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Synthesis and Characterization of Macrocyclictetradentate Ligand Type N_2o_2 and its Complexes with ($Co^{(Ii)}$, $Ni^{(Ii)}$ And $Pd^{(Ii)}$)

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Abstract

The Schiff base ligand [2,3,8,9–tetra -methyl-1,4,5,7,10,12-hexa azo-5,12- dihydro -6,11- dione 1,3,7,10-dudec-tetra-ene] [H_2L] and its complexes with ($Co^{(II)}$, $Ni^{(II)}$ and $Pd^{(II)}$) was prepared in two steps. In the first a solution of (2,5-Hexandion) in methanol react under reflux with (semicarbazidhydrochlorid) in 1:2 mole ratio to give an intermediate compound [2,5-Hexandion bis (Semicarbazone)] which react in the second step with another mole of (2,5-Hexandion) giving the mentioned ligand. The complexes were then synthesized by direct reaction of the corresponding metal chloride with the ligand. The ligand and complexes have been characterized by spectroscopic methods [IR, (UV-Vis), HPLC and (A.A)], chloride content and conductivity measuremenst. The data of these measurements suggest a square planar geometry around $Ni^{(II)}$ and $Pd^{(II)}$ ions and a tetrahedral geometry around $Co^{(II)}$ ion.

Introduction

During the past two decades, considerable attention has been paid to the chemistry of metal complexes of Schiff bases containing nitrogen and oxygen as donor atoms (1,2).This may be attributed to their stability, biological activity(3) and potential application in many fields such as oxidation catalysis(4) and electrochemistry(5). Semi and thiosemicarbazones are widely reported to have biological activity both as free ligands and as metal complexes(6). On the other hand large number of complexes formed by macrocyclic Schiff bases with transition metals, but the number of macrocyclic complexing reagent as such, is much smaller(7). The most important results of extensive studies (syntheses, spectral, magnetic, voltametric and structural characteristics and biological activity) of metal complexes with pyredoxal semi, thio, isothiosemicarbazones have been reported (8). In 2008 bermejo studied Zn^{II}, Cu^{I} and Ag^{I} complexes of some semi and thiosemicarbazones with benzene and pyridin diacetyles(9). Nature of bonding, stereo chemistry and antimicrobial activiteis of p-vanillin semi and thiosemicarbazone have been studied(10). Isatin-thiosemicarbazone and its Cu(II) complexe related to the antiviral drug methisazone was prepared and characterized by different spectroscopic techniques (11). In this research we attend to study a macrocyclic system of semicarbazone and its complexes.

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 (4000-400) cm^{-1}. Electronic spectra of the prepared compounds were measured in the region (200-900) nm for 10^{-3} M solution in (DMSO) 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 spectrophotometer. The chloride contents for complexes was determined by potentiometric titration method on (686-titro processor-665), Dosinat-metrom Swiss. The (HPLC) chromatograms for the complexes were obtained using a Shimadzu 2020 chromatography. Electrical conductivity measurements of the complexes were recorded at 25^0C for $10^{-3}M$ solutions in (DMSO) as a solvent using a PW 9526 digital conductivity meter.

Synthesis of the ligand [H_2L]

Step(1): Preparation of the intermediate compound [2,5-Hexandion bis-(Semicarbazone)]. A solution of 2,5-Hexandion (0.5g, 4.348mmole) in methanol (5ml) was added to semicarbazidhydrochlorid (0.65g, 8.696mmole) dissolved in methanol (5ml), then(2-4) drops of glacial acetic acid was added slowly to the reaction mixture. The mixture was refluxed for 5 hrs, and allowed to dry at room temperature for (24) hrs. Brown solid was obtained. Yield (92%), (0.82g), m.p. (180°C).

Step(2): Preparation of the ligand [2,3,8,9–tetra -methyl-1,4,5,7,10,12-hexa azo-5,12- dihydro - 6,11- dione 1,3,7,10-dudec-tetra-ene] [H_2L]. A solution of [2,5- Hexandion bis–(Semicarbazone)] (0.5g, 2.450mmole) in methanol (5 ml) was added to (2,5-Hexandion) (0.27g, 2.450mmole) dissolved in methanol (5ml), then (2-4) drops of glacial acetic acid was added slowly to the reaction mixture. The reaction mixture was refluxed for 5 hrs with stirring, filtered and the filtrate was allowed to dry at room temperature for 48 hrs, washed with (5ml) diethylether to give the Brownish red solid. Yield (95%), (0.6g), m.p. (205°C).

