Cobalt(II), Nickel(II), and Copper(II) Complexes with Ligands Contain Nitrogen as Donor Atoms type N3 and Azamacrocylic N6 , Synthesis and Characterisation.

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Abstract

Two series of N3 Schiff base complexes [M L^1 Cl] and 22-membered hexaazamacrocyclic complexes [ML^2] (M=Co^{2+}, Ni^{2+}, and Cu^{2+}) have been synthesised via the condensation reaction of para-nitobenzaldehyde with diethelyenetriammine to obtain [HL^1] where [HL^1]= *N-[(4-nitrophenyl)methylene]-N'-(2-{[(4-nitrophenyl)methylene]amino}ethyl)ethane-1,2-diamine* and diethylene triammine with 2,5hexane dione to from [HL^2] where [HL^2] = *8,11,19,22-Tetramethyl-1,4,7,12,15,18hexaaza-cyclodocosa-7,11,18,22-tetraene*, in the presence of acetic acid as a catalyst in ethanol. The prepared compounds were haracterized by FT- IR, ^{1}H-NMR, and electronic spectral studies, conductivity, elemental microanalysis and magnetic moment measurements The mode of bonding and overall geometry of the complexes have been inferred through IR, and electronic spectral studies, conductivity, and magnetic moment measurements.[Co Cl L$^{1]}$ is distorted tetrahedral, [Ni Cl$_3$ L^1] is octahedral, and [Cu Cl L^1] is square planar, An octahedral geometry is proposed for [Co L^2] and [Ni L^2] complexes and square planar for [Cu L^2].

الخلاصة:-

تم تحضير نوعين من المعقدات مع ليكندات مفتوحة السلسلة و الحلقية المحتوية على ستة ذرات نيتروجين كذرات واهبة من خلال تفاعل التكثيف في الايثانول بوجود حامض ألخليك كعامل مساعد حيث تم مفاعله بارا –نايترو بنزالهايد مع ثنائي اثلين ثلاثي أمين ليكونان الليكند

[HL^1] where [HL^1]= *N-[(4-nitrophenyl)methylene]-N'-(2-{[(4-nitrophenyl)methylene] amino}ethyl)ethane-1,2-diamine*

أما تفاعل الهكسان ثنائي كيتون مع ثنائي اثلين ثلاثي أمين ليكونان الليكند

[HL^2] where [HL^2] = *8,11,19,22-Tetramethyl-1,4,7,12,15,18hexaaza-cyclodocosa-7,11,18,22-tetraene*

شخصت المركبات المحضرة بواسطة أطياف الأشعة تحت الحمراء وفوق البنفسجية–المرئية وطيف الرنين النووي المغناطيسي إضافة إلى الحساسية المغناطيسية والتوصيلية المولارية والتحليل الكمي الدقيق للعناصر. ومن خلال المعلومات التي قدمتها دراسات الأطياف الأشعة تحت الحمراء وفوق البنفسجية – المرئية والحساسية المغناطيسية والتوصيلية المولارية أن الشكل الفراغي المتوقع للمعقدات مع الليكند الأول هو لمعقد الكوبالت رباعي السطوح المشوه ولمعقد النيكل الشكل ثماني السطوح بينما اقترح الشكل المربع المستوي لمعقد النحاس ، أما معقدات الليكند الثاني أظهرت إن لمعقدات الكوبالت الثنائي والنيكل الثنائي الشكل ثماني السطوح بينما كان الشكل الفراغي المقترح لمعقد النحاس الثنائي هو المربع المستوي.

Introduction

The interest in the study of macrocyclic complexes continued to expand because of their catalytic properties [1] which has led to industrial applications in addition to their involvement in many important biological processes such as photosynthesis and dinitrogen transport[2]. Recent studies on macrocyclic complexes containing mixed nitrogen, sulfur, and/or oxygen donor atoms [3–8] show that it remains an active area of research. Elegant studies on ligand design and metal ion recognition of macrocyclic complexes have been reported by Lindoy [9–11] and co-workers. Evidently, transition metals can act as templates [12–15] for the synthesis of many macrocyclic complexes. A wide variety of macrocyclic complexes were reported by Martell [16–19] where he added a note on the catalytic activity of Cu complexes [19]. Nasman and co-workers, they are reported [20–24] a variety of macrocyclic complexes.

Certain natural macrocycles are very important, among them are the macrocycles included in chlorophyll, blood heme, and vitamin B12. However, synthetic macrocyclic compounds are of much greater importance for chemical analysis. In general, they have been known for many decades but active research began in the late 1960s[25].

A macrocyclic compound can be formed by linking;

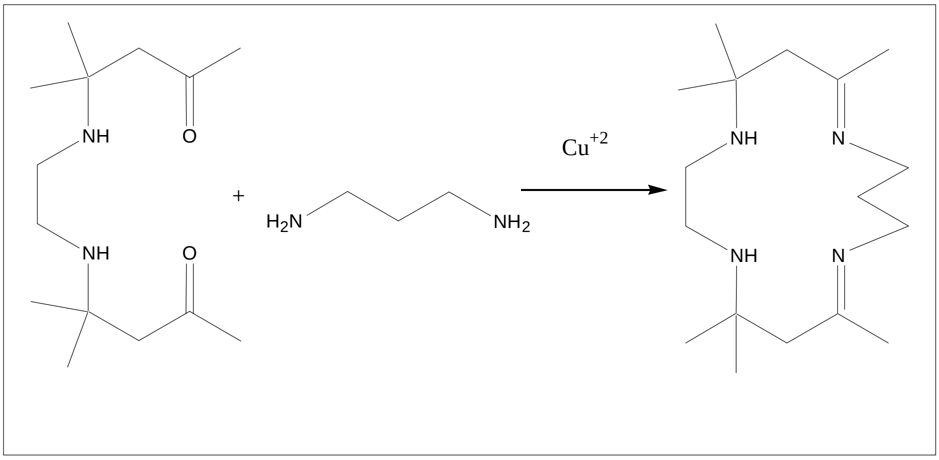
(a) Two heteroatoms (b) A heteroatom and a carbon atom, and (c) Two – carbon atoms.

