Synthesis and Characterization of Novel Tetradentate ligand Type N4 and its Complexes With Co^{II},Ni^{II},and Pd^{II}.

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Abstract

A new Schiff base ligand [2,3,8,9–tetra -phenyl-1,4,5,7,10,12-hexa azo-5,12-dihydro -6,11- dione 1,3,7,10-dudec-tetra-ene] [H2L] and its complexes In general formula [M(H2L)]Cl2 (where : M= Co^{II}, Ni^{II}, and Pd^{II}) were prepared. This ligand was prepared in two steps,in the first step a solution of benzil in methanol was reacted under reflux with semicarbazidhydrochlorid to give an (intermediate compound)[benzyl bis–(Semicarbazone)] which was reacted in the second step with benzil giving the mentioned ligand. The complexes Co^{II}, Ni^{II}, and Pd^{II} were synthesized by direct reaction of the corresponding metal chloride with the ligand [H2L].The ligand and complexes were characterized by spectroscopic methods (IR, UV-Vis, and atomic absorption), chloride content and conductivity measurement.From the data of these measurements, we suggestred a tetrahedral geometry for Co^{II}, Ni^{II} complexs and a square planar for Pd^{II} complex.

Introduction

Schiff bases derived from condensation of semicarbazide with carbonyl compounds were reported as complexing agents for various transition metal ions. 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 2006 kurup and Co-workers [8]reported that the reaction of 2- benzoyl pyridine N(4)-phenylthiosemicarbazone with variety of cupper salts yielded a series of cupper (II) complexes. The present paper reports the synthesis and characterization of new ligand [2,3,8,9-tetra-phenyl-1,4,5,7,10,12-hexa azo-5,12-dihydro-6,11-dione-1,3,7,10-dudec-tetra-ene] [H2L] and its complexes with Co^{II}, Ni^{II} and Pd^{II}.

Experimental

Reagents were purchased from Fluka and Rediel – Dehenge Chemical Co.I.R spectra were recorded as (KBr) disc by 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 $25^{0}C$ 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 by using a Shimadzu A.A 680G atomic absorption spectrophotometer. The chloride contents for complexes were determined by potentiometric titration method on (686-titro processor-665) ,Dosinat-metrom Swiss.Electrical conductivity measurements of the complexes were recorded at 25^0C for 10^{-3}M solutions in (DMSO) as a solvent by using a PW 9526 digital conductivity meter.

Synthesis of the ligand [H2L]

The ligand was prepared in two steps.

Step(1): Preparation of the [benzil bis -(Semicarbazone)] (intermediate compound).

A solution of benzil (0.5g,2.37mmole) in methanol (5ml) was added to semicarbazidhydrochlorid (0.53g,2.37mmole) dissolving in methanol (5ml),and then(2-4) drops of glacial acetic acid were added slowly to the reaction mixture .The mixture was refluxed for 5 hours, and allowed to dry at room temperature for (24) hours. A white solid materal was obtained. Yield (89%),(0.69)g, m.p (215^0C).

Step(2): Preparation of the [2,3,8,9-tetra-phenyl-1,4,5,7,10,12-hexa azo-5,12-dihydro-6,11-dione-1,3,7,10-dudec-tetra-ene] [H2L].

A solution of [benzil bis-(Semicarbazone)](intermediatecompound)(0.5g,1.543 mmole) in methanol (5 ml) was added to benzil (0.32g, 1.543mmole) dissolving in methanol (5ml), then (2-4) drops of glacial acetic acid were 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 for (48) hours. Then , it was washed with (5)ml diethyl ether and dried at room temperature to give the white solid materal. Yield (77%), (0.59) g ,m.p (235^0C).