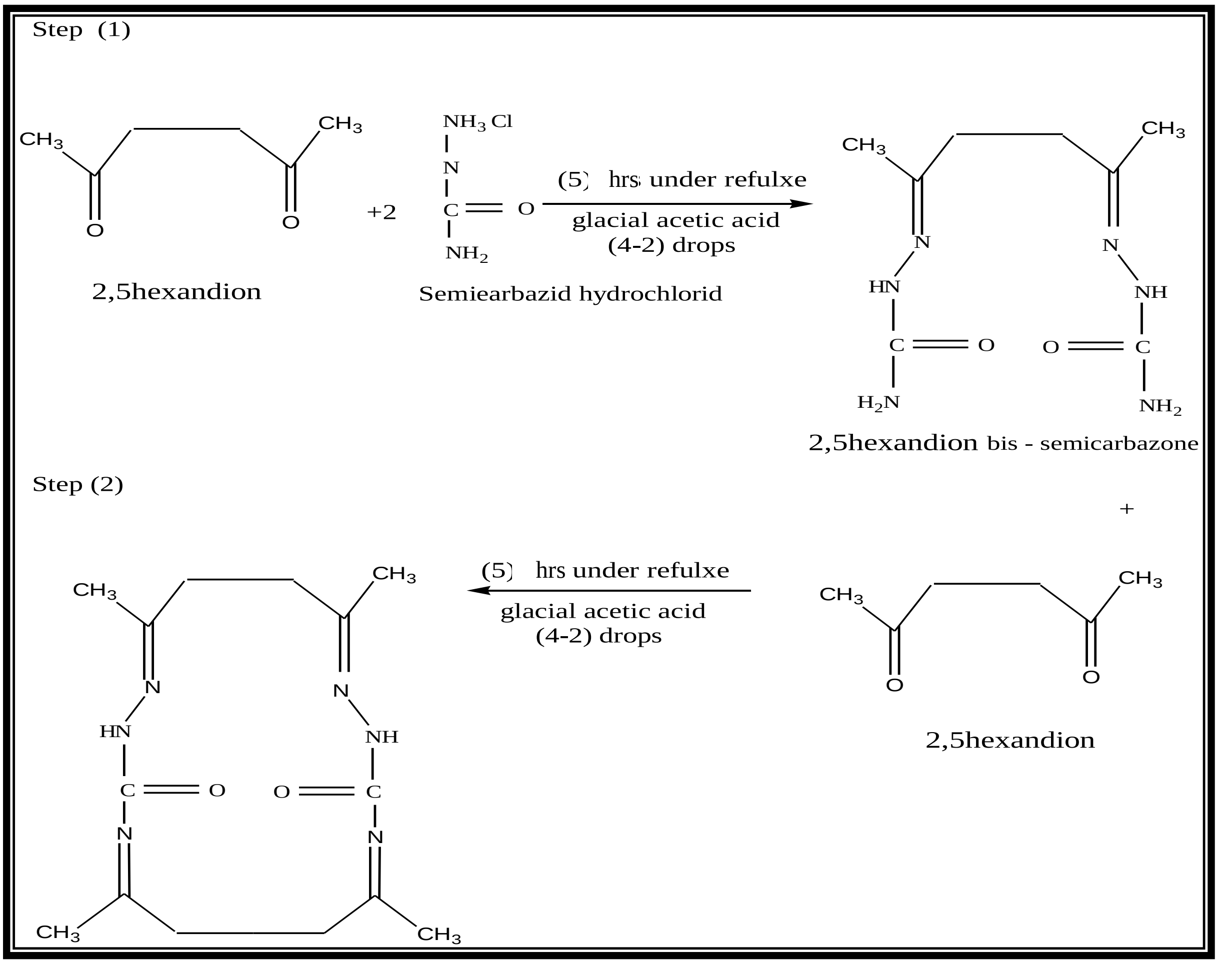
Synthesis of complexes

All complexes were prepared by adding dropwise a solution of the ligand [H_2L] (0.1g, 0.387mmole) in (5 ml) methanol with stirring to a solution of metal chloride $MCl_n.XH_2O$ dissolved in (5ml) methanol, where: [M= Co^{II}, Ni^{II} and Pd^{II}: X = 6, 6 and 0]. The reaction mixture was allowed to reflux for 2hrs until a coloury precipitate formed which was filtered, washed with (5ml) diethylether and dried at room temperature. Table (1) shows the stated weight of starting materials, yield and some physical properties of the prepared complexes.

Results and discussion

The ligand [H_2L] was prepared in two steps according to the general method of preparation of Schiff base ligands(12) shown in Scheme (1).The (I.R) spectrum for [H_2L] Fig.(2), displays a band at 3190 cm^{-1} which assigned to the υ(N-H) stretching vibration, while the band at 1689 cm^{-1} can be attributed to the υ(C=O) stretching vibration(13). The band at 1602 cm^{-1} was attributed to υ(C=N) stretching vibration of imine group (14-16). Finally the band at 1035 cm^{-1} can be attributed to υ(N-N) stretching vibration(17). (U.V-Vis) spectrum, Fig.(3) exhibits a high intense absorption peak at (282 nm) (35461 cm^{-1}) (ε_{max} =1876 $molar^{-1}.cm^{-1}$) which assigned to overlap of ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions (18).