Method (a) is of rather limited use[26]. Preparation of macrocyclic disulfide from terminal dithiols is about the only instance of its application [27]. Uses of method (c) is also infrequent in spite of the great experience gained in organic chemistry in creating extremely complicated carbon skeletens and the abundance of methods for making carbon – carbon bonds [28].

Nearly all of the syntheses of macrocycles are based on method (b), that is, on the formation of a heteroatom – carbon bonds. Moreover, all the macrocycles synthesised to date are the heteroatom (oxygen, nitrogen, and sulfur, etc) behaves as a nucleophilic moiety in this reaction , whereas a carbon atom is an electrophilic centre [29].

Most of the macrocyclic Schiff bases contain nitrogen atoms, and at least two of these form (C=N) bonds [30] .

The transition metal complexes of the macrocyclic Schiff bases with four (C=N) bonds have been thoroughly investigated (especially Cu^{2+} and Ni^{2+} chelates). but very few macrocycles have been isolated in a free state[28].



Experimental

The commercially available pure samples, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, and $CuCl_2.2H_2O$, (Merk), were used as received. Diethelyene triammine (diene) and 2,5 hexanedione (Ubichem), paranitrobenzaldehyde (Fluka), 2,4-pentanedione were used as supplied.

IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in range (4000-400) cm^{-1}. Electronic spectra of the prepared compounds were measured in the region (200-800) nm for 10^{-3} M solution in DMF at 25 °C using Shimadzu 160 spectrophotometer, with 1.000 ± 0.001 cm matched quartz cell.. ^{1}H-NMR were acquired with BRUKER-400 spectrometer in DMSO-d^6. Elemental microanalysis were performed on a (C.H.N) analyser from heraeus (Vario EL). The chloride contents for complexes were determined by using potentiometer titration method on (686-Swiss). Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3} M solution of the sample in DMF using a PW9526 digital conductivity meter. The magnetic susceptibility of complexes were recorded in Guay balance.

Preparation of [HL^1] *N*-[(4-nitrophenyl)methylene]-*N'*-(2-{[(4-nitrophenyl) methylene] amino}ethyl)ethane-1,2-diamine

A solution of diethylenetriammine (2.00g, 19.38 mmole) in ethanol (20 mL) was added slowly to two equivalent of para-nitrobenzaldehyde(5.862g,38.76mmole) dissolved in ethanol (15 mL). The mixture was allowed to reflux for two and half hours under nitrogen blanket, then cooled to room temperature. A yellow solid was collected by filtration, recrystallised from methanol/ H_2O, dried under vacuum to give [HL^1] as a pale yellow solid. Yield 5.60g (75.16%) m.p. (274-276°C).

Preparation of [H_2L^2] *8,11,19,22-Tetramethyl-1,4,7,12,15,18hexaaza-cyclodocosa-7,11,18,22-tetraene*

The preparation of [H_2L^2] carried out under template reaction since two equivalents of diethylenetriammine (4.00 g, 38.78mmole) in (20 mL) ethanol was added to solution of 2,5-hexanedione (8.85g, 38.78 mmole) in (10 mL) ethanol the mixture allowed to stirred under nitrogen atmosphere about 20 minutes through this time the mixture became thick, the result mixture was refluxed under nitrogen for four hours the pale orange precipitate was obtained, cooled at room temperature. A deep orange solid was collected by section filtration, recrystaallised from toluene. Dried under vacuum to give the titled ligand 5.8g (45.6%) mp (198-200°C)

Preparation of [HL^1] complexes

A solution of **[HL^1]** (0.20g, 5.19 X 10^{-4} mmole) in methanol (15 mL) was placed in a round-bottomed flask three neck 250 mL in size. A solution of cobalt (II) chloride hexahydrate (0.12g, 5.19 X 10^{-4} mmole) in (15 mL) methanol was added drop-wise with stirring, then one equivalent from trimethylammine was added to deprotenation the proton. The resulting mixture was heated under reflux for two hrs, during which time the solution became brown in colour. The solution was concentrated by evaporating methanol at room temperature. A deep brown solid was formed, which collected by filtration, washed with diethylether (5 mL) and dried under vacuum to give0.210g (88%) yield, m.p. (267-269°C). **Table(1)** Summarised the stated of quantities, reaction condition and some physical properties of the prepared complexes of nickel(II) and copper (II).

Table (1) Some physical properties of the prepared complexes

Empirical formula	m.p. °C	Colour	Wt .of metal ion = 5.19 X 10^{-4} mmole	Wt. of product	Yield%
[Ni Cl_3 (L^1)]$^{-2}$	256-258	Yellow	0.123g	0.198g	83
[Cu Cl (L^1)]	297-299	Deep pink	1.346g	0.201g	83

Preparation of [H_2 L^2] complexes

A solution of **[H_2L^2]** (0.10g, 2.75 X 10^{-4} mmole) in methanol (15 mL) was placed in a round-bottomed flask. A solution of cobalt (II) chloride hexahydrate (0.065g, 2.75 X 10^{-4} mmole) in (15 mL) methanol was added drop-wise with stirring, then two equivalent from trimethylammine was added to deprotenation the protons. The resulting mixture was heated under reflux for three hrs, during which time the solution became deep red in colour. The solution was concentrated by evaporating methanol at room temperature. A deep brown solid was formed, which collected by filtration, washed with diethylether (5 mL) and dried under vacuum to give 0.09g (78%) yield, m.p. (205-207°C). **Table(2)** Summarised the stated of quantities, reaction condition and some physical properties of the prepared complexes of nickel(II) and copper (II)..

Table (2) Some physical properties of the prepared complexes

Empirical formula	m.p. °C	Colour	Wt .of metal ion = 2.75 X 10^{-4} mmole	Wt. of product	Yield%
[Ni (L^2)]	213-215	White-yellow	0.065g	0.110g	95
[Cu (L^2)]	239-241	Wine	0.322g	0.100g	86

Results and Discussion

Synthesis and characterisation of [HL^1] and [H_2L^2]

The condensation reaction of one equivalent of diethylene triammine with two equivalent from *para*-nitrobenzaldehyde formed the ligand [HL^1] according to the general method was summarised in **Scheme (1).** The prepared ligand was characterised by FT-IR, UV-Vis, HNMR spectroscopies. As well as the physical methods. The [H_2L^2] was prepared in the similar methods since the condensation reaction of two equivalent of diethylene triammine with two equivalent of hexane dione resulted in the ligand preparation according to the general method were Summarised in **Scheme (2)**, the IR, UV-Vis, and HNMR spectroscopies was used to characterised the prepared ligand.

