions (Co<sup>(II)</sup>, Ni<sup>(II)</sup>, Cu<sup>(II)</sup>, and Pd<sup>(II)</sup>) in methanol in the presence of methyl ethyl keton peroxide as an initiator with (1:1) metal : ligand ratio to give a series of new polymeric complexes of the general formula [Ni(HL)Cl<sub>2</sub>·H<sub>2</sub>O], [M(HL)Cl<sub>2</sub>], where ( M= Co<sup>(II)</sup>, Ni<sup>(II)</sup>, Cu<sup>(II)</sup>, and Pd<sup>(II)</sup> ). All compounds were characterised by spectroscopic methods (I.R, U.V-Vis), atomic absorption, (EI-mass for the ligand), microanalysis (C.H.N) along with conductivity measurements. The obtained data propose a tetrahedral structure for Co and Cu complexes and square planar for Ni and Pd complexes.

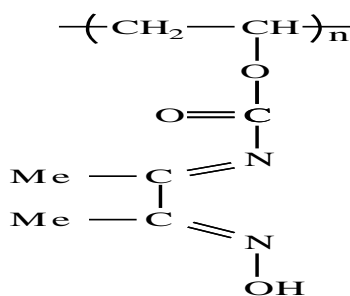
// الخلاصة

تضمن البحث تحضير الليكند نوع (امين-اوكسيم) ثنائي السن (N<sub>2</sub>) (N-acryloyl-2-3-butaylidine mono-imine mono oxime) [HL] وذلك من مفاعلة (acrylamide) مع [diacetylmonoxime] تحت التصعيد الارجاعي في الميثانول . ثم مفاعلة الليكند مع بعض العناصر الفلزية باستخدام (بيروكسيد ميثيل اثيل كيتون) والميثانول وسطا للتفاعل وبنسبة (1:1) حيث تكونت معقدات بوليمرية جديدة ذوات الصيغة العامة: [Ni(HL)Cl<sub>2</sub>·H<sub>2</sub>O] و [M(HL)Cl<sub>2</sub>] حيث M=Co<sup>(II)</sup>, Cu<sup>(II)</sup>, Ni<sup>(II)</sup> and Pd<sup>(II)</sup>

شخصت جميع المركبات بالطرق الطيفية التالية ( الاشعة تحت الحمراء والاشعة فوق البنفسجية -المرئية و C.H.N وطيف الكتلة بتقنية القصف الالكتروني EI لليكند) و كذلك شخصت المركبات بوساطة ،التحليل الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائية وقياس محتوى الكلور. من نتائج البحث كان الشكل الفراغي المقترح لمعقدات الكوبلت والنحاس هي رباعية السطوح مشوه بينما النيكل و البلاديوم فكان شكل معقداتها مربعا مستويا مشوه.

### Introduction

Oxime polymer derivatives and their coordination compounds with metal ions have a great importance in medicine, industry and biochemistry (1). Polymers have been used in protective coating, semiconductors, catalyses and analytical methods (2-4). Chelat polymers containing an amidoxime group show high selectivity towards uranium to separate it easily from west water (5,6). In (2004) Ahmed reported the synthesis and characterization of a new type (N<sub>2</sub>) polymeric bidentate imine–oxime proligand Fig (A) and it's polymeric metal complexes with Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Hg<sup>II</sup> ions (7).



**Fig (A) the chemical structure of the polymeric ligand [HL]**

The ligand and its complexes were characterized by elemental analysis [(C.H.N), (A.A)], IR, (U.V-Vis) spectroscopic and molar conductance measurements. In this paper the synthesis of a new mono-imine mono-oxime ligand [N-acryloyl-2-3-butaylidine mono-imine mono oxime] [HL], and some of its polymeric complexes with (Co, Ni, Cu, and Pd) are reported.

## **Experimental**

Reagents were purchased from Fluka and Rediel- Dehenge Chemical Co. IR spectra were recorded as (KBr) discs using a Shimadzu (8400) FTIR spectrophotometer in the range (4000-400)  $\text{cm}^{-1}$ . Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for  $10^{-3}$  M solution in (DMSO) at 25  $^{\circ}\text{C}$  using a Shimadzu, 160 spectrophotometer with 1  $\text{cm}^{-1}$  matched quartz cell. Mass spectrum for the ligand was obtained by Electron-Impact (EI) on a Shimadzu GCMSQPA 1000 spectrometer at the University of Free Berlin, Germany. Elemental microanalyses were performed on a (C.H.N) analyzer from Heraeus (Vario E.L) at the University of Free Berlin, Germany, while 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  $^{\circ}\text{C}$  for  $10^{-3}$  M solutions of the samples in (DMF), using a PW 9526 digital conductivity meter. The chloride content for complexes was determined by using potentiometric titration method on (686-Titro processor -665-Dosimate Metrohom. Swiss)

