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SYNTHESIS AND CHARACTERIZATION OF NEW SCHIFF-BASE LIGAND TYPE N_2O_2 AND ITS COMPLEXES WITH ($Co^{(II)}$,$Ni^{(II)}$,$Cu^{(II)}$ AND $Zn^{(II)}$) IONS.

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Abstract

A new ligand [1-(ortho hydroxy-benzylidene),2-Sodium pyruvalidene hydrazine] [NaHL] was prepared and its complexes ($Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$, and $Zn^{(II)}$). This ligand was prepared in two steps. The first step a solution of salicyladehyed in methanol react under reflux with hydrazinemonohydrate to give an (intermediate compound) [(1-ortho hydroxy benzylidene) hydrazine] which react in the second step with Sodium pyruvate giving the mentioned ligand. The complexes were synthesized in direct reaction of the corresponding metal chloride with the ligand. The ligand and complexes have been characterized by spectroscopic methods (IR, UV-Vis, atomic absorption), chloride content and conductivity measurement. The obtained data propose a chemical formula [M (L)] and geometries structure as a tetrahedral distorted about metal ion for the studied complexes.

Key words: Schiff-base ; oxidatioin catalyst ; Sodium pyruvate.

Introduction

Many chemists have reported on the chemical, structural and biological properties of Schiff bases. Schiff bases are characterized by the –N=CH-(imine) group which is very important in elucidating the mechanism of transmission rasemination reaction in some biological systems (1,2). During the past two decades, considerable attention has been paid to the chemistry of metal complexes of Schiff bases containing nitrogen and other donor atoms (3,4).This may be attributed to their stability, biological activity (5)and potential application in many fields such as oxidatioin catalysis (6) and electrochemistry (7). In 2005 Halabi and Co-worker (8).prepared a schiff base kind (N_2O_2) which is derived from amino–1,2,3,6 – oxatrizain and salicylaldeyed with some transition metal complexes (Ni $^{(II)}$, Cu $^{(II)}$, and Pd $^{(II)}$). The present paper we synthesis and characterization of new ligand [1-(ortho hydroxy-benzylidene),2-Sodium pyruvalidene hydrazine] [NaHL] and its complexes with divalent ions. To prepare the ligand, a solution of salicyladehyed in methanol was mixed with hydrazinemonohydrate (1:1) then the resultant of reaction (intermediate compound) was added to Sodium pyruvate 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 (200-900) nm for 10^{-3}M solution in (DMF) at 25^0C using a Shimadzu 160 spectrophotometer with 1.000±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 Spectro-photometer. Electrical conductivity measurements of the complexes were recorded at 25^0C for 10^{-3}M solutions of the samples in (DMF) using a PW 9526 digital conductivity meter.

Preparation

Synthesis of the ligand [NaHL]

The ligand was prepared in two steps.

Step (1): Preparation of the [(1-ortho hydroxy benzylidene) hydrazine] (intermediate compound).

A solution of salicyladehyde 0.6 g, (4.913 mmole) in methanol (5ml) was added to hydrazine monohydrate 0.245 g, (4.89 mmole) which was dissolving in methanol (5 ml), and (2-4)drops of glacial acetic acid was added slowly to the reaction mixture. The mixture was refluxed for 5 hours, and allowed to dry at room temperature during (24) hours. Deep Yellow solid was obtained. Yield (80%), 0.53 g, m.p (178 ^{0}C).

Step (2): Preparation of the [2-Sodium pyruvalidene hydrazine, 1-(ortho hydroxy benzylidene)] [NaHL].

A solution of [(1-ortho hydroxyl benylidene) hydrazine] (intermediate compound) 0.4g,,(2.941mmole) in methanol (5 ml) was added to Sodium pyruvate 0.32 g, (2.941 mmole) which was dissolving in methanol (5 ml), then (2-4) drops of glacial acetic acid was added slowly to the reaction mixture.The reaction mixture was refluxed for (5) hours with stirring, filtered and the filtrate was allowed to dry at room temperature during (48) hours,then, washed with (5) ml diethyl ether and dried at room temperature to give the pale yellow solid was obtained. Yield (88%), (0.59) g,m.p (225^{0}C).

Results and discussion

The new ligand [NaHL] was prepared in two steps according to the general method of preparation of Schiff base ligands (9) as shown in Scheme (1).The (I.R) spectrum for [NaHL]

Synthesis of (NaHL) complexes

1-Synthesis of [Co (L)] (1).