Synthesis and characterisation of the complexes

All complexes were prepared by a similar method, shown in **Scheme(3) and Scheme(4)** . The complexes were prepared from the reaction of the ligand with metal chloride salt at reflux in ethanol, triethyl ammine was used as a base to deprotenation of protons. The complexes are stable in solution and in solid state. The molar conductance of the prepared complexes in (DMF) lies in the range (15–37) (S cm^2 $mole^{-1}$) range, indicating all complexes are non electrolytes. Except [Ni Cl_3 L^1] $^{2-}$

complex gave (135 S cm^2 $mole^{-1}$) indicating the complex is electrolyte with 1:2 ratio.**Table (4)** The magnetic susceptibility of complexes were determined by Faraday's method the results was listed in **Table (4)**. The microanalysis of elements and metal analysis were in good agreements with expected values. **Table (5)**

IR Spectra

The IR spectrum for [HL^1] , **Fig. (1)** appears the bands at (3180, 3035, 2920 cm^{-1}) ascribed to ν(N-H) , aromatic ν(C-H) and aliphatic ν(C-H) stretching respectively. The intense strong band at (1635 cm^{-1}) assigned to ν(C=N) stretching, the NO_2 group displays bands at (1602 cm^{-1}). The other bands were listed in **Table (3).**

The IR spectra of complexes [Co Cl L^1]. [Ni Cl_3 L^1]$^{-2}$ and [Cu Cl L^1] **Figs. (2,3,4)** exhibited the disappear of band at (3180 cm^{-1}) which that attributed to ν(N-H) in free ligand, indicating of the deprotenation of NH proton and bonded to metal ion , the spectra shows the shifting of band which that due to C=N at (1635 cm^{-1}) that shifting to higher frequencies at (1685, 1690, and 1675 cm^{-1}) of [Co Cl L^1]. [Ni Cl_3 L^1]$^{-2}$ and [Cu Cl L^1] complexes respectively[31]. The new bands of ν(M-N) stretching were shows between (415- 435 cm^{-1}) of these complexes. Indicating to coordination between the ligand and metal was occur.

While the IR spectrum for [H_2L^2] , **Fig. (5)** appears the bands at (3313, 3095cm^{-1}) ascribed to ν(N-H) , and the bands at (2931, 2910, 2889 cm^{-1}) assigned to aliphatic ν(C-H) stretching these values refer to the two groups exist in two different environments. The band at (1662 cm^{-1}) assigned to ν(C=N) stretching. The other bands were listed in **Table (3).**

The IR spectra of complexes [Co L^2]. [Ni L^2] and [Cu L^2] **Figs. (6,7,8)** exhibited the disappear of band at (3313 cm^{-1}) which that attributed to ν(N-H) in free ligand, indicating of the deprotenation of NH proton and bonded to metal ion , the spectra shows the shifting of band which that due to C=N at (1662 cm^{-1}) that shifting to lower frequencies at (1625, 1620, and 1635 cm^{-1}) of [Co Cl L^1]. [Ni Cl L^1] and [Cu Cl L^1] complexes respectively This shifting can be attributed to the delocalisation of the electron density of the metal ion into the π-system of the ligand (HOMO → LUMO) [where

HOMO= Highest Occupied Molecular Orbital; LUMO= Lowest Unoccupied Molecular Orbital] [32]. The new bands of ν(M-N) stretching were shows between (405- 430 cm^{-1}) of these complexes. Indicating to coordination between the ligand and metal was occur. The other bands were listed in **Table (3).**

UV-Vis spectra

The electronic spectrum of [HL^1] **Fig. (9),** exhibits the peaks at (301 nm) (33222 cm^{-1}) (ε_{max}= 1841 $molar^{-1}cm^{-1}$) and (328 nm) (30487 cm^{-1}) (ε_{max}= 1890 $molar^{-1}cm^{-1}$) assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively[33], **Table (4).**

The (U.V–Vis) spectra for complexes [Co Cl L^1]. [Ni Cl_3 L^1]$^{-2}$ and [Cu Cl L^1] are shown in **Figs (10, 11, 12)** respectively. The absorption data for the complexes are given in **Table (4)** .In general the spectra showed an intense peak in the (U.V) region at (266nm) (37593cm^{-1}) (ε_{max}=542 $molar^{-1}cm^{-1}$),(260nm) (38461cm^{-1}) (ε_{max}=1503) and (274 nm) (36496cm^{-1}) (ε_{max}=1305 $molar^{-1}cm^{-1}$) for these complexes respectively, due to the ligand field and charge transfer .

Additional peaks were observed at (395nm) (25316cm) (ε_{max}=85 $molar^{-1}cm^{-1}$) and (375nm) (26666cm^{-1})(ε_{max}=110 $molar^{-1}cm^{-1}$) for the complexes Co^{II} and Ni^{II} respectively, attributed to charge transfer transitions. For complex Cu^{II} the charge transfer peak may overlapped with the (d-d) transition.

In the [Co Cl L^1] spectrum the two peaks at (608nm) (16447cm^{-1}) (ε_{max} =44 $molar^{-1}cm^{-1}$) and at (664nm) (15060 cm^{-1}) (ε_{max}=48 $molar^{-1}cm^{-1}$) which can be assigned to (${}^4A_2{}^{(F)} \rightarrow {}^4T_1{}^{(F)}$) and (${}^4A_2{}^{(F)} \rightarrow {}^4T_1{}^{(P)}$) d–d transition suggesting an tetrahedral structure around the cobalt (II) ion.