### **Synthesis of the ligand (HL) (N-acryloyl-2-3-butaylidine mono-imine mono oxime).**

A solution of acrylamide 0.5g, (7.0 m mole) in (12 mL) methanol was added slowly with stirring to a solution of diacetylmonooxime 4.9g, (49 m mole) dissolved in (10mL) methanol with a few drops of HBr (48%). The mixture was refluxed for 90 min with stirring, and then allowed to cool at room temperature for (24 hr), to give the ligand as a white solid. Yield (75%) m.p (155 $^{\circ}\text{C}$ ).

### **Synthesis of [Co (HL) Cl<sub>2</sub>] 1-**

A solution of (HL) 0.1g, (0.65mmole) in methanol 7 mL was added slowly to a stirred solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  0.3g, (1.30 m mole) in MeOH 13 mL along with mixture 0.5 mL methyl ethyl ketone peroxide in 15 mL methanol. The reaction was refluxed for 1.5 hr. The solution was concentrated by removing the solvent under low pressure. A deep blue precipitate was formed, yield 0.343 g (85%), m.p (210 $^{\circ}\text{C}$ ) dec.

### **2-Synthesis of [Ni (HL) Cl<sub>2</sub>.H<sub>2</sub>O]**

The method used to prepare [Ni (HL) Cl<sub>2</sub>] was analogous to the procedure given for the complex [Co (HL) Cl<sub>2</sub>] but with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  0.309g, (1.3 m mole) in stead of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . The quantities of the other reagents were adjusted accordingly and an identical work -up procedure gave a green yellow 0.35 g (88%), (m.p) (145 $^{\circ}\text{C}$ ) dec.

### **3- Synthesis of [Cu (HL) Cl<sub>2</sub>]**

The method used to prepare [Cu (HL) Cl<sub>2</sub>] was analogous to the procedure given for the complex [Co (HL) Cl<sub>2</sub>] but with  $\text{CuCl}_2$  0.221 g, (1.3 m mole) instead of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . The quantities of the other reagents were an adjusted accordingly and an identical work -up procedure gave a brown precipitate 0.24 g (67%), m.p (110 $^{\circ}\text{C}$ ) dec.

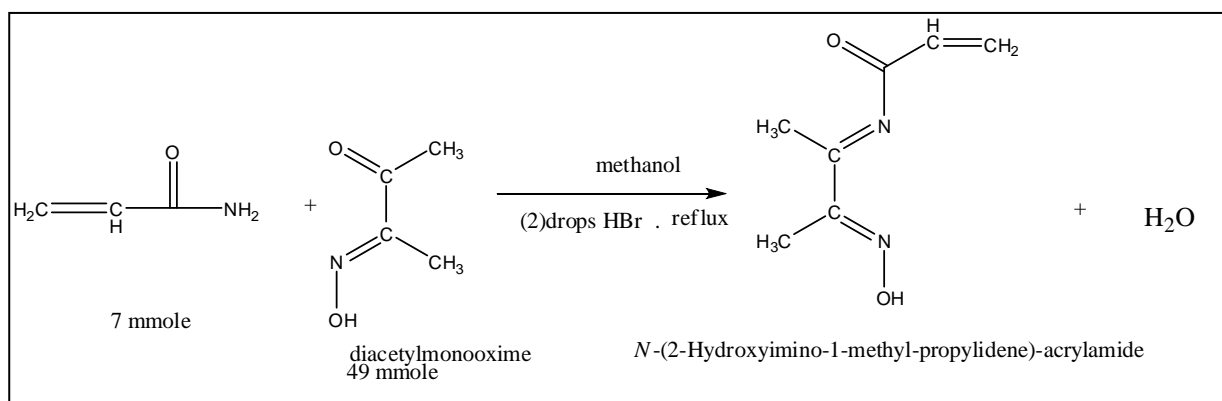
#### 4- Synthesis of [Pd (HL) Cl<sub>2</sub>]

The method used to prepare [Pd (HL) Cl<sub>2</sub>] was analogous to the procedure given for the complex [Co (HL) Cl<sub>2</sub>] but with PdCl<sub>2</sub> 0.231 g, (1.3 m mole) instead of CoCl<sub>2</sub>.6H<sub>2</sub>O. The quantities of the other reagents were an adjusted accordingly and an identical work -up procedure gave a brown precipitate 0.26 g (45%), m.p (240<sup>0</sup>C) dec.