A solution of (NaHL) (0.2g, 0.877mmole) in methanol (5ml) was added to solution of CoCl2.6H2O (0.2g, 0.877 mmole) in methanol (5ml) with stirring. 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 during (24 hrs). A blue solid which decompose (195 ^{0}C) was obtained. Yield (91%), (0.21 g).

Synthesis of [Ni (L)] (2), [Cu (L)] (3) and [Zn (L)] (4) Complexes.

The method used to prepare these complexes was similar to that mentioned in the preparation of [Co (L)] complex. Table (1) states the weight of starting materials, yield reaction conditions and some physical properties of the prepared complexes.

Table (1)

Some physical properties of the complexes and their reactants quantities.

Compound	Metal chloride	M.p ^{0}C	Color	Weight of metal chloride		Weight of product (g)	Yield %	chloride content	Metal content
				g	mmole				
[Co (L)]	$CoCl_2$.6H2O	195 Dec	blue	0.2	0.877	0.21	91	nil	21.62 (22.41)
[Ni(L)]	$NiCl_2$.6H2O	200 Dec	green Yellow	0.2	0.877	0.19	82	nil	21.03 (22.34)
[Cu(L)]	$CuCl_2$.2H2O	270 Dec	blue green	0.14	0.877	0.22	95	nil	22.39 (23.75)
[Zn(L)]	$ZnCl_2$. H2O	285 Dec	Yellow	0.11	0.877	0.20	86	nil	23.51 (24.27)

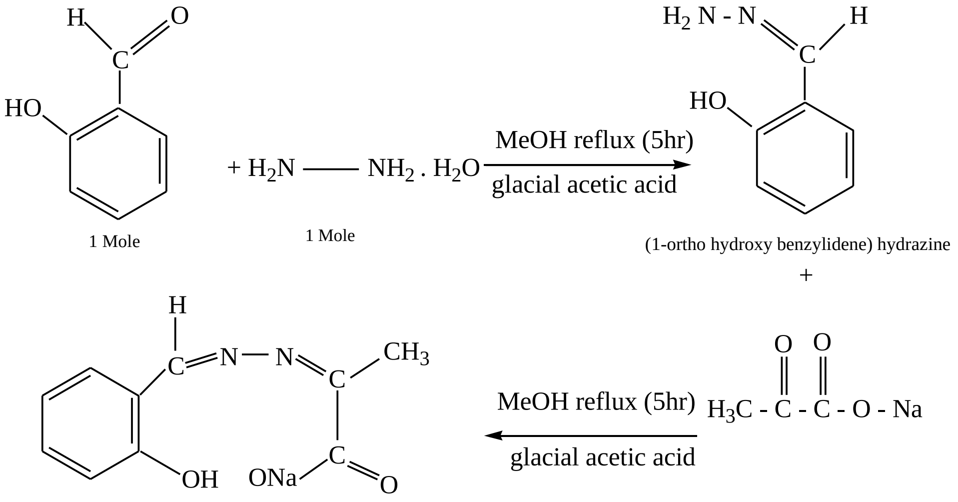
(Calc): Calculated.

Dec: Decomposition.

Fig. (2), display a broad band at 3450 cm^{-1} which is due to the υ (O-H) stretching of the phenolic hydroxyl group (10). The band at 1708cm^{-1} is attributed to the υ (C=O) stretching vibration (11).The two bands at 1630 and 1573cm^{-1} are attributed to υ (N=C-CH3) and υ (N=C-H) stretching frequency for the imine group vibration (12-14).The sharp band at 983 is attributed to (N-N) stretching stretching vibration (15). (U.V-Vis) spectrum.

shifting of υ (N=C-H) group appeared in the lower frequency at 1541,1545, 1541 and 1540cm^{-1}, showing a reducing in the bond order. This can be attributed to delocalization of metal electrons density at (t2g) in the π

Fig.(3) exhibits a high intense absorption peaks at (293 nm) (34129 cm^{-1}) (ε_{max} = 1815 molar $^{-1}$.cm^{-1}),(344) nm (29069 cm^{-1}) (ε_{max} = 2287 molar $^{-1}$.cm^{-1}) and (372) nm (26881cm^{-1}) (εmax 1180 molar $^{-1}$.cm^{-1}) which assigned to overlap of (π →π*), (n →π*) and (n →π*) transitions (16).