The ^1H NMR spectrum of the ligand [H_2L] is shown in Fig. (3). The spectrum reveales that the N (2) *H* resonance is found as a sharp singlet at lower field (9.95ppm) consistent with its interaction with DMSO-d_6. The resonance is equivalent to two protons. The proton resonance of the four methyl groups are equivalent and appears as a sharp singlet at (δ=1.9ppm). The resonance is equivalent to twelve protons. Also the protons resonance of the four methylene groups are equivalent and found as a sharp singlet at (δ=3.1ppm). The resonance is equivalent to eight protons(19), the results are summerised in Table (4).

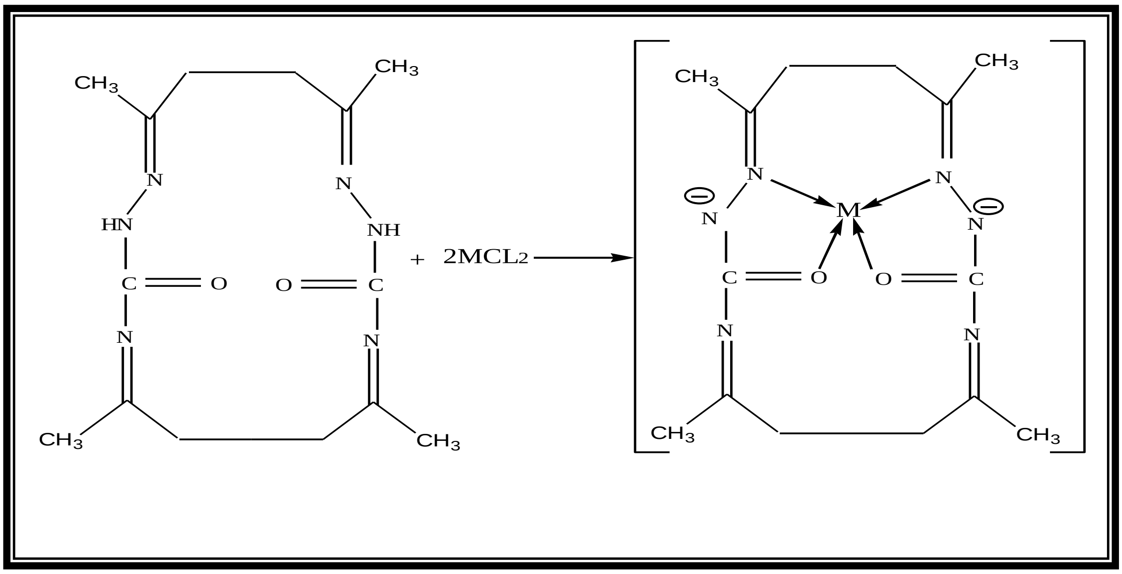


Scheme (1) Preparation of the ligand [H_2L].

The synthesis of the complexes was carried out by the reaction of [H_2L] with [$MCl_2.H_2O$] [where; M = (Co, Ni and Pd)] in methanol under reflux. The analytical and physical data (Table-1) and spectral data (Table (2) and (3)) are compatible with the suggested structures. Figs.(2a),(2b) and (2c) represent the (I.R) spectra of [Co(H_2L)](1), [Ni (H_2L)](2) and [pd(H_2L)](3) complexes respectively. The spectra show bands at 1677, 1679 and 1680 cm^{-1} for compounds (1), (2) and (3) respectively, assigned to υ(C=O) stretching vibration. These bands has been shifted to lower frequency in comparison to that of the free ligand at 1687 cm^{-1}(20), this can be attributed to the delocalization of metal electrons density into π-orbital of the ligand and formation of π–back bond (dπ -pπ)(21). The shift indicates involving of the oxygen atoms in the coordination with the metal center. The strong band in free ligand [H_2L] at 1650 cm^{-1} for the imine group υ (C=N) was shifted to higher frequency and appeared at 1660, 1657 and 1663 cm^{-1} for compounds (1),(2) and (3) respectively, this can be attributed to the weak coordination between the metals and Nitrogen atom(22-27). Comparison of the ligand spectrum with the complexes spectra shows no changes in azomethin band υ (C=N) at 1612 cm^{-1} indicating that the two lower azomethine groups did not coordinate to metal ions. This may be belong to the difficult of formation of four member ring.

The bands at 1033,1030 and 1025 cm^{-1} were assigned to υ (N-N) stretching vibration(17) in the complexes (1), (2) and (3) respectively. The appearance of the bands at 759-574 cm^{-1} and 594-401cm^{-1} are due to υ(M-N) and υ(M-O) stretching respectively suggesting that the oxygen atom in addition to the nitrogen are involved in coordination with the metal ion. The (I.R) spectral data of the complexes are presented in (Table (2)).