#### Results and discussion

The reaction of [HL] with [ MCl<sub>2</sub> .XH<sub>2</sub>O] (where M= Co<sup>(11)</sup>, Ni<sup>(11)</sup>,Cu<sup>(11)</sup> , and Pd<sup>(11)</sup> ) was carried out in methyl ethyl keton peroxide and MeOH under reflux . These complexes are stable in solution. The analytical and physical data were listed in Table (1) and spectral data in Table (2, 3).

The N-acryloyl 1-2-3-butyldine monoamine monooxime [HL] ligand was prepared according to general method shown in scheme (1).



**Scheme (1) the synthesis route of the ligand (HL)**

The (FT-IR) spectrum for ligand (HL) fig (1), display two bands at (1620) and (1441) cm<sup>-1</sup> due to the  $\nu(\text{C}=\text{N})$  stretching for the imine and oxime groups respectively (8). The broad bands at (3346, 3200) cm<sup>-1</sup> are attributed to the, (OH) stretching for oxime group and traces of methanol or hydrate water (9). The band at (966) cm<sup>-1</sup> are attributed to  $\nu(\text{N}-\text{O})$  stretching, while the band at (1685) cm<sup>-1</sup> is due to  $\nu(\text{C}=\text{O})$ . The characteristic band for the ligand are listed in Table (2).

(U.V-Vis) spectrum for the ligand fig (2) exhibits a high intents absorption peak at (240) nm and (285) nm which assigned to ( $\pi \rightarrow \pi^*$ ) and ( $n \rightarrow \pi^*$ ) Transition respectively (10).

The EI (+) mass spectrum of the ligand fig (3), (Table 4) shows the parent ion peak at ( $M/Z=154$ ) (11) which corresponds to ( $M^+$ ), and the fragments at , (123 ,108, 95 , 80 , 65 and 53 are assigned to [ $M-\{\text{N}-\text{OH}\}^+$ ], [ $M-\{\text{CH}_3-\text{N}-\text{OH}\}^+$ ], [ $M-\{\text{CH}_3-\text{CH}-\text{N}-\text{OH}\}^+$ ], [ $M-\{\text{CH}_3-\text{CH}_3-\text{CH}-\text{N}-\text{OH}\}^+$ ], [ $M-\{\text{CH}_3-\text{CH}_3-\text{CH}-\text{CH}_2-\text{N}-\text{OH}\}^+$ ], [ $M-\{\text{CH}_3-\text{CH}_3-\text{CH}-\text{CH}_2-\text{C}=\text{N}-\text{OH}\}^+$ ], respectively , other fragments are summarised in Table (4).

The (C.H.N) and Chloride contents with metal contents of the prepared complexes were in a good agreement with the calculated values Table (1). The (FT-IR) spectral data of the complexes are presented in Table (2) fig (1a and 1b). In general the (FT-IR) spectra of the complexes show bands at (1610 and 1404) cm<sup>-1</sup> which assigned to the  $\nu(\text{C}=\text{N})$  for the imine and oxime groups respectively .The band of imine groups at (1620) cm<sup>-1</sup> in the ligand spectrum was shifted to lower frequency (1610) in the complexes spectra as a result of decrease in the bond order. This can be attributed to the delocalization of metal electron density into the ligand  $\pi$ -system (12).On the other hand the  $\nu(\text{C}=\text{N})$  for the oxime groups around (1441) cm<sup>-1</sup> were shifted, as expected, to lower frequency (1404) cm<sup>-1</sup>. This is indicative of nitrogen oxime (with hydroxyl group) coordination to the metal ion. The  $\nu(\text{N}-\text{O})$  stretching band at (966) cm<sup>-1</sup> for the ligand was shifted to higher frequencies in the range (1076-1039) cm<sup>-1</sup> upon coordination with metals. This may be due to the

partially double bond character of (N-O) occurred upon complexation, and confirmed that, the ligand coordinated with the metal ions through the nitrogen's of the oxime groups (13). The  $\nu$  (O-H) stretching band of the oxime group in the free ligand at  $(3200) \text{ cm}^{-1}$  is still present at the range  $(3350-3170) \text{ cm}^{-1}$  in the spectra of the complexes. The  $\nu(\text{C}=\text{O})$  stretching band at  $(1685) \text{ cm}^{-1}$  for the free ligand is shifted to higher frequencies and appeared at  $(1728) \text{ cm}^{-1}$ ,  $(1710) \text{ cm}^{-1}$ ,  $(1715) \text{ cm}^{-1}$  and  $(1718) \text{ cm}^{-1}$  respectively. This may be due to the ( ) due to resonance

$\text{H}_2\text{C}=\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{N}=\overset{\text{O}}{\text{C}}$  delocalization of electrons of (C=O) along ( ). The (C=O) group is not involved in complexation with metal and it's another evidence of the coordination between the metal ions and the ligand. The bands at  $(605-428) \text{ cm}^{-1}$  were assigned to  $\nu$  (M-N) stretching indicating that the imine and oxime nitrogen's were involved in coordination with metal ion (14). The electronic spectral data of the complexes are summarised in table (3).