Scheme (1) Preparation of the ligand [NaHL].

The synthesis of the complexes was carried out by the reaction of [NaHL] with [$MCl_2.H_2O$] where M= [Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}] in methanol under reflux. The analytical and physical data (Table-1) and spectral data Table (3) are compatible with the suggested structures. The (I.R) spectra of complexes are presented in Table (2). In general the (I.R) spectra of the complexes show a band at 1623,1620,1626, and 1625 cm^{-1} which are due to υ(C=O) stretching vibration for compounds (1),(2),(3) and (4) respectively. These bands has been shifted to lower frequency in comparison to that of the free ligand at 1708cm^{1}(17,18).This can be attributed to delocalization of metal electrons density into π-orbital of the ligand and formation of π–back bond (dπ -pπ) (19).The strong band in free ligand [NaHL] at 1630 cm^{-1} for the imine group υ (N=C-CH3) was shifted to lower frequency and appeared at 1571,1574,1583 and1573 cm^{-1} for compounds (1),(2),(3) and (4) respectively (13-15). In the same way the

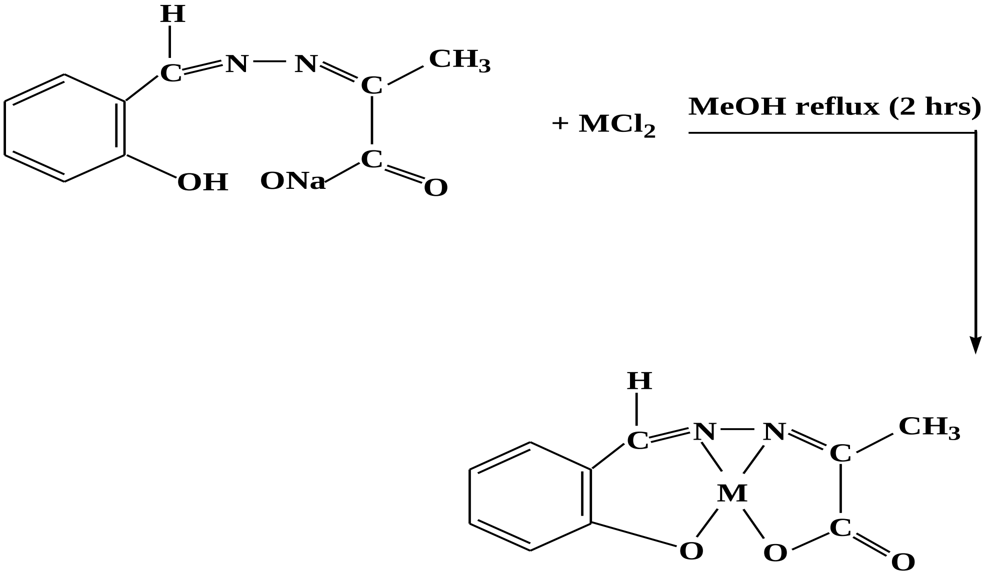
system of the ligand (HOMO → LUMO) (20), where:

HOMO = highest occupied molecular orbital.

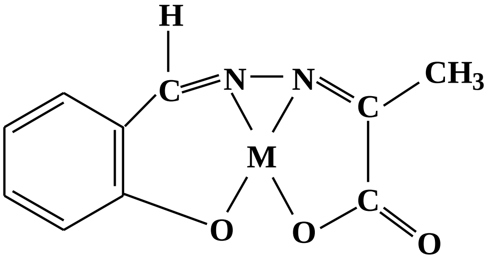
LUMO = lowest unoccupied molecular orbital.

While the bands at (1471-1446),(1487-1471),(1487-1471) and(1480-1472) cm^{-1} which are due to υas(COO^{-}) and υs(COO^{-}) stretching vibration for all compounds. The bands at 1031,1025,1028and 1030 cm^{-1} were assigned to υ (N-N) stretching vibration (15) in all complexes. The bands at (489-565),(565 -586) (532-590) and (565-584) cm^{-1} were assigned to υ(M-N) for compounds indicating that the imine nitrogen is in addition to the oxygen involved in coordination with metal ions (21-23). The bands at (422-459), (422 -459), (459-499) and (405-459) cm^{-1} were assigned to υ(M-O) for compounds (1),(2),(3) and (4), indicating that the phenolic oxygen of the ligand is involved in coordination with metal ions (23,24) Figs.(2a) and (2c) represent the (I.R) spectra of [Co(L) and [Cu (L)].The