The (U.V-Vis) spectra for the complexes (1), (2) and (3) are shown in Figs.(3a), (3b) and (3c) respectively. The absorption data for complexes are given in (Table (3)). Each spectrum shows two intense peaks in the U.V region at (278 and 369nm); (285 and 385nm) and (284 and 371nm) for complexes (1), (2) and (3) respectively, these peaks were assigned to ligand field and charge transfer transitions(27). Complex (1) exhibited peaks at 608 and 680 nm, which can be attributed to (d-d) transition type ($^4A_2 \rightarrow ^4T_{1(p)}$). The observed peak in spectrum of complex (2) at 465 nm is assigned to (d-d) transition type ($^1A_{1g} \rightarrow ^1A_{2g}$).The spectrum of complexes (3) exhibited very intense peak at 412 nm which can be attributed to (d-d) transition type ($^1A_{1g} \rightarrow ^1B_{1g}$). These U.V-Vis data suggest a tetrahedral structure to $Co^{(II)}$ and a square planar to $Ni^{(II)}$ and $Pd^{(II)}$ions (28), Fig.(1). The molar conductance values determined in (DMSO) solution (10^{-3} M) were found in the range (42.0-51.1) Λm ($\Omega^1.cm^2.Mole^{-1}$) (Table (3)) which indicates that the complexes are non electrolytes (27). The (H.P.L.C) results of the complexes are presented in Table (3).Figs.(4a and 4b) exhibit the chromatograms of [Co (H_2L)] and [Ni (H_2L)] complexes which show one signal at (t_R = 5.949 and 6.020 min) respectively, indicating the purity of the complexes and appear as a single species in solution. The atomic absorption analysis and the chloride content results of the complexes are in a good agreement with suggested formula [M(H_2L)].



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

Scheme (2) Preparation of the metal complexes.

Table (1)
Some physical properties of the complexes and its reactants quantities.

Compound	*decomposition temperature* ^0C	*Color*	*Weight of metal chloride*		*Weight of product g*	*Yield %*	*chloride content*	*Metal ion % Prac. (Theo.)*
			g	*mmole*				
[Co (H_2L](1)	245	Brown Yellow	0.18	0.387	0.15	88	nil	24.77 (26.38)
[Ni (H_2L)](2)	275	Deep brown	0.18	0.387	0.16	94	nil	25.01 (26.30)
[pd (H_2L)](3)	292	Brown	0.13	0.387	0.18	90	nil	37.67 (39.28)

Prac.= practical, (Theo.) = Theoretical

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

Compound	***υ (N-H)***	***υ(C=O)***	***υ (C=N)***	***υ (N-N)***	***M-O M-N***	***Othor bands***
[H_2 L]	3190	1689	1650	1035	-	υ (c-H) alph 2920
[Co (H_2L]	-	1677	1660	1033	594 759	υ (c-H) alph 2924
[Ni (H_2L)]	-	1679	1657	1030	401 574	υ (c-H) alph 2985
[pd (H_2L)]	-	1680	1663	1025	589 765	υ (c-H) alph 2925

Table (3)
Electronic spectral data , and conductance measurement for the ligand[H_2L] 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***
[H_2 L]	282	35461	1876	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
[Co (H_2L)]	278	35971	1747	Ligand field	51.1	tetrahedral
	369	27100	733	charge transfer		
	608, 680	16447	448	$^4T_{1(P)} \leftarrow {}^4A_2$		
[Ni (H_2L)]	285	3508	2082	Ligand field	49.2	Square planar
	385	25974	930	charge transfer		
	465	21505	1009	$^1A_{2g} \leftarrow {}^1A_{1g}$		
[pd (H_2L)]	284	35211	2075	Ligand field	42.1	Square planar
	371	26954	915	charge transfe		
	412	24271	611	$^1B_{1g} \leftarrow {}^1A_{1g}$		

Table (4)
^{1}H, NMR data for the ligand in DMSO–d_6 and chemical shift in ppm(δ).

Funct .group	***δ (p.p.m)***
N(2)*H*	9.95(2H, s)
CH_3	1.9, 2.6 (12H s)
CH_2	3.5(8H, s)