The (U.V-Vis) spectra of the complexes display absorption between (296-301) nm assigned to the ligand field (15). In the  $[\text{Co}(\text{HL})\text{Cl}_2]$  complex fig(2a), the three bands shown at (381), (526), and (680) nm are attributed to charge transfer and (d-d) electronic transitions ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_2$ ) and ( ${}^3\text{T}_1 \rightarrow {}^3\text{T}_2$ ) respectively, suggesting a distorted tetrahedral about Co(II) ion fig(4a). The band at (409 and 753) nm in the spectrum of  $[\text{Ni}(\text{HL})\text{Cl}_2] \cdot \text{H}_2\text{O}$ , fig (2b) which assigned to ( ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ ) and ( ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ ) (d-d) transitions respectively, suggesting distorted square planar about Ni (II) ion. The (U.V-Vis) spectrum of  $[\text{Cu}(\text{HL})\text{Cl}_2]$  which exhibit absorption at (850) nm assigned to ( ${}^2\text{B}_2 \rightarrow {}^2\text{E}_1$ ) (d-d) transition, suggesting distorted tetrahedral around Cu (II) (16). In the (U.V-Vis) spectrum of  $[\text{Pd}(\text{HL})\text{Cl}_2]$  complex, the band at (390) nm was attributed to (d-d) transition of type ( ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ ) suggesting a square planar structure about Pd (II) ion fig (4b).

The molar conductance of the complexes in (DMF) solution  $10^{-3}$  (M) lie in the (31-34)  $\text{S} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$  range Table (5), indicating their non electrolytic nature (17).

**References**

1. Patel .M. and Patel, S. H., Synth. React, Inorg. Mct–Org. Chem. (1983), **13**, 133.
2. J. E. Katon (ed.), Organic Semi conducting Polymers (Macel Dekker), New York, (1968)
3. R. Riedere and W. Sawodny, Eng. Chem., (1977), **16**, 859.
4. J. Hodgkin, “Encyclopaedia of Polymer Science and Engineering”. 1985, 2<sup>nd</sup>. ed. (Jonn Wiley, New York,).
5. N. Sahiner, N. Pekel, and O. Guven, Radiate Phys. Chem., (1998), **52**, 271.
6. H. Guler, N. Sahiner, GA. Ayccik, O. Guven, J. Appl. Polym. Sci., (1997), **66**, 2475–2480.
7. D. J. Ahmed, MSC. Thesis. University of Baghdad, Education College, (2004).
8. J.M Lo and K.S liu, Appl. Radiat. Isot, (1993),44,1139.
9. G. Socrats “Infrared Characteristics Group Frequencies” Wiley – Interscience publication, (1980), **7**, 132.
10. K. Nakomoto, “Infrared Spectra of Inorganic and Coordination Compound” 4<sup>th</sup>, J. Wiely and Sons, New York, (1996), **8**, 241.
11. William Kemp “Organic Spectroscopy” (1987), 2<sup>nd</sup>, Edition.
12. J. R. Chapman, “Practical Organic Mass Spectrometry” (1995), 2<sup>nd</sup>. Ed. J. Wiley.
13. D. Hadz. And L. Premra, Spectro Chem. Acta (1967),**23A**, 35.
14. D. Hadzi, J. Chem. Soc., (1956), **15**, 2725.
15. R. W. Adams, R. L. Martin, and G. Winter, Aust. J. Chem., (1967), **20**, 773.
16. N. N. Green Wood and A. Earnshow “Chemistry of the Elements” J. Wiley and Sons Inc. New York, (1998), **9**, 314.
17. A. B. P. Lever “Inorganic Electronic Spectroscopy”, New York; (1968), **6**, 121.
18. V. Ramesh, P. Umasundari, and Kalyank Das, Spectro Chem. Acta, Part A, (1998), **54**, 285.