(U.V-Vis) spectra for the complexes (1), (2), (3) and (4) are shown in Figs.(3a),(3b),(3c) and (3d). The absorption data for complexes are given in Table (3). In general, the spectra show two intense peaks in the U.V region at (300,322), (299,344), (300,343) and (293,344) nm for complexes (1), (2), (3) and (4) respectively. These peaks were assigned to ligand field and charge transfer transition (25). Besides that other bands appear. Complex (1) exhibited peak at 608 nm, which can be attributed to (d-d) transition type ($^4A_2 \rightarrow {}^4T_{1\,(p)}$). The observed peak in spectrum of complex (2) is at 411 nm is assigned to (d-d) transition type($^3T_2 \leftarrow {}^3T_1$). The spectra of complexes (3) exhibited peak at 404 nm. They can be attributed to (d-d) transition type ($^2B_2 \leftarrow {}^2E$). A relative shifting in the band of complexe (4) this is due to (d^{10}) configuration of metal ions. These U.V-Vis data suggest a tetrahedral configuration around the metal ion for the four studied complexes (26). Fig (1). The molar conductance values determined in (DMF) solution (10^{-3} M) were found in the range (5.31-11.29) $S.cm^2.mole^{-1}$ Table (3) which indicates that the complexes are non-electrolytes (27). The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with suggested formula [M(L)].



Scheme (2) Preparation of the metal complexes.



M^{II}=Co, Ni,Cu and Zn

Fig. (1) : The suggested structure for the complexes.

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

Compound	υ (O-H) phenol	υ(C=O)	υ (N=C- CH3)	υ (N=C-H)	υ(COO⁻)	υ (N-N)	M-O M-N	Othor bands
[L]	3450	1708	1630	1573	as 1488 s 1448	983	- -	υ (C=C) 1406 υ (c-H) alph2985 υ (C-H) arom3045
[Co(L)]	-	1623	1571	*1541*	as 1471 s1446	1031	422 459 489 565	υ (C=C) 1388 υ (c-H) alph 2848 3043υ (C-H) arom
[Ni (L)]	-	1620	*1574*	*1545*	as 1487 s 1471	1025	422 459 565 586	υ (C=C) 1388 υ (c-H) alph 2844 υ (C-H) arom 3043
[Cu(L)]	-	1626	*1583*	*1541*	as 1487 s 1471	1028	459 499 532 590	υ (C=C) 1386 υ (c-H) alph 2846 υ (C-H) arom 3042
[Zn (L)]	-	1625	*1573*	*1540*	as 1488 s 1470	1030	404 459 565 584	υ (C=C) 1388 υ (c-H) alph 2844 υ (C-H) arom 3040

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

Compound	λ nm	Wave number Cm^{-1}	ε_{max} Molar Cm^{-1}	Assignment	Λm $(\Omega^{1}.cm^{2}.Mole^{-1})$	Propose structure
[L]	293	34129	2815	$\pi \rightarrow \pi^*$	-	-
	344	29069	2287	$n \rightarrow \pi^*$		
	373	26809	1196	$n \rightarrow \pi^*$		
[Co(L)]	300	33333	1864	Ligand field	11.29	tetrahedral
	322	31055	1902	charge transfer		
	608	16447	416	$^{4}T_{1(P)} \leftarrow {}^{4}A_{2}$		
[Ni (L)]	299	33444	2152	Ligand field	7.12	tetrahedral
	344	29069	2004	charge transfer		
	411	23430	1846	$^{3}T_{2} \leftarrow {}^{3}T_{1}$		
[Cu(L)]	300	33333	2437	Ligand field	5. 31	tetrahedral
	343	29154	2302	charge transfer		
	404	24752	549	$^{2}B_{2} \leftarrow {}^{2}E$		
[Zn (L)]	293	34129	1625	Ligand field	10.25	tetrahedral
	310	32258	1136	Ligand field		
	344	29069	1651	charge transfer		
	367	27247	979	charge transfer		