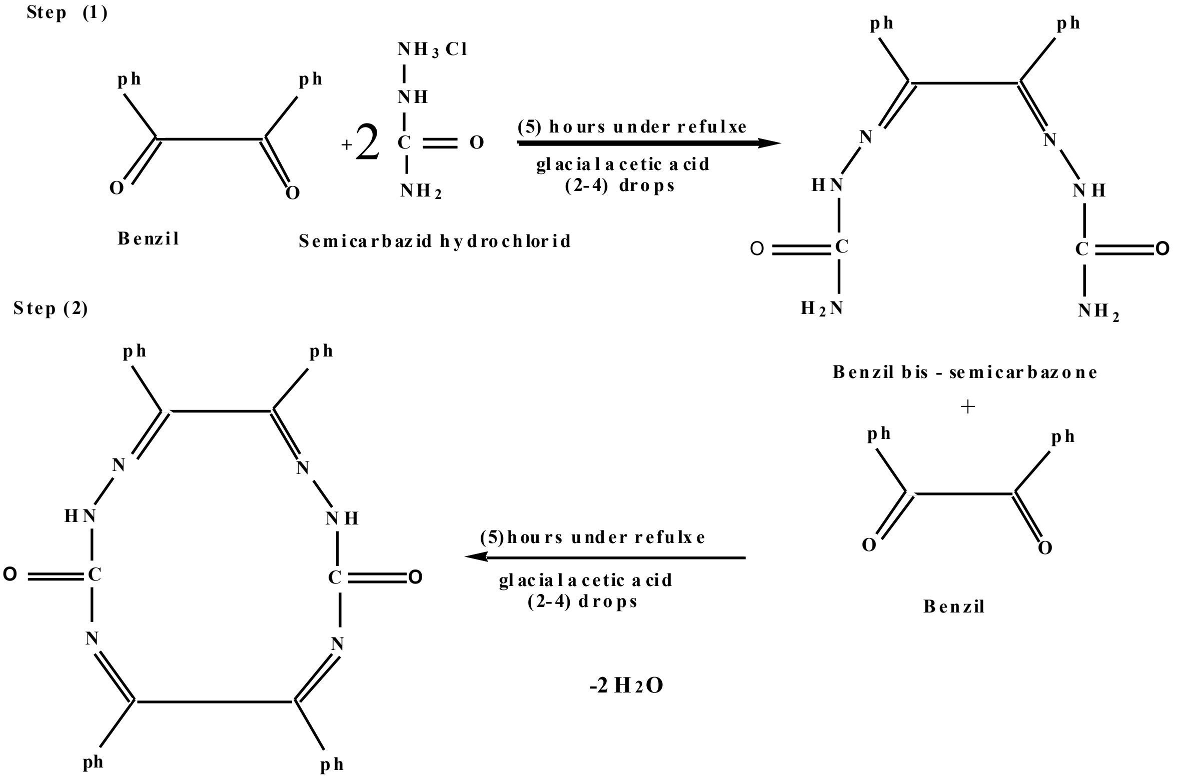
Synthesis of complexes

All complexes were prepared by adding a dropwise of a solution of the ligand (H_2L) (0.1g,0.2008mmole)in (5) ml methanol with stirring ,to 0.2008mmole of a solution of metal chloride salt $MCl_2.XH_2O$ dissolved in(5) ml methanol ,where:[M=Co^{II},Ni^{II} and Pd^{II};X=6 for Co^{II},Ni^{II} and X=0 for Pd^{II}]. The reaction mixture was allowed to be refluxed for (2)hrs , let the coloury precipitate formed which was filtered,washed with (5) ml diethyl ether and dried at room temperature.Table(1)shows the stated weight of metal chloride salt ,% yield and some physica properties of the prepared complexes.

Results and Discussion

A-The ligand [H2L]

The new ligand [H2L] was prepared in two steps according to the general method of preparation of Schiff base ligands [9] shown in scheme (1).The (I.R) spectrum for [H2L] (Fig. -2) , display a band at 3209 cm^{-1} which is due to the υ(N-H) stretching vibration [10]. The band at 1687 cm^{-1} is attributed to the υ(C=O) stretching vibration [11].The band at 1612 cm^{-1} is attributed to υ (C=N) stretching frequency for the imine group vibration [12-13],while the two bands at 1025 cm^{-1} and 935 cm^{-1} were attributed to the foramation of macrocycle [14] .And finaly , the band at 1062 cm^{-1} is attributed to (N-N) stretching vibration [15].The (U.V-Vis) spectrum(Fig.-3) exhibits a high intense absorption peak at (300 nm) (33333 cm^{-1}) (ε_{max} = 2128 $molar^{-1}.cm^{-1}$) which is assigned to overlap of ($n \rightarrow \pi^*$) electronic transitions [16].