s = singlet

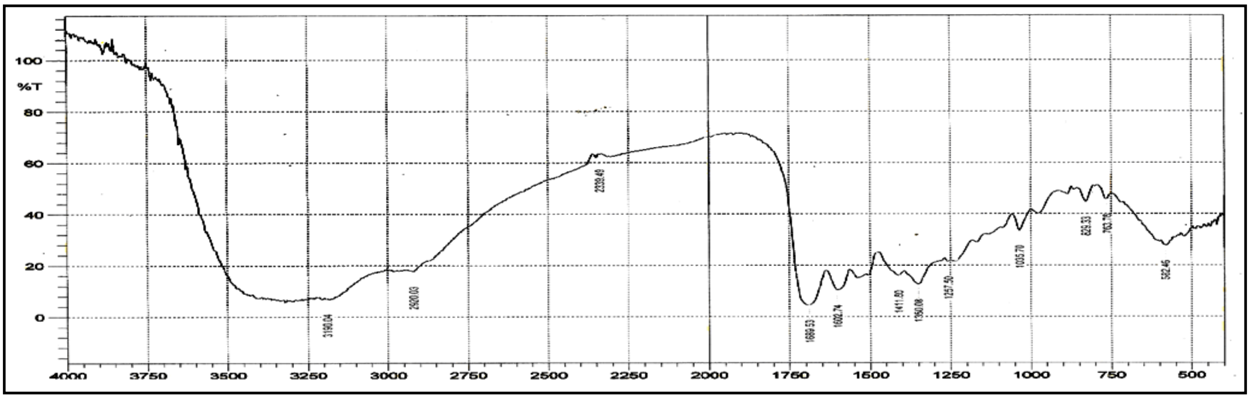


Fig. (2) The I.R. Spectrum of the ligand [H_2L].

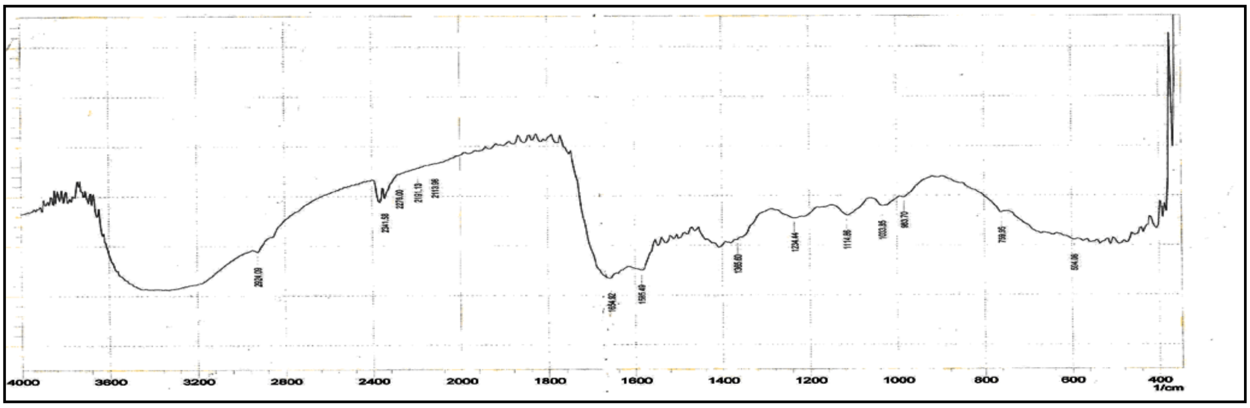


Fig. (2a) The I.R. Spectrum of the [Co (H_2L)].

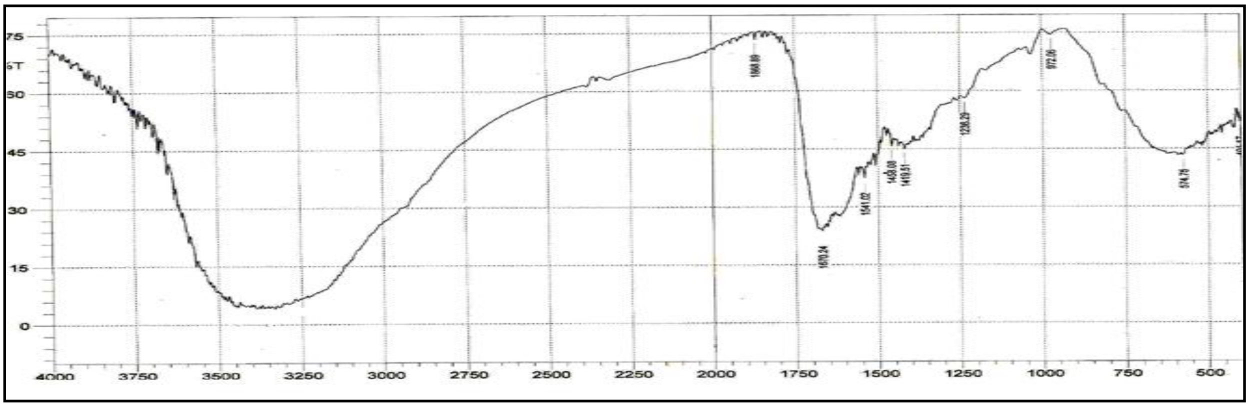


Fig. (2b) The I.R. Spectrum of the [Ni (H_2L)].