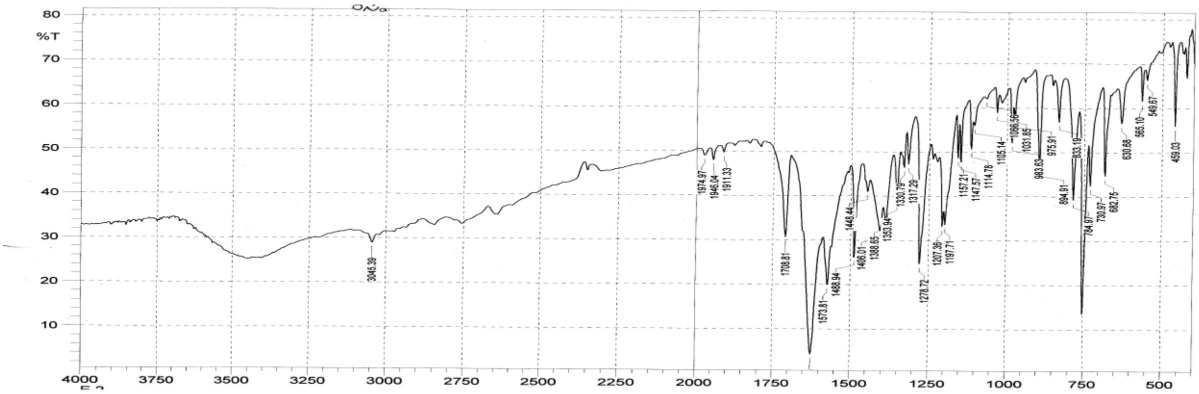


Fig.(2) : The I.R. Spectrum of the ligand [NaHL].

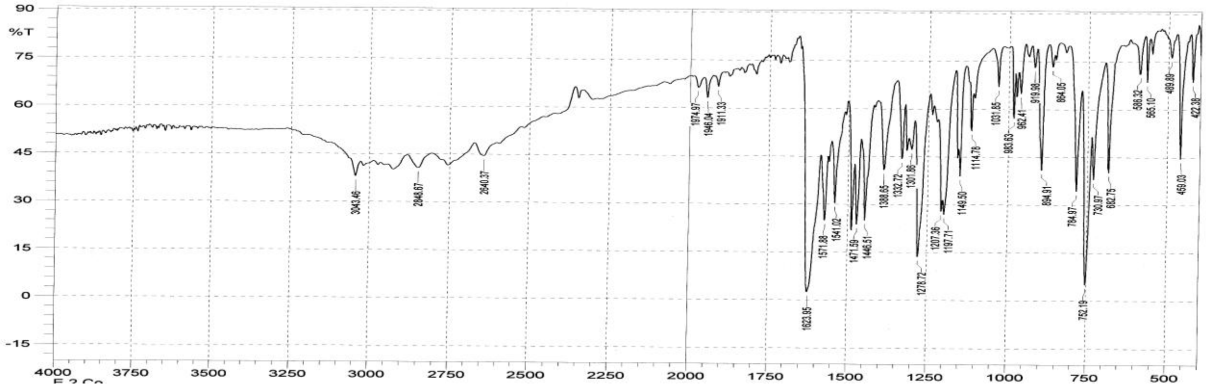


Fig. (2a) : The I.R. Spectrum of the [Co(L)].

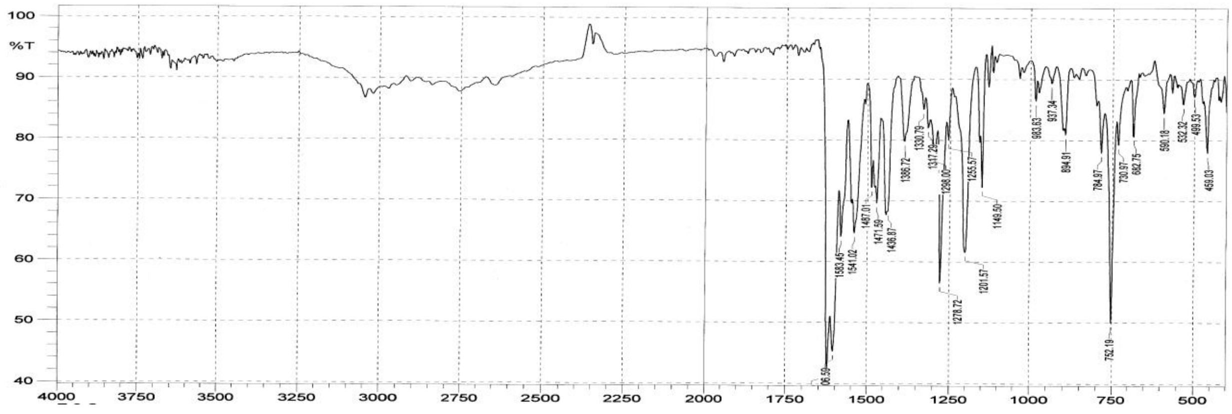


Fig. (2c) : The I.R. Spectrum of the [Cu(L)].