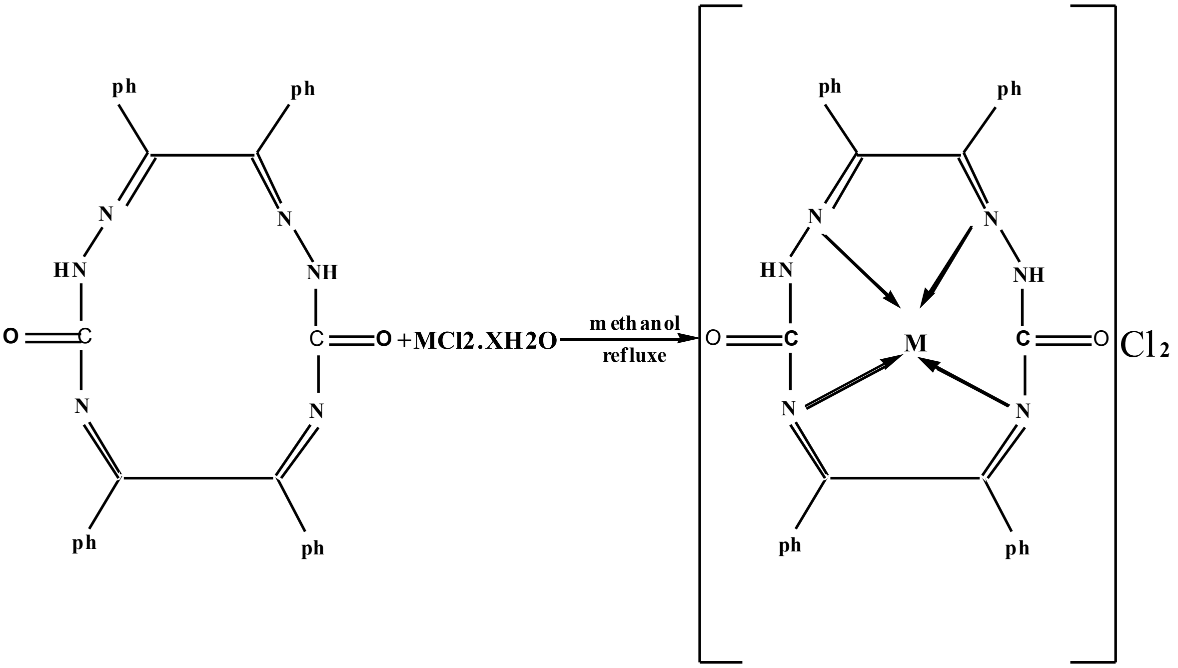
Scheme (1) : Preparation of the ligand [H2L]

B- Complexes of Co^{II}, Ni^{II} and Pd^{II} with [H2L]

The synthesis of the complexes was carried out by the reaction of [H2L] with $[MCl_2.XH_2O]$ where M= [Co^{II} ;X=6, Ni^{II} ;X=6 and Pd^{II} ;X=0] in methanol under reflux. These complexes are stable in solution and electrolyte (1:2) systems in (DMSO) (Table-3).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). The (I.R) spectra of the complexes show a band at 1679 ,1675 and 1670 cm^{-1} which are due to υ(C=O) stretching vibration for complexes (1) , (2) and (3) respectively. These bands were shifted to a lower frequency in comparison with that of the free ligand at 1687 cm^{-1}[17,18]. The strong band in free ligand [H2L] at 1612 cm^{-1} for the imine group υ (C=N) was shifted to a lower frequency and appeared at 1602,1605 and 1598 cm^{-1} for complexes (1),(2) and (3) respectively [12-14], showing a reducing in the bond order. This can be attributed to delocalization of metal electronic density at (t2g) in the π system of the ligand (HOMO → LUMO) [19].

Where HOMO = highest occupied molecular orbital.
LUMO = lowest unoccupied molecular orbital.