In the (UV–Vis) spectrum of complex [Ni(L^1) Cl_3]$^{-2}$ displays two weak peaks in the visible region at (750nm) (13333cm^{-1}) (ε_{max}=8 $molar^{-1}cm^{-1}$) and(810 nm) (12345 cm^{-1}) (ε_{max}=11 $molar^{-1}cm^{-1}$) were assigned to (${}^3A_2g^{(F)} \rightarrow {}^3T_1g^{(F)}$) and (${}^3A_2g^{(F)} \rightarrow {}^3T_1g^{(P)}$) d–d transition confirming octahedral structure around nickel (II) ion. In the [Cu^{II}(L^1) Cl] spectrum the peak at (465nm) (21505 cm^{-1}) (ε_{max}=200 $molar^{-1}cm^{-1}$) which can assigned to(${}^2B_2g \rightarrow {}^2B_1g$) confirming a square planer structure around the copper (II) ion.

while the spectrum of [H_2L^2] **Fig. (13)** displays the broad peak at (358 nm) (

27929 cm^{-1}) (ε_{max}= 3311 $molar^{-1}cm^{-1}$) attributed to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions respectively(112), **Table (4).** And the UV-Vis spectra of [Co L^2]. [Ni L^2] and [Cu L^2] complexes **Figs. (14,15,16)** showed an intense peaks in the (U.V) region at (265nm) (37735 cm^{-1}) (ε_{max}=300 $molar^{-1}cm^{-1}$) for cobalt(II), (264nm) (37879cm^{-1}) (ε_{max}=2033 $molar^{-1}cm^{-1}$) (320 nm) (31250 cm^{-1}) (ε_{max}=125$molar^{-1}cm^{-1}$) for nickel(II) and at (262nm) (38168cm^{-1}) (ε_{max}=2750 $molar^{-1}$ cm^{-1}) for copper (II) complexes. These peaks were assigned to ligand field and charge transfer transitions.

the peaks (590nm) (16949cm^{-1}) (ε_{max}=300$molar^{-1}cm^{-1}$) (657nm) (15221cm^{-1}) (ε_{max}=490$molar^{-1}cm^{-1}$) for cobalt(II) , the peak at (555nm) (18018cm^{-1}) (ε_{max}= 8 $molar^{-1}cm^{-1}$) for nickel(II) and the peak at (530nm) (18868cm^{-1}) (ε_{max}=50$molar^{-1}cm^{-1}$) for copper(II) complexes are assigned to d-d transitions type ($^4T_1g^{(F)} \rightarrow {}^4T_2g^{(F)}$) ($^4T_1g^{(F)} \rightarrow {}^4T_1g^{(P)}$),($^3A_2\rightarrow{}^3T_{1g}$) and ($^2B_2g \rightarrow {}^2B_1g$) for Co^{II}, Ni^{2+} and Cu^{2+} complexes respectively, suggesting an octahedral, octahedral and square planer structure around Co^{2+}, Ni^{2+}, and Cu^{2+} ions respectively [33].

^{1}H NMR spectra

The ^{1}H NMR spectrum of the ligand [HL^1] **Fig. (17),** in DMSO-d^6 displays. The resonance at (δ= 8.38 ppm, 2H) is attributed to (N=C-*H*) protons. These protons are equivalent and appears as a singlet, (N.*H*) proton appear at chemical shift (δ= 8.20 ppm, 1H) [34]. The signal sat (δ= 8.15, 7.60 ppm,8H) assigned to aromatic ring vibration protons. The ethyl groups protons resonance appears at (δ= 3.35, 2.20 ppm, 8H), while the signal at (δ= 2.5 ppm) due to DMSO-d^6

The ^{1}H NMR spectrum of the ligand [H_2 L^2] **Fig. (18),** in DMSO-d_6 appears the chemical shifts at (δ= 3.90 ppm, 8H, δ= 3.20 ppm, 8H, δ= 2.20 ppm, 8H, δ= 2.05 ppm, 12H) attributed to (NH-C-*H*), (C-H_2-C-H_2), (C=N-C-H_2) and (C-H_3) respectively, while the N-*H* groups displays the resonance at (δ= 8.30 ppm, 2H) [35].

Magnetic Susceptibility and molar conductivity

The magnetic moments μ_{eff} (B.M.) , **Table 4**, correspond to high-spin d^7 systems, consistent [36] with the tetrahedral and octahedral environment around cobalt(II) for [Co Cl L^1] and [CoL^2] respectively. The electronic spectra of the cobalt complexes show two bands in the

16447, 15060 and 16949, 15221 cm^{-1} regions corresponding [36] to $^4T1g^{(F)} \rightarrow {}^4A_2g^{(F)}$, and $^4T_1g^{(F)} \rightarrow {}^4T_1g^{(P)}$ transitions, respectively. The band expected to appear below 8,500 cm^{-1}, corresponding to the transition $^4T_1g^{(F)} \rightarrow {}^4T_2g^{(F)}$, could not be recorded as it lies beyond the range of the instrument. The observed magnetic moments for the nickel(II) complexes, **Table 4**, are typical for high-spin species establishing the triplet ground state. Their electronic spectra show two main bands in the 13333, 12345 and 18018 cm^{-1} assignable to $^3A_2g^{(F)} \rightarrow {}^3T_1g^{(F)}$ and $^3A_2g^{(F)} \rightarrow {}^3T_1g^{(P)}$ transitions, respectively, suggesting an octahedral geometry around the nickel(II) ions [33]. While the copper complexes shows magnetic moments corresponding with one unpaired electron, the proposed square planar geometry around the cooper ion, they are agree well with electronic spectra of theses complexes.

The molar conductivity of complexes **,** **Table (4)** illustrated the complexes are no electrolytes excepts the [Ni Cl_3 L^1] is electrolytes with 1:2 ratio.

Finally, it has not escaped us that the procedure outlined for preparing the macrocyclic complexes under study may well have wider applicability. It should prove useful for investigating the complexes of a range of other ligand types as well as for the study of metal-containing—biological molecules such as metallo-enzymes.

