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SERIT-LIBYA

THE SYNTHESIS AND CHARACTERISATION OF SOME TRANSITION METALS M(II) COMPLEXES OF SCHIFF'S BASE.

THIS THESIS SUBMITTED AS PARTIAL FULLFILLMENTS FOR THE
REQUIRMENTS OF THE MASTER DEGREE OF SCIENCE IN CHEMISTRY

BY

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Contents

Chapter (I)

1. Introduction

Chapter (II)

2. Experimental

Chapter (III)

3. Results and Discussion

LIST OF TABLES

LIST OF FIGURES

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ABSTRACT

The Schiff base ligands and their complexes of divalent metals of Ni(II), Co(II) and Cu(II) were investigated in terms of synthesis, elemental analysis, molar conductivity, thermal analysis, infrared spectra, ultraviolet-visible and magnetic susceptibility measurements. The ligands have been synthesized by condensation of benzoylacetone and ethylenediamine, o-phenylenediamine and 1,6-hexanediamine to gives $H_2L^1 = C_{22}H_{24}N_2O_2$, [N,Ṅ-bis(benzoylacetone)ethylenediamine]; $H_2L^2 = C_{26}H_{24}N_2O_2$ [N,Ṅ-(benzoylacetone)-o-phenylenediamine]; $H_2L^3 = C_{26}H_{32}N_2O_2$, [N.Ṅ-bis (benzoylacetone)-1,6- hexanediamine] respectively. The fourth ligand is formed by the condensation of benzoin and o-phenylenediamine $H_2L^4 = C_{34}H_{28}N_2O_2$, [N,Ṅ.bis(Benzoin)-o-phenylene- diamine]. The ligands and their fifteen complexes have been synthesized by two different methods and their geometries were investigated. A synthesis and characterization of novel ligand and complexes of benzoin derivatives has been achieved. The study also confirmed the formation of mon- and binuclear metal. The binuclear metal complexes are synthesized by new methods.

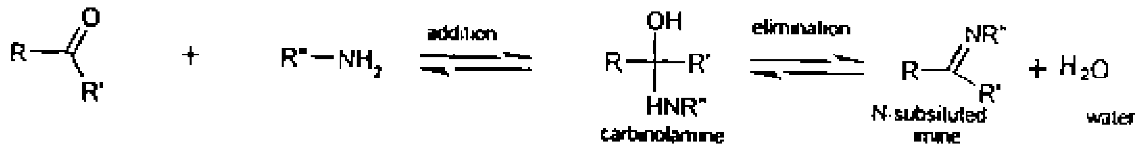
Chapter (I)

Introduction

1.1. Schiff base complexes

Schiff bases are well known classes of organic compounds. These compounds are in which both hydrogen atoms of the amine group (an aromatic or aliphatic primary amines) are replaced by one hydrocarbon group are known as imines, azomethine, or more commonly known Schiff base and containing the structure (C=N—). An imine is a nitrogen analog of an aldehyde or ketone in which the (C=O) group is replaced by a (C=NR) group where R = alkyl, aryl or H(1).

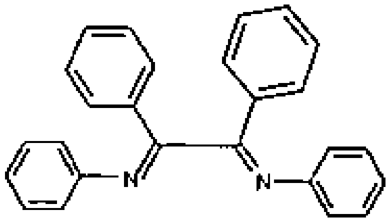
Imines formation is an example of a large class of reactions in which two or more organic compounds were condensed together with elimination of water molecules. Formation of imine is reversible and generally takes place with acid or base catalysis or with heat. The mechanism of imine formation begins as nucleophilic addition to the carbonyl group in this case the nucleophilic is the amine which reacts with the aldehyde or ketone to give an imines (2). In the first stage of the reaction the amine add to the carbonyl group to give a species known as a carbinolamine, Scheme (I). Once formed the carbinolamine undergoes dehydration to yield the product of the reaction, an N—alkyl or N—aryl substituted imines (3).



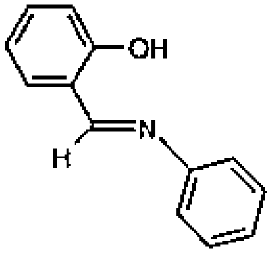
Scheme (I). Formation of Schiff base.

If one or both reagents are aromatic the Schiff bases are formed because the presence of the aromatic ring in conjugation with the double bond in the product is apparently necessary to provide stability (4). Imines are important in many biochemical reactions because many enzymes use a NH_2 group of an amino acid to react with an aldehyde or ketone to form an imine linkage (5). Both imine formation and hydrolysis have been studied extensively because of their relevance to biochemical processes. Many biological reactions involve initial binding a carbonyl compound to an enzyme or coenzyme by way of imine formation. Recently they used imidazole containing Schiff base ligands in synthesis of transition metal complexes as structural models of some metalloenzyme (6, 7). Schiff bases represent an important class of chelating agents, the metal complexes of which have been studied widely. During the past decades, there has been a great deal of interest in the synthesis and characterization of transition metal Schiff base chelate because of their important as catalysts in many reactions such as carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis (8-12). Metal complexes of Schiff base have contributed widely to the inorganic chemistry of chelate system. Many of these transition metal complexes derivatives of Schiff bases have been prepared and investigated and are studied extensively due to synthetic flexibility of these compounds and selectivity as well as sensitivity toward the central metal (13, 14).