While the bands at 1074,1087 and 1085 cm^{-1} were assigned to υ (N-N) stretching vibration (15) in the complexes(1), (2) and (3) which were shifted to a higher frequency when it compared with free ligand. The appearance of the band at 698-507 cm^{-1} is due to υ(M-N) stretching .This suggests that the nitrogen of imine group was involved in coordination with the metal ion [20-23].Figs.(2a),(2b) and (2c) represent the (I.R) spectra of$[Co (H2L)]Cl_2$, $[Ni (H2L)]Cl_2$ and $[Pd (H2L)]Cl_2$.The (U.V-Vis) spectra for the complexes (1), (2) and (3) are shown in Figs.(3a) ,(3b) and (3c). The absorption spectral data for complexes are given in (Table -3). The spectra show two intense peaks in the U.V region at (300,357), (300,361) and (300,371) nm for complexes (1), (2) and (3) respectively. These peaks were assigned to ligand field and charge transfer transition respectively (24).Complex (1) exhibited the peak at 609 nm which can be attributed to (d-d) electronic transition type ($^4A_2 \rightarrow {}^4T_{1(p)}$). The observed peak in spectrum of complex (2) at 420 nm is assigned to (d-d) electronic transition type ($^3T_1 \rightarrow {}^3T_2$) . The spectrum of complexe (3) exhibited the very intense peak at 412 nm which can be attributed to (d-d) electronic transition type ($^1A_1 \rightarrow {}^1B_1$). These U.V-Vis data suggest a tetrahedral structure for Co^{II} ,Ni^{II} complexes and a square planar for Pd^{II} complexe [25]. (Fig.-1). The molar conductance values were determined in (DMSO) solution (10^{-3} M) at 298^5 k were found in the range (72.03-79.11) Λm (Ω.cm^2.Mole^{-1}) (Table-3) which indicated that the complexes are electrolytic in nature with 1:2 ratio for all complexes [26]. The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with the suggested formula [M (H2L)]Cl_2.



M=Co^{II}, Ni^{II} and Pd^{II}

Scheme (2) : Preparation of the metal complexes

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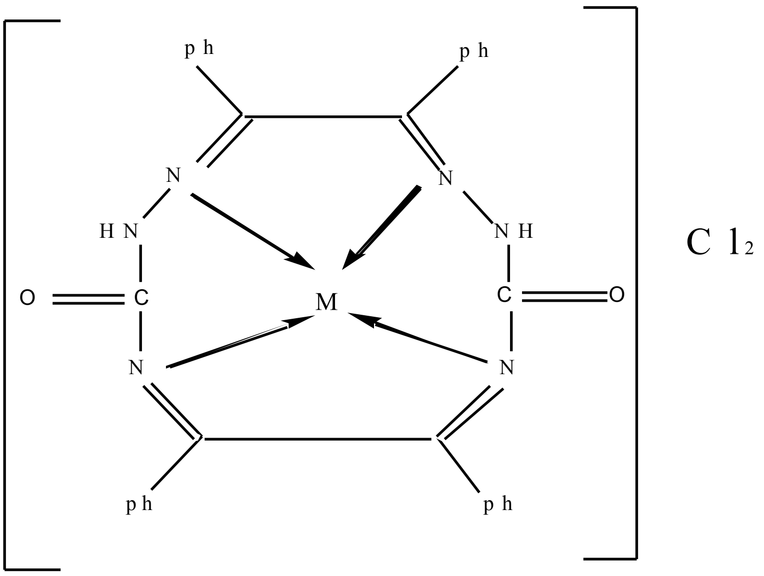

M=Co^{II}, Ni^{II} and Pd^{II}

Fig (1): The suggested structure for the complexes

Table(1): Some physical properties of the complexes and the weight of metal chloride salt.

complexes	decomposition temperature ^{0}C	M.W	Colour	metal chloride Salt	Weight of metal chloride(g) =0.2008 mmole	Weight of product g	Yield %	chloride content	Metal ion % Prac. (Theo.)
[Co (H_2L] Cl_2	295	627.83	pink	$CoCl_2$.6H2O	0.04	0.11	87	Nill	8.11 (9.386)
[Ni (H_2L)] Cl_2	270	627.59	green	$NiCl_2$.6H2O	0.047	0.1	79	Nill	7.97 (9.351)
[pd (H_2L)] Cl_2	255	675.3	Pale pink	pd Cl_2.	0.035	0.12	88	Nill	14.13 (15.755)

Table (2): I.R spectral data of the ligand and it's complexes (cm^{-1}).