Table (3) Infrared spectral data (wave number) cm^{-1} of the ligand $[HL^1]$, $[H_2L^2]$ and its complexes

Compound	υ(N–H)	υ(C=N)	Ring vibrations	υ(M–N)	δ(N-H)	Additional bands
$[HL^1]$	3180 m	1635s	1506s, 1072s, 833s	-	1411m	3035m υ(C–H) arom. 2920w υ(C–H) aliph 2839 w υ(C–H) aliph
$[Co(L^1)Cl]$	-	1685s	1550m, 1010m, 815s	413w	-	3150w υ(C–H) arom. 2950vw υ(C–H) aliph 1418m δ(C-N)
$(NH_4)_2[Ni(L^1)Cl_3]$	-	1690s	1560s, 1005s, 810s	435m	-	3090w υ(C–H) arom. 2850m υ(C–H) aliph 1510m δ(C-N) 3250, 3330 m υ(NH_4)
$[Cu(L^1)Cl]$	-	1675s	1575s,1015m, 820m	410w	-	3000wυ(C–H) arom. 2878w υ(C–H) aliph 1480w δ(C-N)
$[H_2L^2]$	3313m	1662m	-	430w	1365	2931w υ(C–H) aliph 1517m δ(C-N)
$[Co(L^2)]$	-	1625m	-	412w	-	2900w υ(C–H) aliph 1416m δ(C-N)
$[Ni(L^2)]$	-	1620 s	-	415w	-	2890w υ(C–H) aliph 1405m δ(C-N)
$[Cu(L^2)]$	-	1635s	-	415m	-	2900w υ(C–H) aliph 1410m δ(C-N)

(s) strong, (m) medium, (w) weak,

Table (4) Electronic spectral data, magnetic moments and molar conductance values of the ligands $[HL^1]$, $[H_2L^2]$ and its complexes

Compound	μ eff B.M	Molar conductivity $molar^{-1}cm^{-1}$	Band position	ε_{max} $molar^{-1}cm^{-1}$	Assignment	Suggested geometry
$[HL^1]$	-	-	301 328	1841 1890	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	-
$[Co(L^1)Cl]$	4.56	15	608 664	44 48	${}^4A_2{}^{(F)}\rightarrow{}^4T_1{}^{(F)}$ ${}^4A_2{}^{(F)}\rightarrow{}^4T_1{}^{(P)}$	Distorted tetrahedral
$(NH_4)_2[Ni(L^1)Cl_3]$	3.11	135	750 810	8 11	${}^3A_2g^{(F)}\rightarrow{}^3T_1g^{(F)}$ ${}^3A_2g^{(F)}\rightarrow{}^3T_1g^{(P)}$	Octahedral
$[Cu(L^1)Cl]$	1.71	31	465	200	${}^2B_2g\rightarrow{}^2B_1g$	Square planar
$[H_2L^2]$	-	-	358	3311	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	-
$[Co(L^2)]$	4.62	22	590 657	300 490	${}^4T_1g^{(F)}\rightarrow{}^4T_2g^{(F)}$ ${}^4T_1g^{(F)}\rightarrow{}^4T_1g^{(P)}$	Octahedral
$[Ni(L^2)]$	3.19	28	555	8	${}^3A_2g^{(F)}\rightarrow{}^3T_1g^{(F)}$	Octahedral
$[Cu(L^2)]$	1.69	37	530	50	${}^2B_2g\rightarrow{}^2B_1g$	Square planar

Table (5) Elemental analysis data and some physical properties of [H_3L] and its metal complexes

Empirical Formula	M.Wt	Colour	Micro analysis found (calc) %				
			C	H	N	Cl	Metal
$C_{19}H_{23}N_5O_4$	385.42	Pale yellow	59.01	5.98	8.24	-	-
			(59.21)	(6.01)	(8.17)	-	-
$C_{18}H_{18}ClCoN_5O_4$	462.78	Deep brown	46.66	3.88	15.09	7.53	12.30
			(46.72)	(3.92)	(15.13)	(7.66)	(12.74)
$C_{18}H_{18}C_{l3}N_5NiO_4$	533.42	Yellow	40.41	3.26	13.20	19.82	10.91
			(40.53)	(3.40)	(13.13)	(19.94)	(11.00)
$C_{18}H_{18}ClCuN_5O_4$	467.37	Deep pink	46.10	3.69	15.09	7.34	13.49
			(46.26)	(3.88)	(14.98)	(7.59)	(13.60)
$C_{20}H_{38}N_6$	362.56	Pale orange	66.12	10.41	23.23	-	-
			(66.26)	(10.56)	(23.18)	-	-
$C_{20}H_{36}CoN_6$	419.47	Deep red	57.13	8.40	20.21	-	13.88
			(57.27)	(8.65)	(20.03)	-	(14.05)
$C_{20}H_{36}N_6Ni$	419.23	White yellow	57.13	8.54	2012	-	13.87
			(57.30)	(8.66)	(20.05)	-	(14.00)
$C_{20}H_{36}CuN_6$	424.09	wine	56.43	8.47	19.98	-	14.79
			(56.64)	(8.56)	(19.82)	-	(14.98)

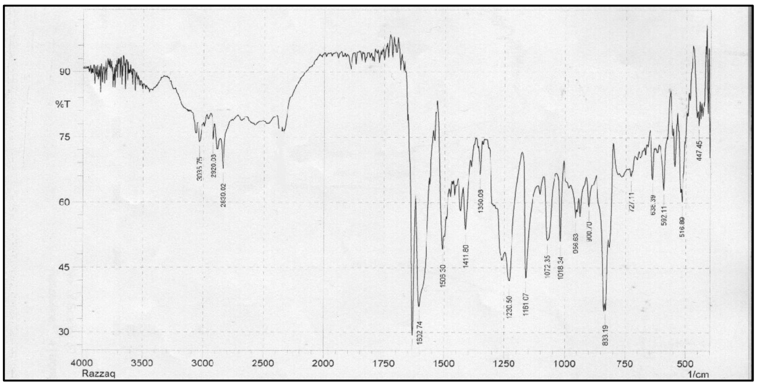


Fig (1) FT-IR spectrum of [HL^1]