The transition metal complexes with Schiff bases have been amongst the most widely coordination compounds. In general the azomethine group (C=N—) which is functional group of the Schiff base is aided in the formation of stable complexes by either a such group (I) an acid group like a phenolic OH (II) or another donor group (III) the formation of a chelate ring seems essential for the production of stable complexes with ligand containing the azomethine group(7).



(I)



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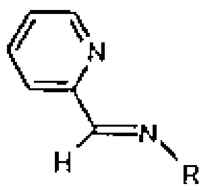


(III)

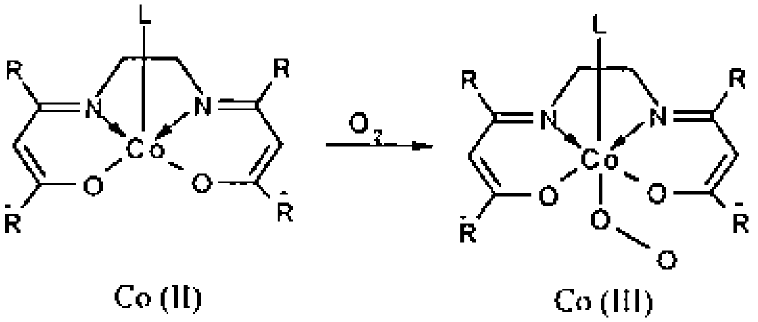
During the past two decades considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor, this may be attributed to their stability, biological activity and potential application in fields such as oxidation catalysis and electrochemistry(15-17).

1.2. Application of some Schiff base complexes

The biological activity of Schiff bases and their complexes that have received attention owing by many of prior research. In recent years metal complexes of Schiff bases have attracted considerable attention due to their remarkable antifungal antibacterial and antitumor activities$^{(18, 19)}$.

Earlier work has shown that some drugs showed increased activity when administered as metal chelate rather than as organic compound, the Schiff base of o-phenylenediamine and it is complexes have a variety of applications including biological, clinical,$^{(20)}$ analytical,$^{(21)}$ and the coordinating possibility of o-phenylenediamine has been improved by condensing with a variety of carbonyl compounds$^{(22-24)}$.

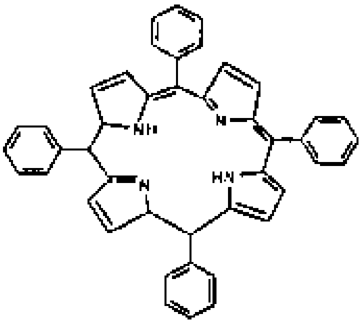
Several new transition metal using Schiff base containing, pyridine and amide moieties were prepared, $^{(25)}$ their antibacterial activities have been studied by microcolorimetry, the result shows that the ligand and all complexes are potential antibacterial reagent and their inhibitory capacities are concentration depended. The antibacterial activity of ligand and its complexes have been carried out against bacteria like S.qureus, E.Coli, B.Subtilis and the fungus A-niger, using nutrient agar medium by the well diffusion method. The neutral tetradentate 2N2O type complexes of Cu(II), Ni(II), Co(II), and Zn(II) have been investigated, $^{(26)}$ by using the Schiff base ligand formed by the condensation of acetylacetone and p-anisidine, they found all the complexes were screened for antimicrobial activity. Antibacterial activities of the ligand and its complexes have been carried out against bacteria like S.aureus, E.Coli, B.subtils and A.niger, using nutrient agar medium by the well diffusion method. From these studies they observed that metal chelates have a higher activity than free ligands. Some metal studies have involved the reactions of O_2 with certain Co (II) Schiff base complexes. Reactions such as that represented in **scheme (II)** yield Co (III) compounds in which the O_2 molecule is bond end-on to the metal centre. The Co (II) complexes formed can be considered to contain coordinated [O_2] but the presence of the axial base L is Crucial to the formation of the monomeric product.



L= monodentate ligand e.g.py

Scheme (II)

A logical ligand to model the active sites in myoglobin and haemoglobin is one derived from porphyrin Tetraphenylporphyrin scheme (III) is readily available, but the reaction of the Fe(II) complex $Fe(tpp)_2$ with O_2 lead to a peroxobridged Fe(III) complex (27).