Compound	υ (N-H)	υ(C=O)	υ (C=N)	υ (N-N)	υ (M-N)	Othor bands
$[H_2 L]$	3209	1687	1612	1062	-	υ (C=C) 1444 υ (c-H) alph 2925 υ (C-H) arom 3047
$[Co (H_2L] Cl_2$	3217	1679	1602	1074	613 698	υ (C=C) 1446 υ (c-H) alph 2898 υ (C-H) 3060 arom
$[Ni (H_2L)] Cl_2$	3220	1675	1605	1087	603 636	υ (C=C) 1431 υ (c-H) alph 2985 υ (C-H) arom 3053
$[Pd (H_2L)] Cl_2$	3215	1670	1598	1085	507 557	υ (C=C) 1442 υ (c-H) alph 2962 υ (C-H) arom 3074

Table (3) : Electronic spectral data , and conductance measurement for the ligand[H2L] and it's complexes

Compound	λ nm	Wave number Cm^{-1}	ε_{max} $Molar^{-1}.Cm^{-1}$	Assignment	$\Lambda m(\Omega.cm^2.Mole^{-1})$	Propose structure
$[H_2L]$	300	33333	2128	$n \rightarrow \pi^*$	–	–
$[Co(H_2L)]Cl_2$	300	33333	2111	Ligand field	77.55	tetrahedral
	357	28011	747	charge transfer		
	609	16420	121	$^4A_2 \rightarrow {}^4T_{1(p)}$		
$[Ni(H_2L)]Cl_2$	300	33333	2362	Ligand field	79.11	tetrahedral
	361	27700	870	charge transfer		
	420	23809	1846	$^3T_1 \rightarrow {}^3T_2$		
$[Pd(H_2L)]Cl_2$	300	33333	2123	Ligand field	72.03	Square planar
	371	26954	915	charge transfe		
	412	24271	611	$^1A_1 \rightarrow {}^1B_1$		

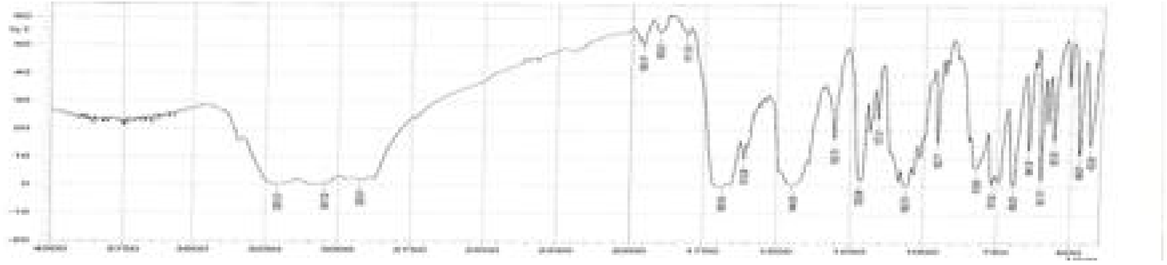

Fig. (2) .The I.R. Spectrum of the ligand [H2L]