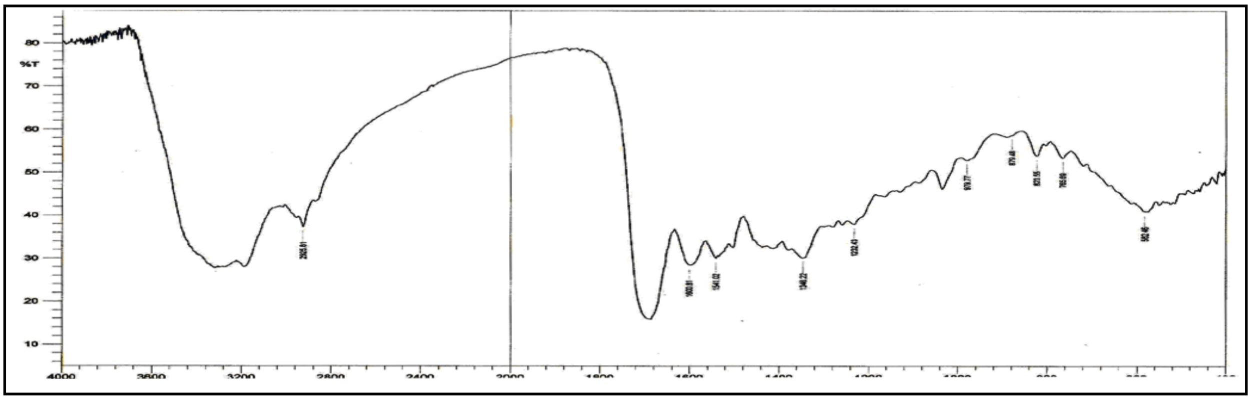


Fig. (2c) The I.R. Spectrum of the [Pd (H_2L)].

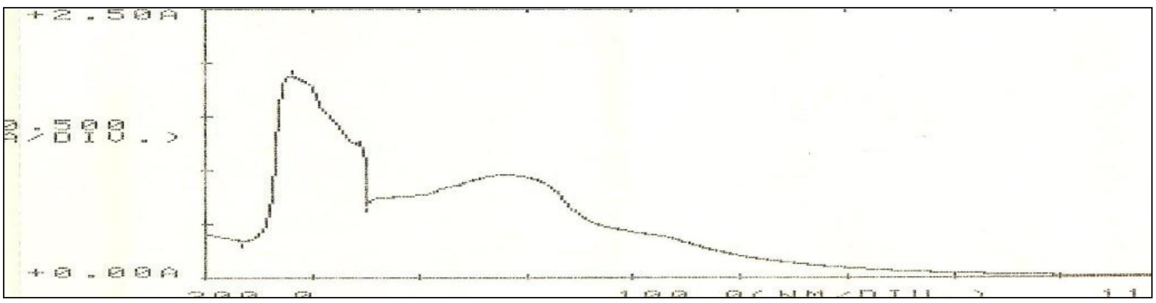


Fig. (3) The U.V. Spectrum of the ligand [H_2L].

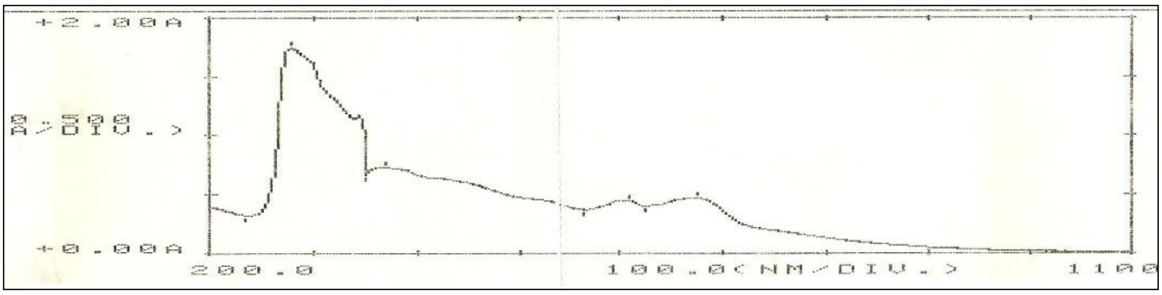


Fig. (3a) The U.V. Spectrum of the [Co (H_2L)].