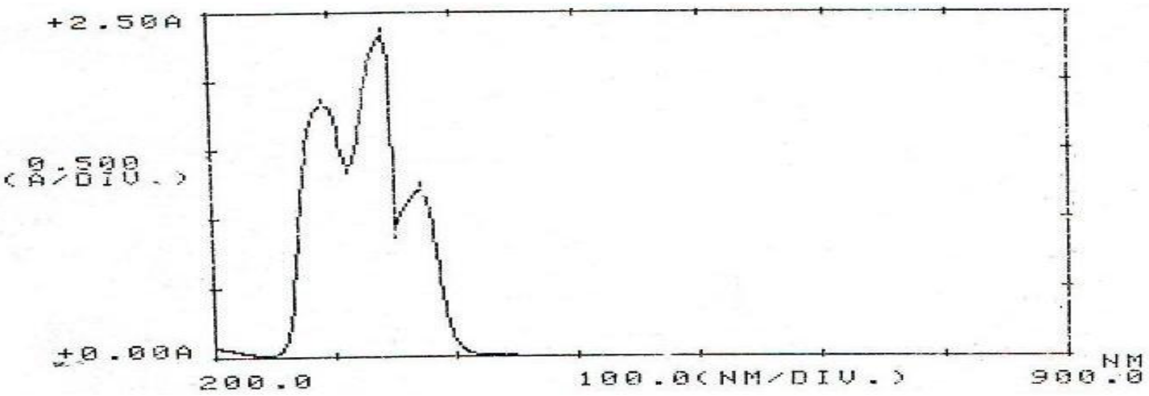


Fig. (3) : The U.V. Spectrum of the ligand [NaHL].

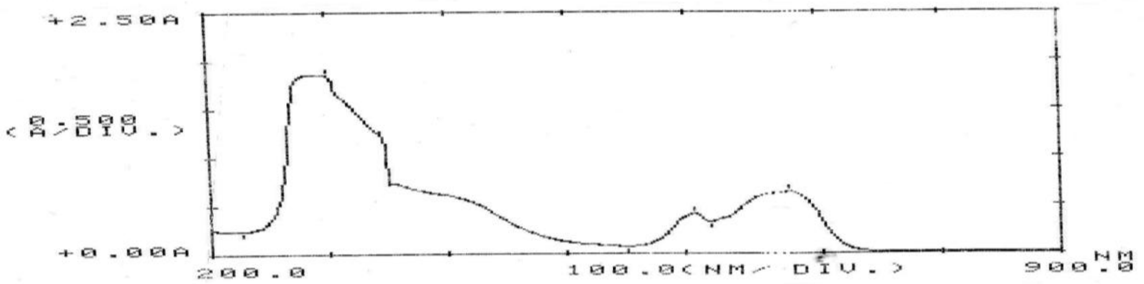


Fig. (3a) : The U.V. Spectrum of the[Co(L)].

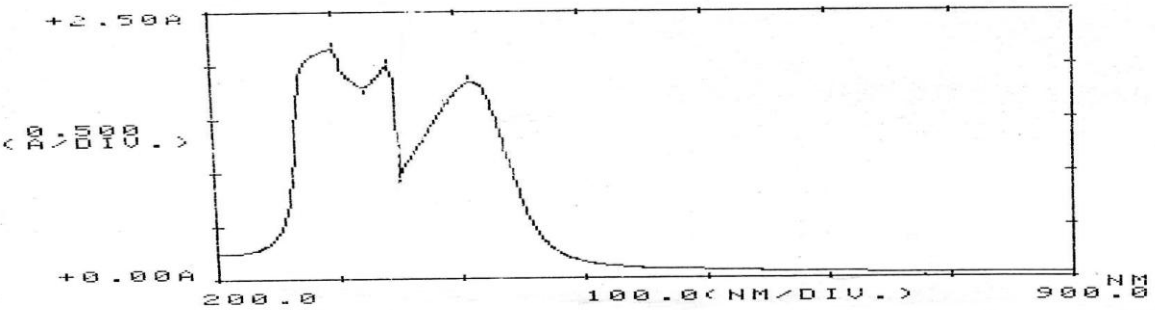


Fig. (3b) : The U.V. Spectrum of the [Ni(L)].