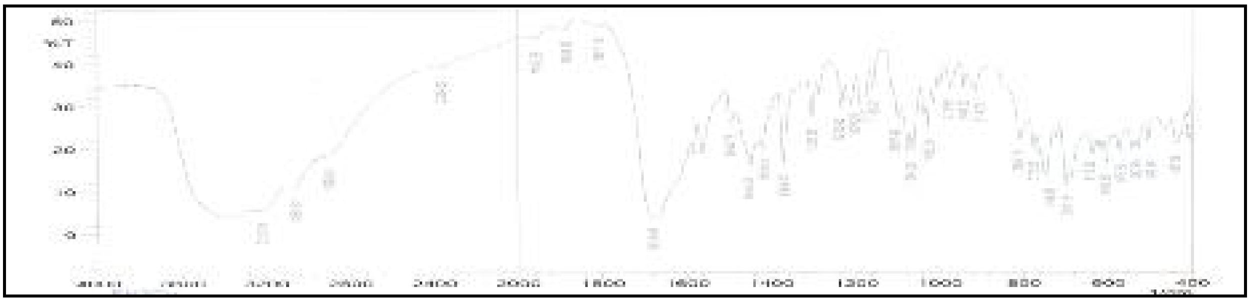

Fig. (2a) .The I.R. Spectrum of the [Co (H_2L)] Cl_2

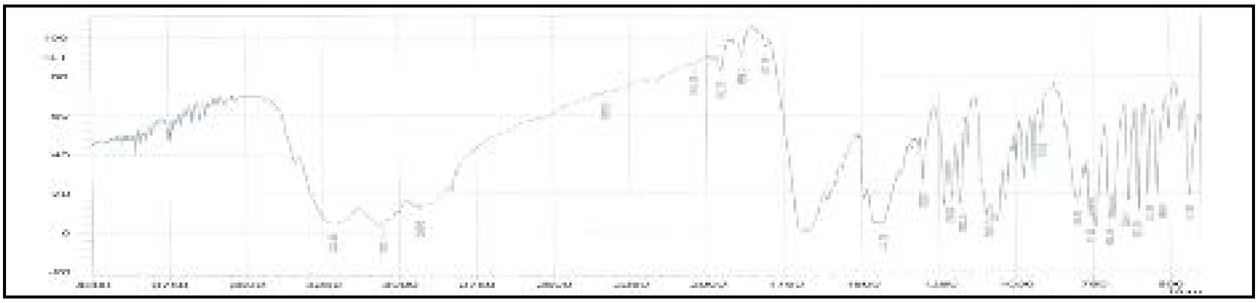

Fig. (2b) .The I.R. Spectrum of the [Ni (H_2L)] Cl_2

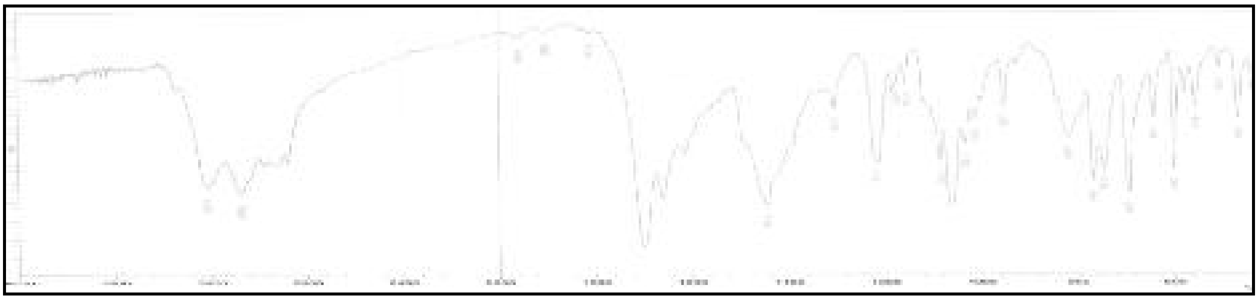

Fig. (2c) .The I.R. Spectrum of the [Pd (H_2L)] Cl_2

Fig. (3) .The U.V. Spectrum of the ligand [H2L]