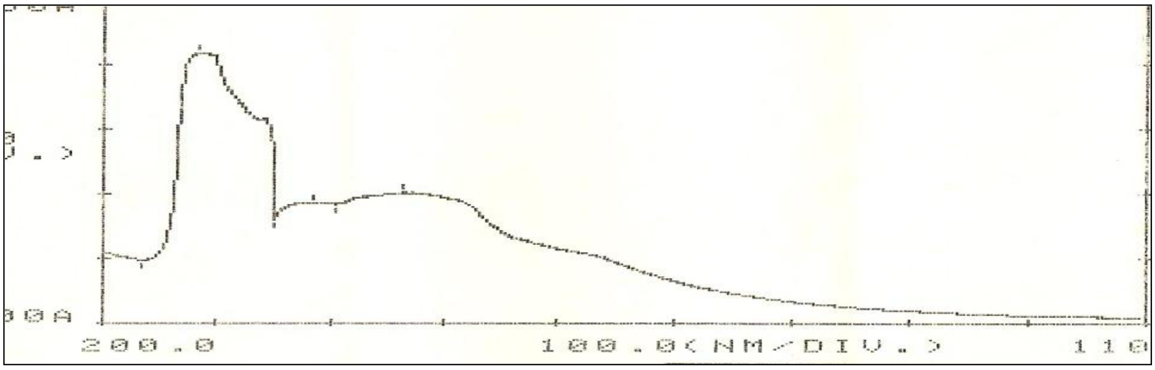


Fig. (3b) The U.V. Spectrum of the [Ni (H_2L)].

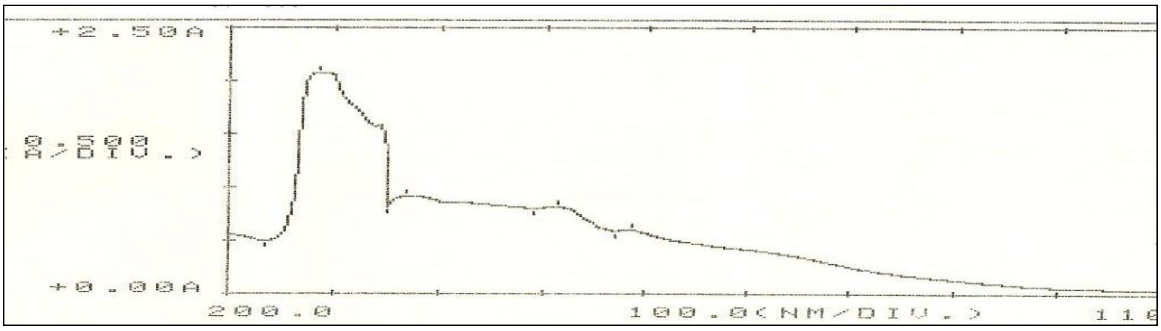


Fig. (3c) The U.V. Spectrum of the [Pd (H_2L)].

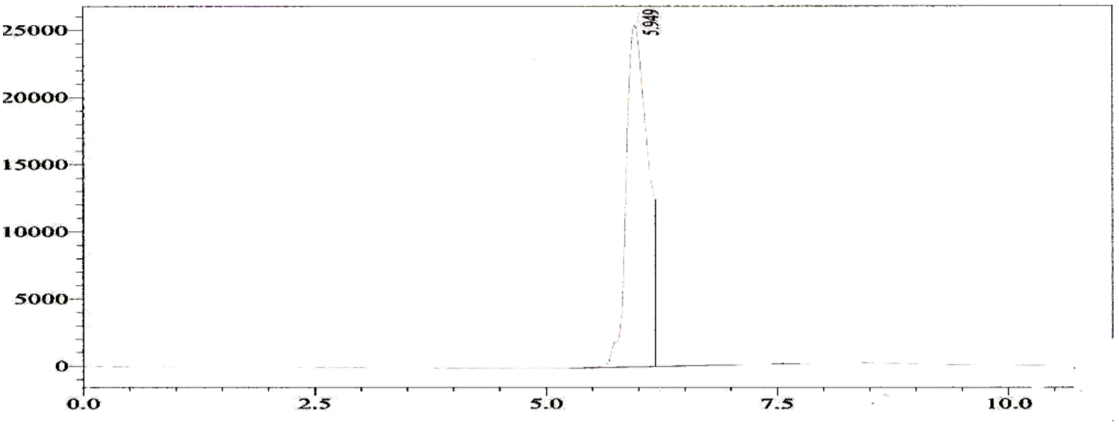


Fig. (4a) The HPLC chromatogram of the [Co(H_2L)].