**Table (1) Elemental analysis and some physical properties of (HL) and its metal Complexes**

Compound	M.W	Found (C.H.N.) %				
		C	H	N	Cl	Metal
(HL)	154	(54.54) 54.35	(6.49) 6.40	(18.18) 18.15	-	-
[Co(HL)Cl <sub>2</sub> ]	283.93	(29.58) 29.44	(3.52) 3.48	(9.86) 9.81	(25.00) 24.25	(20.76) 21.90
[Ni(HL)Cl <sub>2</sub> ] H <sub>2</sub> O	301.7	(27.8) 27.7	(3.98) 3.91	(9.27) 9.25	(23.52) 22.88	(19.46) 19.24
[Cu(HL)Cl <sub>2</sub> ]	288.5	(29.12) 29.08	(3.47) 3.42	(9.71) 9.66	(24.61) 24.61	(22.01) 23.18
[Pd(HL)Cl <sub>2</sub> ]	331.4	(25.38) 25.33	(3.02) 2.98	(8.46) 8.39	(21.45) 20.11	(32.02) 33.61

Calc.=Calculated

**Table (2) Infrared spectral data (wave number ) cm<sup>-1</sup> for ligand and its metal Complexes**

Compound	$\nu(\text{O-H})$ oxime	$\nu(\text{C-H})$	$\nu(\text{C=N})$ imine $\nu(\text{C=N})$ oxime	$\nu(\text{C=O})$	$\nu(\text{N-O})$	$\nu(\text{M-N})$	Additional peaks
(HL)	3200(br) 3374	2827	1620(m) 1441(sh)	1685(m)	966(m)		1364 $\delta(\text{C-H})$ 1145 $\nu(\text{C-N})$ 914 $\nu(\text{C-C})$
[Co(HL)Cl <sub>2</sub> ]	3170(br) 3350	2815(w)	1610(s.sh) 1404(s.sh)	1728(m)	1076(m)	475 428	1296 $\delta(\text{C-H})$ 1128 $\delta(\text{C-N})$ 746 $\nu(\text{C-C})$
[Ni(HL)Cl <sub>2</sub> ] H <sub>2</sub> O	3380(br)	2813(w)	1610(m) 1400(m)	1710(w)	1039(w)	497 430	1124 $\delta(\text{C-N})$ 1294 $\delta(\text{C-H})$ 1388 $\delta(\text{C-H})$
[Cu(HL)Cl <sub>2</sub> ]	3197(br) 3350	2817(w)	1604(s) 1404(s.sh)	1715(m)	1075(w)	447 428	1128 $\delta(\text{C-N})$ 750 $\nu(\text{C-C})$ 1294 $\delta(\text{C-H})$
[Pd(HL)Cl <sub>2</sub> ]	3200(m)	2956(w) 2925(w)	1610(m) 1404(s)	1718(w)	1049(w)	580 493	1128 $\delta(\text{C-N})$ 1331 $\delta(\text{C-H})$

Recorded as KBr disc br = broad, w = weak, m = medium, s = strong,  $\nu$  = stretching,  $\delta$  = bending, sh = sharp

**Table (3) Electronic spectral data of (HL) and its metal complexes.**

Compound	$\lambda_{nm}$	$cm^{-1}$	$\epsilon_{max}$ ( $L.mol^{-1}.cm^{-1}$ )	Assignment	Proposed Structure
(HL)	240 285	41666 35087	360 404	$(\pi \rightarrow \pi^*)$ $(n \rightarrow \pi^*)$	----
[Co(HL)Cl <sub>2</sub> ]	300 381 526 680	33333 26264 19011 14705	920 271 219 70	Ligand field Charge transfer ( $^4A_2(p) \rightarrow ^4T_2$ ) ( $^3T_1 \rightarrow ^3T_2$ )	Tetrahedral
[Ni(HL)Cl <sub>2</sub> ].H <sub>2</sub> O	296 409 753	33783 24449 13280	990 567 223	Ligand field ( $^1A_{1g} \rightarrow ^1B_{1g}$ ) ( $^1A_{1g} \rightarrow ^1A_{2g}$ )	Square planar
[Cu(HL)Cl <sub>2</sub> ]	301 850	33222 11560	1407 24	Ligand field Charge transfer	Tetrahedral
[Pd(HL)Cl <sub>2</sub> ]	299 350 390	33444 28571 25640	1183 650 300	Ligand field Charge transfer	Square planar