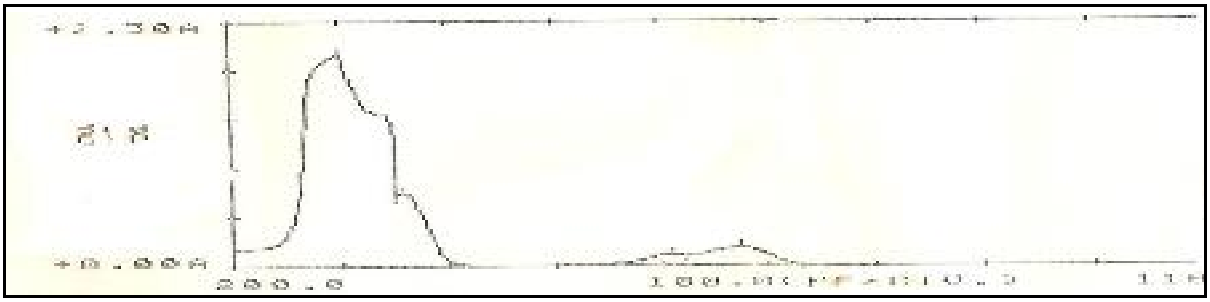

Fig. (3a) .The U.V. Spectrum of the [Co (H_2L)] Cl_2

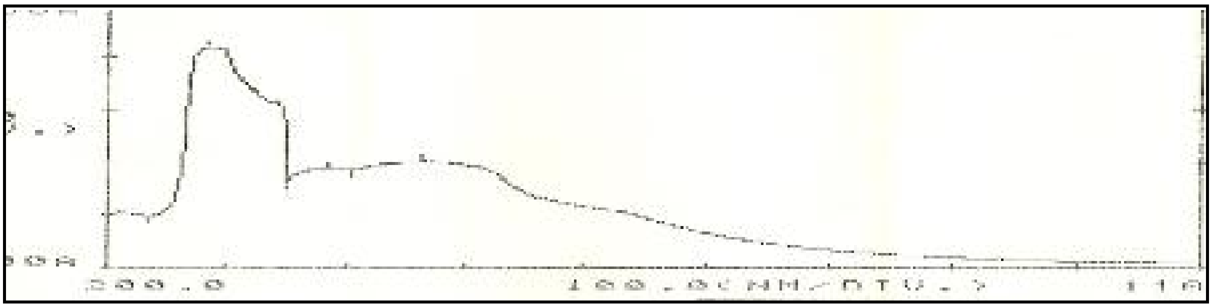

Fig. (3b) .The U.V. Spectrum of the [Ni (H_2L)] Cl_2

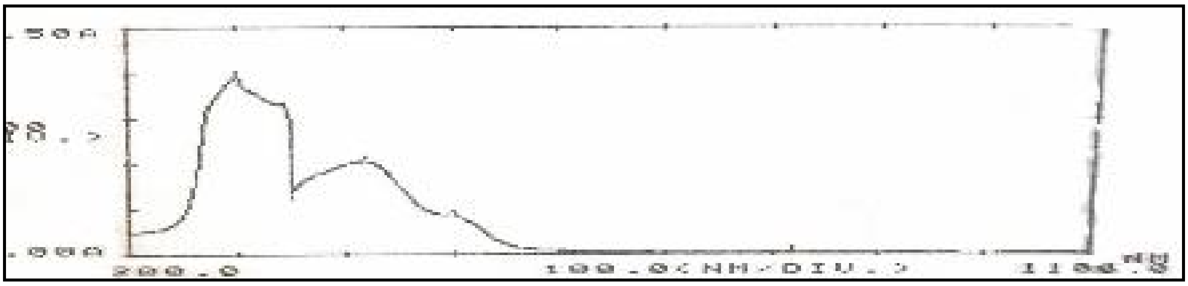

Fig. (3c) .The U.V. Spectrum of the [Pd (H_2L)] Cl_2

تحضير وتشخيص ليكاند رباعي السن جديد نوع N4 ومعقداته مع
Co^{II} , Ni^{II} and Pd^{II}

إنعام إسماعيل يوسف

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الخلاصة

تضمن البحث تحضير الليكاند الجديد[H2L]الذي يمثل :-
[2,3,8,9-tetra-phenyl-1,4,5,7,10,12-hexaazo-5,12-dihydro-6,11-dione-1,3,7,10-dudec-tetra-ene]
بخطوتين:

الخطوة الاولى مفاعلة (benzil) مع (semicarbazidhydrochlorid)

وتكوين [benzil bis -(Semicarbazone)]

والخطوة الثانية مفاعلة ناتج الخطوة الاولى مع (benzil)

لتحضير الليكاند الجديد[H2L]

ثم مفاعلة الليكاند [H2L] مع كل من Co^{II}, Ni^{II} and Pd^{II}

وباستعمال الميثانول وسطا للتفاعل وبنسبة (1:1) للحصول على معقدات جديدة ذوات الصيغة العامة:

$[M\ (H2L)]Cl_2$

اذ:

$M = Co^{II}, Ni^{II}$ and Pd^{II}

شخصت جميع المركبات المحضرة بالطرائق الطيفية الآتية: (الأشعة تحت الحمراء، والأشعة فوق البنفسجية – المرئية، ومطيافية الامتصاص الذري للعناصر) ومحتوى الكلور ودرجات الانصهار ، مع قياس التوصيلية المولارية الكهربائية. من نتائج التقنيات السابقة فان الشكل الفراغي المقترح لمعقدات الكوبالت و النيكل هو رباعي السطوح المشوه، بينما يتخذ البلاديوم شكل مربع مستو.