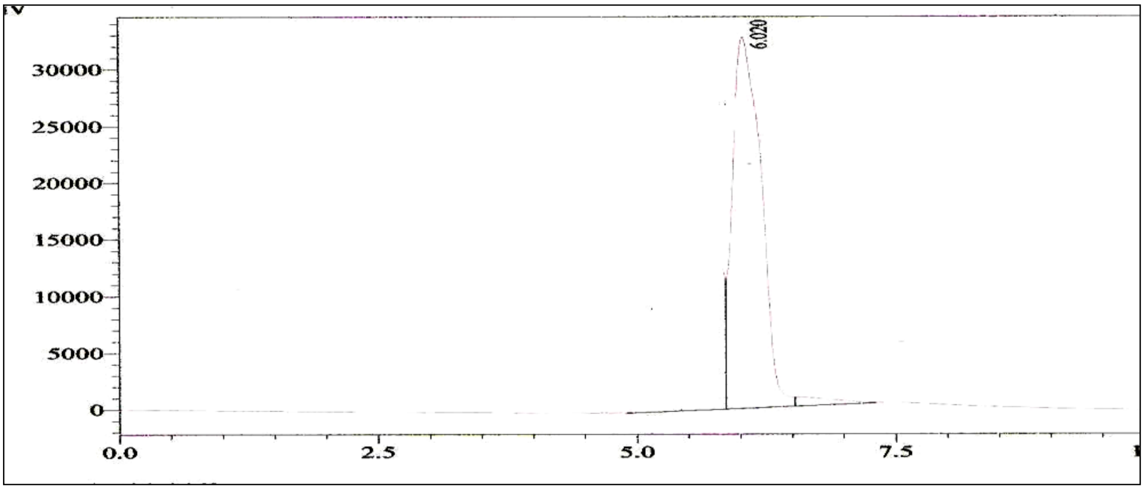


Fig. (4b) The HPLC chromatogram of the [Ni(H_2L)].

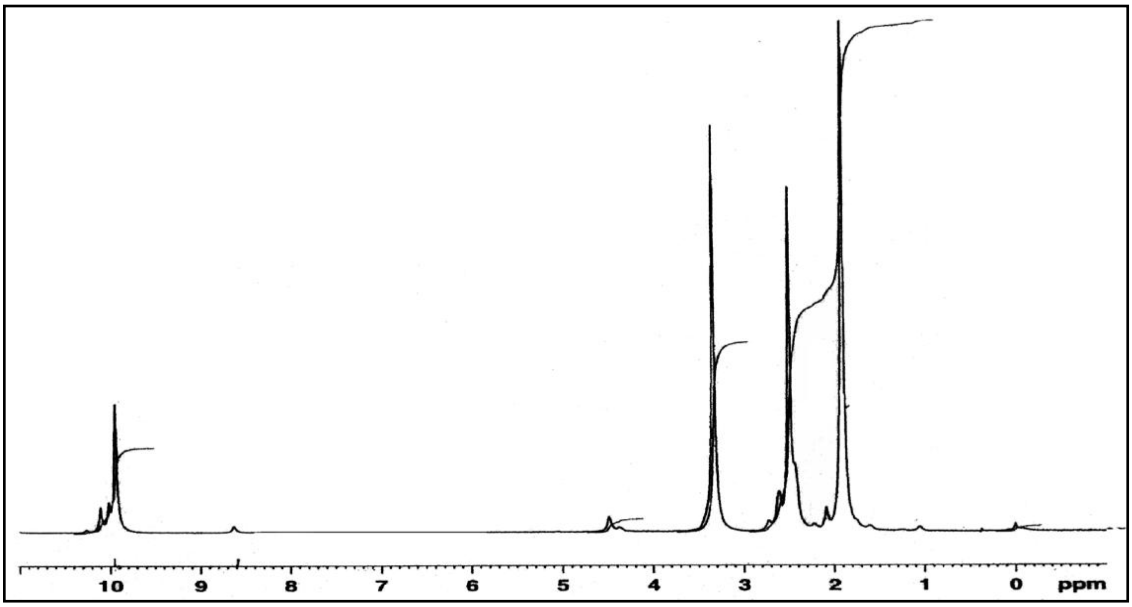


Fig. (4) The H NMR spectrum of the ligand.

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الخلاصة

تضمن البحث تحضير الليكاند الجديد

[2,3,8,9–tetra -methyl-1,4,5,7,10,12-hexa azo-5,12- dihydro -6,11- dione 1,3,7,10-dudec-tetra-ene]

بخطوتين:

الخطوة الاولى مفاعلة (2,5-Hexandion) مع (semicarbazidhydrochlorid)

وتكوين [2,5-Hexandion bis -(Semicarbazone)]

والخطوة الثانية من مفاعلة ناتج الخطوة الاولى مع (2,5-Hexandion)

لتحضير اليكاند الجديد

[2,3,8,9–tetra -methyl-1,4,5,7,10,12-hexa azo-5,12- dihydro -6,11- dione 1,3,7,10-dudec-tetra-ene]

ثم مفاعلة مع بعض العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (1:1) و بوجود حامض الخليك الثلجي حيث تكونت معقدات جديدة ذات الصيغ العامة:

[M(L)]

حيث:

M^{II} = Co, Ni and Pd

شخصت جميع المركبات بالطرق الطيفية التالية (الأشعة تحت الحمراء والأشعة فوق البنفسجية– المرئية (HPLC) ومطيافية الامتصاص الذري للعناصر) ومحتوى الكلور ودرجات الانصهار ، مع قياس التوصيلية المولارية الكهربائية والحساسية المقناطيسية، من النتائج أعلاه كان الشكل الفراغي المقترح لمعقدات النيكل والبلاديوم مربع مستوي بينما يتخذ الكوبلت شكل رباعي السطوح المشوه.