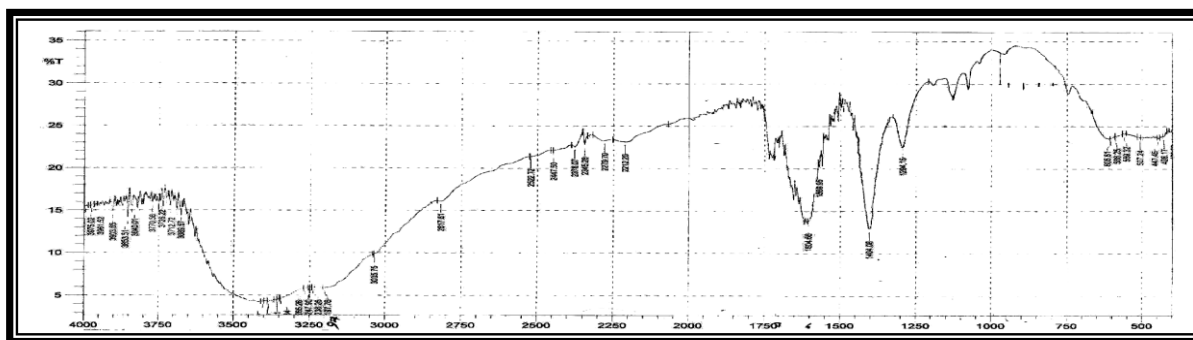
**Table (4) EI-Mass spectral data of (HL)**

Fragment	Mass charge M/Z	% of Relative abundance
[M] <sup>+</sup>	154	2
[M-{N-OH}] <sup>+</sup>	123	100
[M-{CH <sub>3</sub> -N-OH}] <sup>+</sup>	108	93
[M-{CH <sub>3</sub> -CH-N-OH}] <sup>+</sup>	95.2	6
[M-{CH <sub>3</sub> -CH <sub>3</sub> -CH-N-OH}] <sup>+</sup>	80	25
[M-{CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -N-OH}] <sup>+</sup>	65	6
[M-{CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C=N-OH}] <sup>+</sup>	53	10

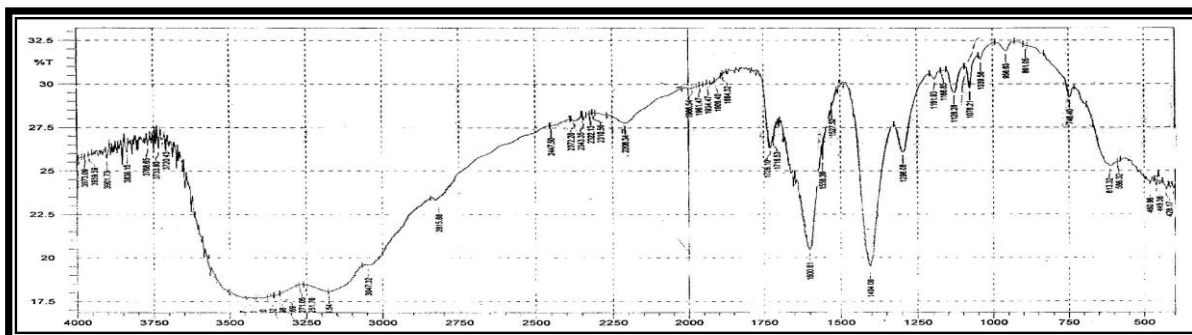
**Table (5) the molar conductance of the Complexes recorded in DMF solvent**

Compound	$\Lambda_m$ (S. cm <sup>2</sup> mol <sup>-1</sup> )
[Co(HL)Cl <sub>2</sub> ]	33.7
[Ni(HL)Cl <sub>2</sub> ].H <sub>2</sub> O	32.8
[Cu(HL)Cl <sub>2</sub> ]	34.2
[Pd(HL)Cl <sub>2</sub> ]	35.00

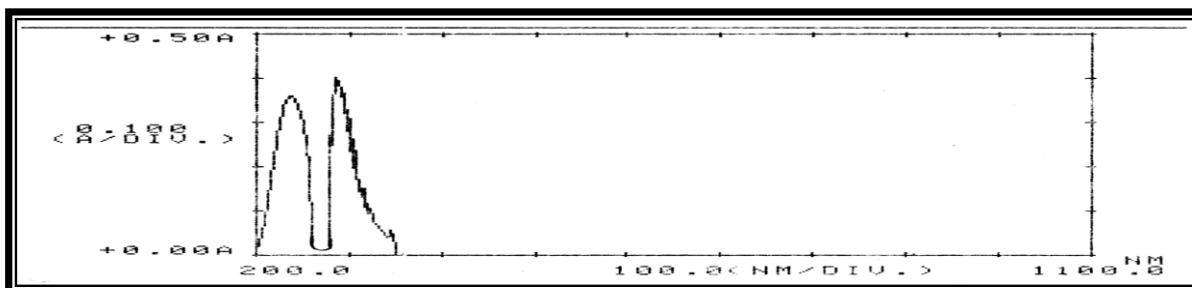
**Fig (1) Infrared spectrum of the ligand**