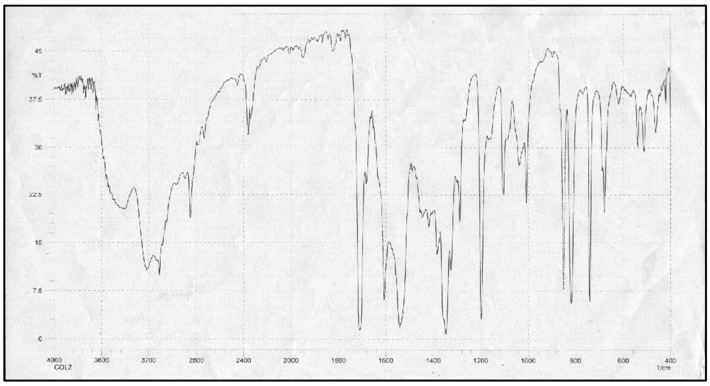


Fig (2) FT-IR spectrum of [Co Cl L^1]

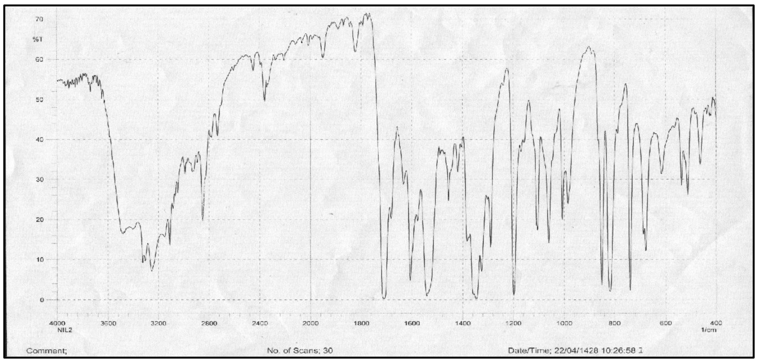


Fig (3) FT-IR spectrum of [Ni Cl_3 L^1]$^{-2}$

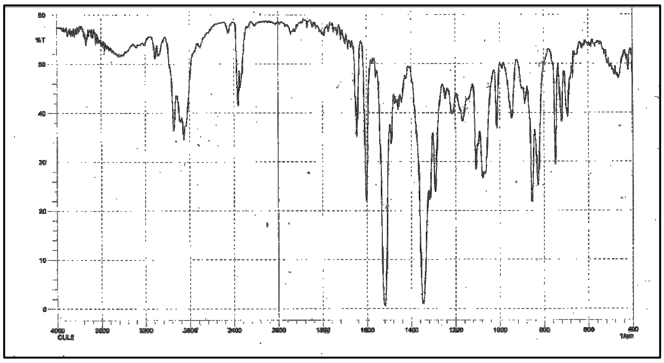


Fig (4) FT-IR spectrum of [Cu Cl L^1]

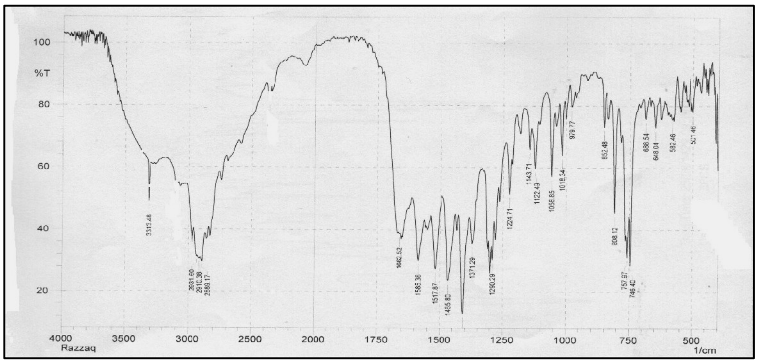


Fig (5) FT-IR spectrum of [H_2 L^2]

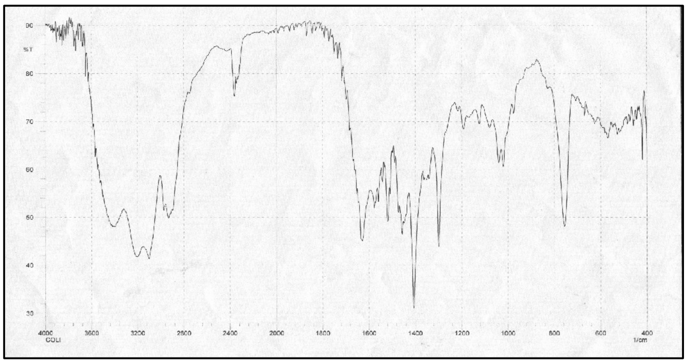


Fig (6) FT-IR spectrum of [CoL^2]

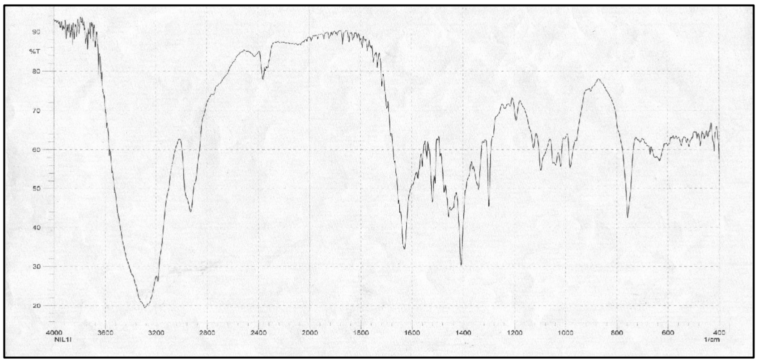


Fig (7) FT-IR spectrum of [Ni L^2]

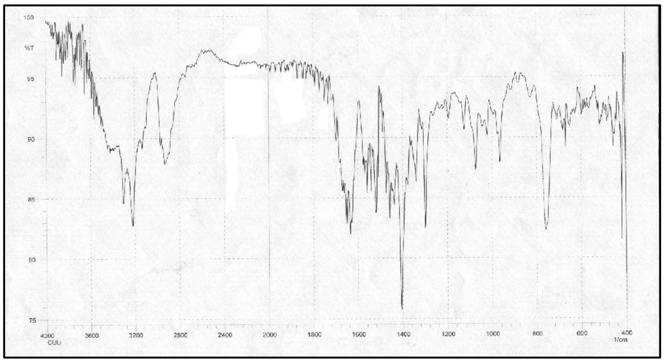


Fig (8) FT-IR spectrum of [Cu L^2]