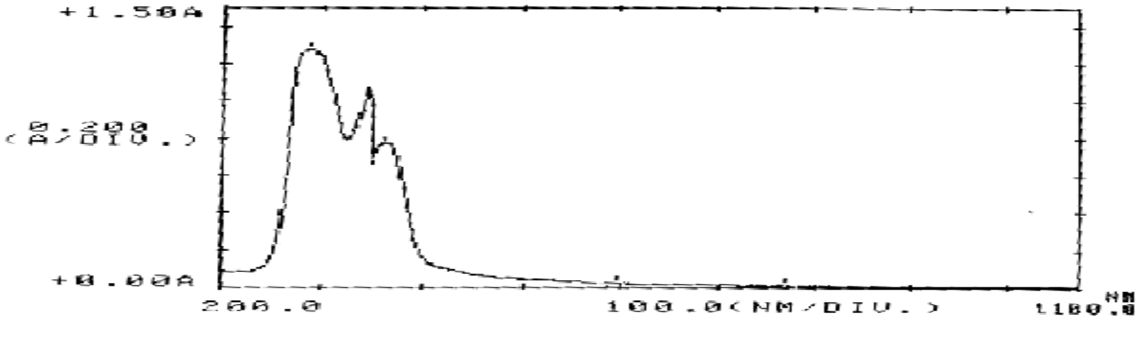


Fig. (3c) : The U.V. Spectrum of the [Cu(L)].

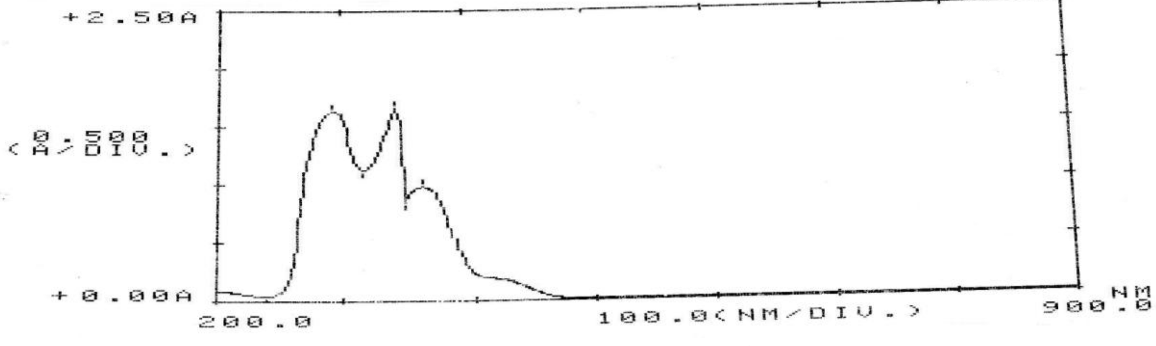


Fig. (3d) : The U.V. Spectrum of the [Zn(L)].

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الخلاصة

تضمن البحث تحضير الليكاند الجديد [2-Sodium pyruvalidene hydrazine,1-(ortho hydroxy benzylidene)] بخطوتين:

الخطوة الاولى : مفاعلة (salicyladehyed) مع(hydrazine monohydrate) وتكوين[(1-ortho hydroxy benzylidene) hydrazin]

والخطوة الثانية: من مفاعلة ناتج الخطوة الاولى مع Sodium pyruvate [2-Sodium pyruvalidene hydrazine,1-(ortho hydroxy benzylidene)] لتحضير الليكاند الجديد ثم مفاعلة مع بعض العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (1:1) و بوجود حامض الخليك الثلجي حيث تكونت معقدات جديدة ذوات الصيغ العامة:

[M(L)]

حيث:

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

شخصت جميع الم10ركبات بالطرق الطيفية التالية (الأشعة تحت الحمراء والأشعة فوق البنفسجية – المرئية ومطيافية الامتصاص الذري للعناصر ومحتوى الكلور ودرجات الانصهار) , مع قياس التوصيلية المولارية الكهربائية. من النتائج أعلاه تم اقتراح الشكل الفراغي للمعقدات المحضرة على انها رباعية السطوح.