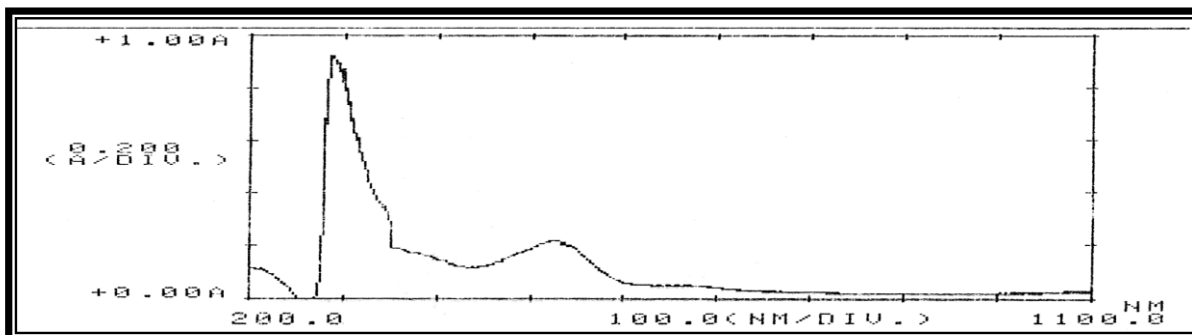
**Fig (1a) Infrared spectrum of [Co (HL) Cl₂] complex**



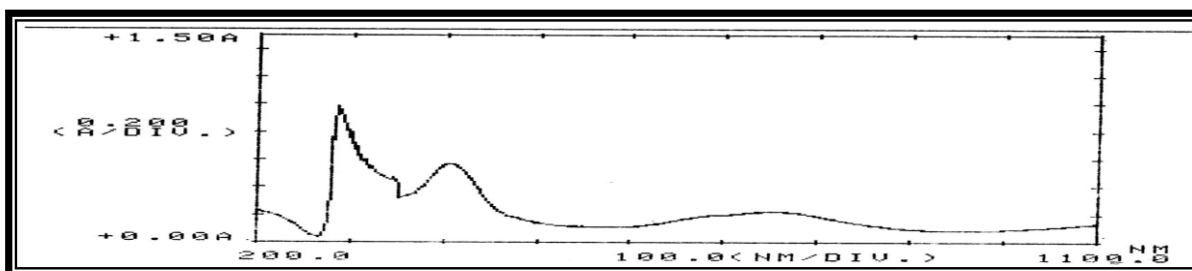
**Fig (1b) Infrared spectrum of [Cu (HL) Cl₂] complex**