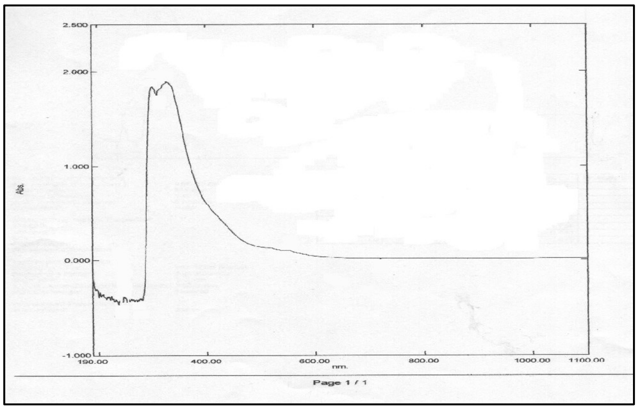


Fig. (9) UV-Vis spectrum of [HL]

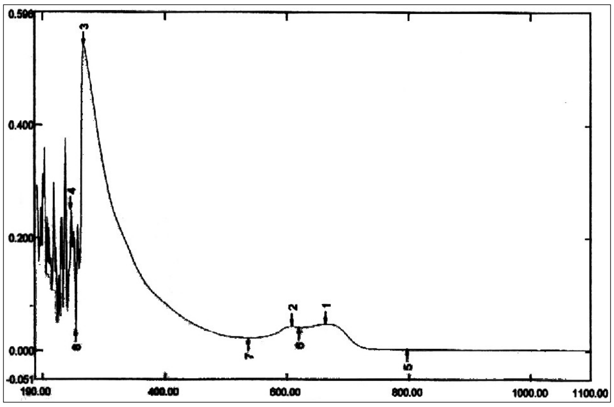


Fig (10) UV-Vis spectrum of [CoL^1Cl]

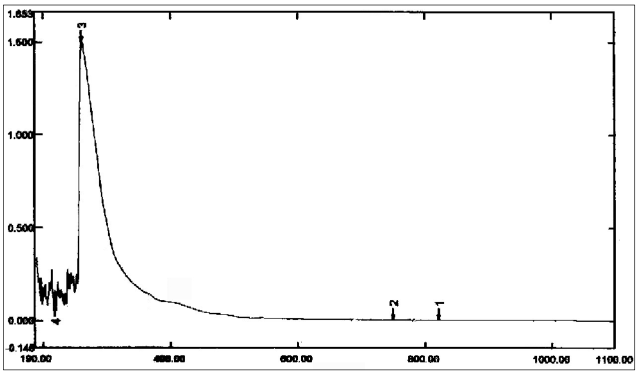


Fig (11) UV-Vis spectrum of [$NiL^1Cl_3]^{-2}$

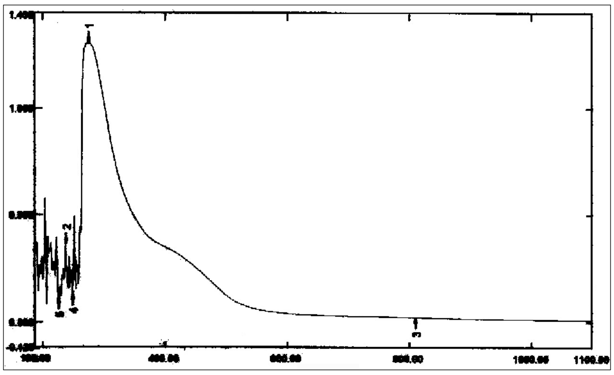


Fig (12) UV-Vis spectrum of [CuL^1Cl]

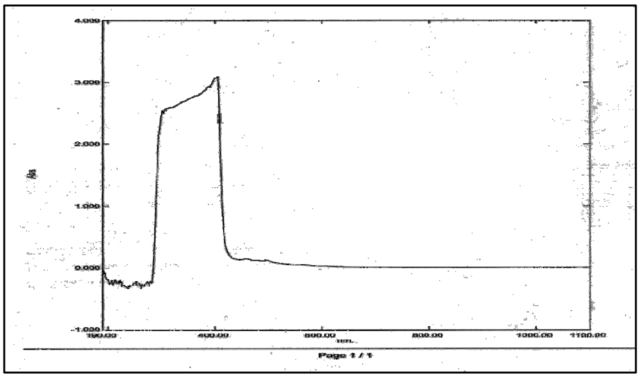


Fig.(13) UV-Vis spectrum of [H_2L^2]

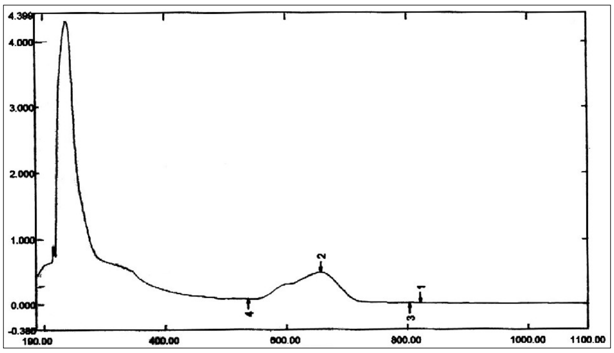


Fig (14) UV-Vis spectrum of [CoL^2]

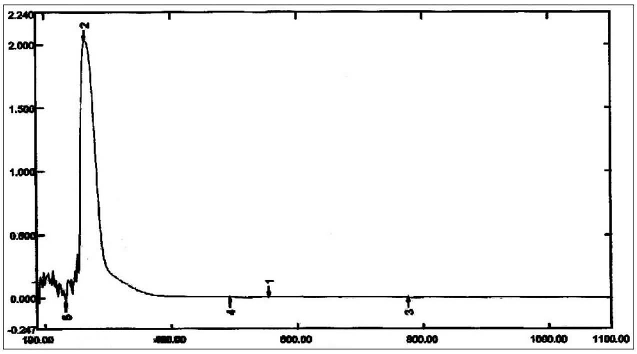


Fig (15) UV-Vis spectrum of [NiL^2]