**Fig (2) Electronic spectrum of the ligand**

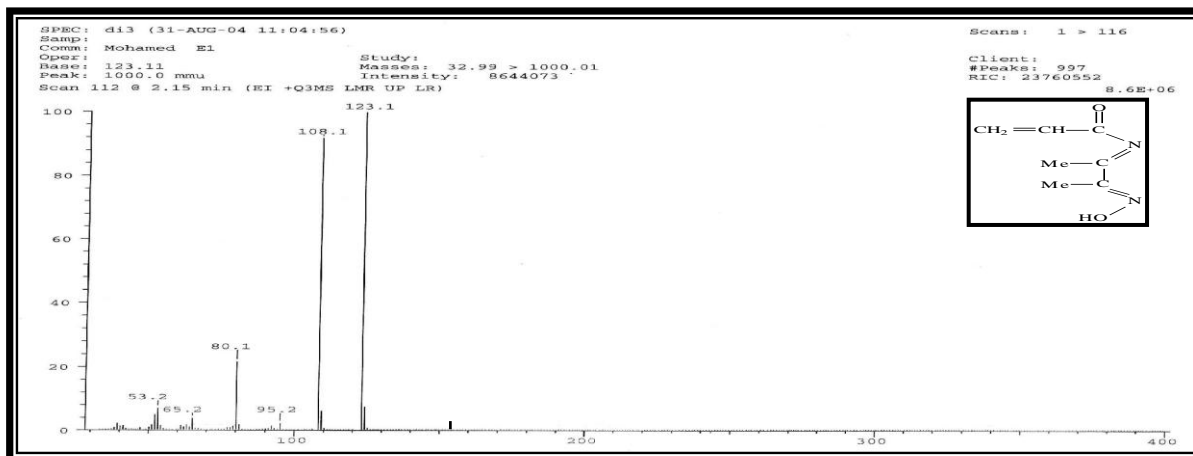


**Fig (2a) Electronic spectrum of the [Co (HL) Cl₂]**

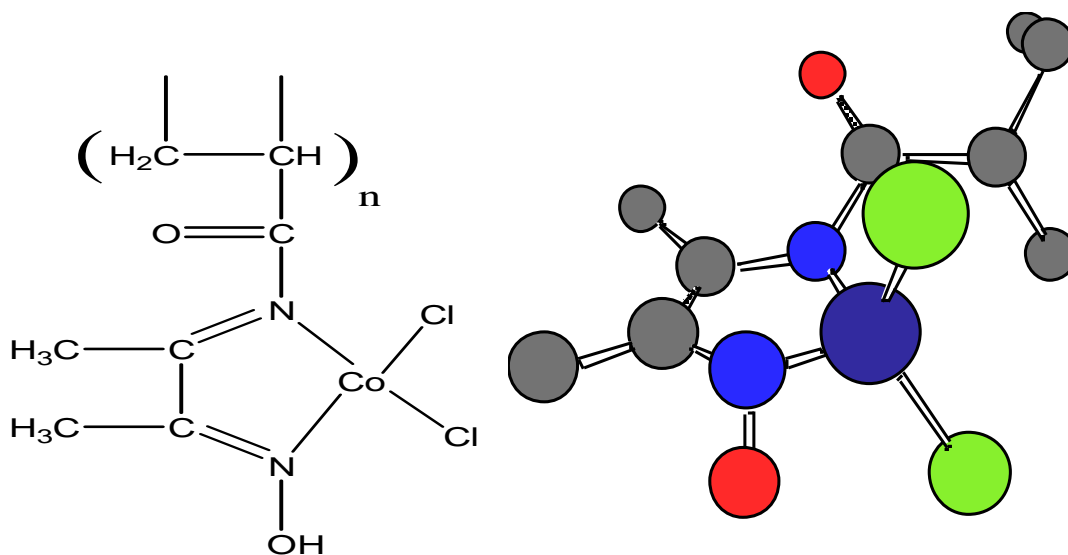


**Fig (2b) Electronic spectrum of the [Ni (HL) Cl₂].H₂O**

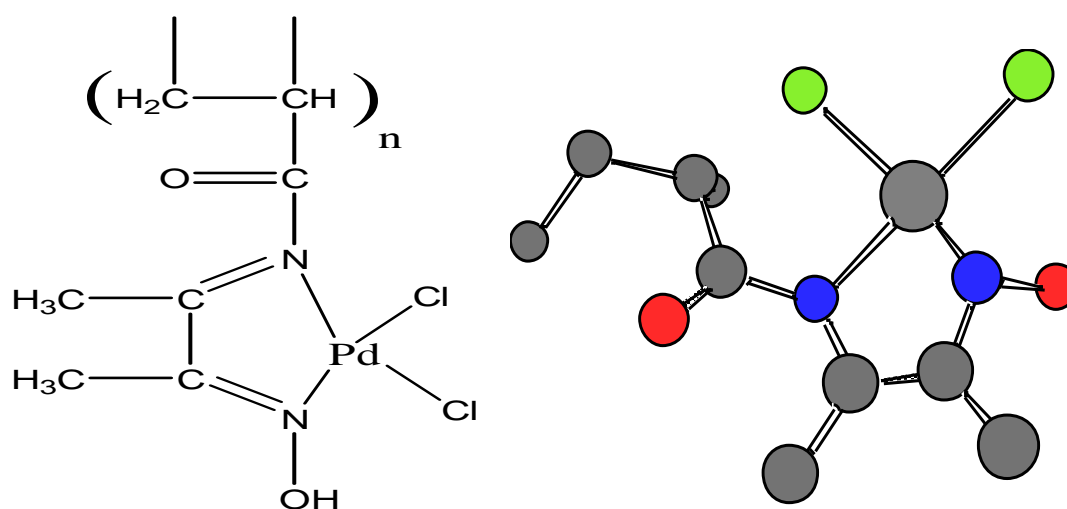




**Fig (3) the mass spectrum for the ligand**



**Fig (4a) the proposed molecular structure of [Co (HL) Cl<sub>2</sub>]**



**Fig (4b) the proposed molecular structure of [Pd (HL) Cl<sub>2</sub>]**