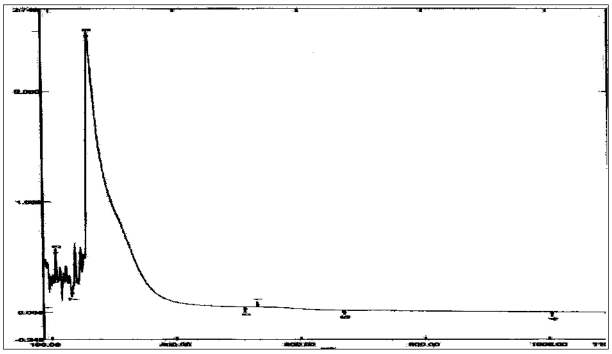


Fig (16) UV-Vis spectrum of [CuL^2]

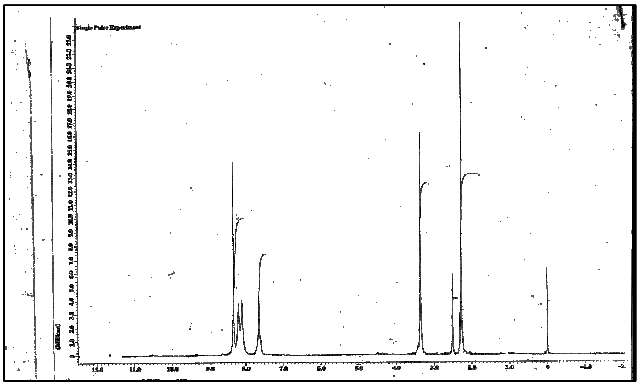


Fig. (17) ^{1}H-NMR spectrum of [HL^1]

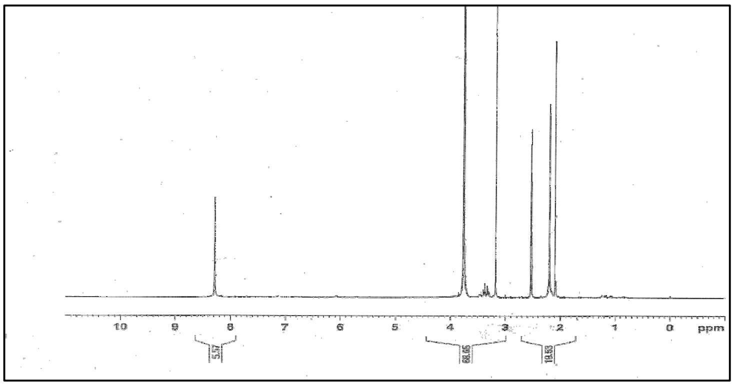
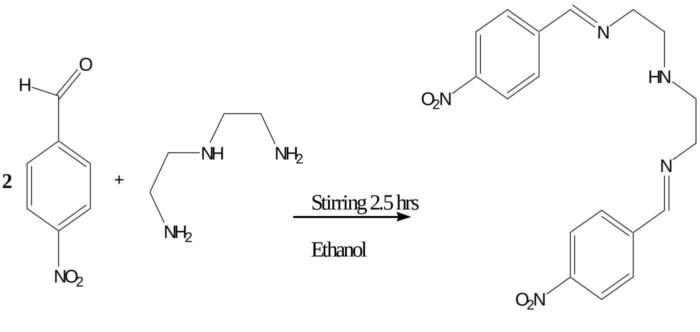
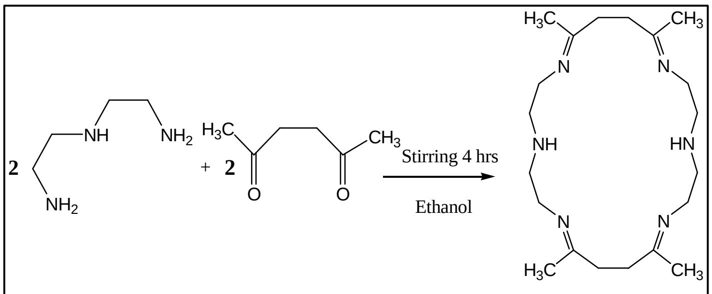


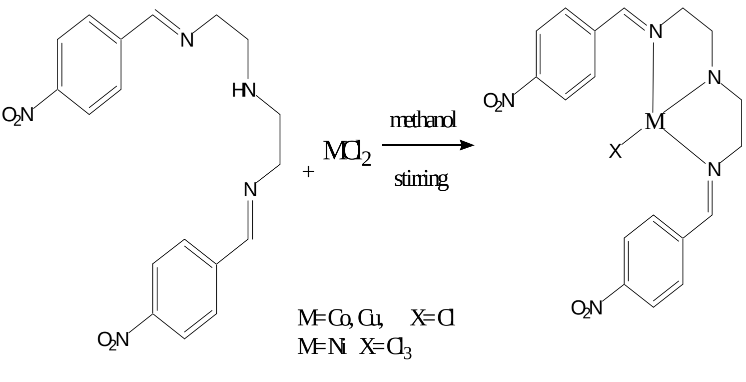
Fig. (18) ^{1}H-NMR spectrum of [H_2 L^2]



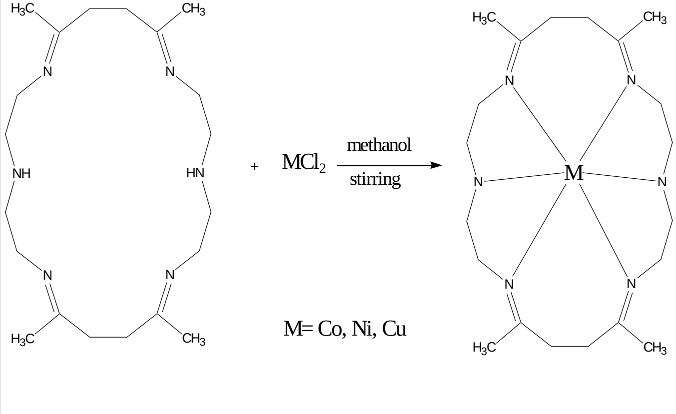
Scheme (1) The synthetic route of the ligand [HL^1]



Scheme (2) The synthetic route of the ligand [H_2L^2]



Scheme (3) The synthetic route of the ligand [HL^1] complexes



Scheme (4) The synthetic route of the ligand [H_2L^2] complexes

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