Scheme (III)

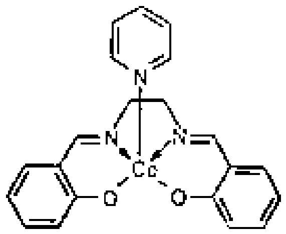
Among the d-block metals that bind O_2 acts as helpful model system like simple Fe(II) complexes , Co(II) complexes react with O_2 by electronic transfer.

$$[\mathrm{L\ Co}]^{2+} + O_2 \rightarrow [\mathrm{L\ Co(III)}\ O_2^-]$$

The product is formally a Co (III) complex of the superoxide ion O_2^-

$$[\mathrm{L\ Co(III)}\ O_2^-] + [\mathrm{L\ Co(II)}] \rightarrow [\mathrm{L\ Co(III)}\text{-}(O_2^{2-})\text{-}\mathrm{Co(III)\ L}]$$

This reaction may be occurs on macro Schiff ligands analogy to haemoglobin, the Co(II) complexes of ligands such as Salen the Schiff base chelating ligands in **scheme (IV)** and a base such as pyridine react with O2 in rapid reversible reaction which is suggestive of the reactions of Mb or Hb (28) .



$$[\mathrm{Co(salen)\ (Py)}] + O_2 \rightleftharpoons [\mathrm{Co}(O_2)\ \mathrm{(Py)\ (salen)}]$$

Scheme (IV)

The current model for O_2 binding to the low-spin Fe (III) centre in haemoglobin and myoglobin is that coordination is accompanied by electron transfer. Oxidizing high spin Fe (II) to low spin Fe (III) and reducing O_2 to O_2^- . Other Π-acceptor ligands can take the place of O_2 in haemoglobin or myoglobin and this is the basis of the toxicity of CO.

Cyanide however although a Π-acceptor ligand favours higher oxidation state metal centres and binds to Fe(III) in cytochromes CN poisoning is not caused by CN blocking the O_2 binding sites in haemoglobin(27).

Carbon monoxide CO is a common Cause of accidental poisonings. The carbon monoxide enters the blood stream in the alveoli of the lungs. In the blood it reacts with blood haemoglobin (O_2Hb) to carboxyhemoglobin (COHb). In this case haemoglobin is the receptor acted on by the carbon monoxide toxicant. Carboxyhemoglobin is much more stable than oxyhemoglobin so that its formation prevents haemoglobin from binding wit oxygen and carrying it to body tissues.

1.3. Coordination compounds

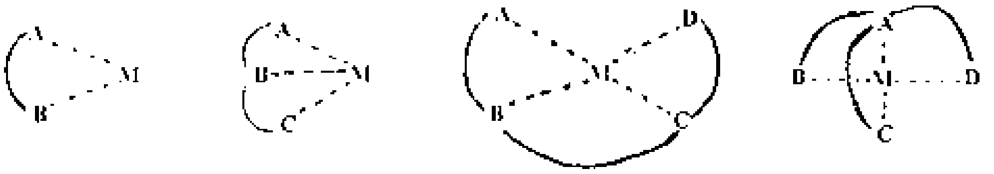
The transition elements are known for their ability to form many complex compounds in which the metal action is surrounded by two or more ions or molecules generally refered to as ligands. These complexes are also called coordination compounds, because one way to the bonds between the metal ion and the ligands are as coordinate covalent bonds. Coordination compounds have many numbers of properties such as several colors, magnetic properties, structures and chemical reaction, therefore the study of coordination compounds has received a major attention in inorganic chemical researches. Also these compounds have a number of important uses such as softening of water by formation of a complex ion and as catalysts in variety of industrial processes (29). In 1893 Werner proposed of coordination theory to explain how bonding occurs between the metal action and ligands in coordination compounds. He saw the valences of the metal in a stable compound having the formula $CoCl_3.6NH_3$ have two types of valence primary and secondary valences. In $CoCl_3.6NH_3$ according to Werner cobalt has a primary valence of three and a secondary valence of six. Today we use the formula $[Co(NH_3)_6]Cl_3$ to indicate that the ammonia molecules and the cobalt atom form a complex ion, the chloride ions are not part of the complex but are held to it by ionic forces (30). The coordination process is an Lewis acid-base interaction. In general an increase in basicity of the ligand and or an increase in the acidity of the metal enhance the stability of the complex formed (31). As a rule ligands are Lewis bases that have one or more unshared pairs of electrons that they can use to form coordinate covalent bonds. Coordination compounds have many applications in biochemistry as a complex ion such as "Blood hemoglobin" containing iron (II) is a well known example. Other example is green chlorophyll, which formed from the reaction between the porphyrin (tetradentate ligand) with Mg^{+2} in the plants. The plants used the chlorophyll as catalytic agent and sunlight in the photosynthesis process, where carbon dioxide and water are combined to form carbohydrates (32).

1.3.1. Structure of Complex ions

A complex ion described by the metal ion and the number and types of ligands attached to it. Therefore, its structure is related to three characteristics (coordination number, geometry and number of donor atom per ligands).

- **Coordination number** In coordination compounds is defined as the number of donor surrounding the central metal atom in a complex ion. For example the coordination number of Ag(I) in $[Ag(NH_3)_2]^+$ is two, that of Cu(II) in $[Cu(NH_3)_4]^{+2}$ is four and that of Fe(III) in $[Fe(CN)_6]^{-3}$ is six.
- **Ligands** The ligands in the complex ions known as the ability to donate electron pairs to central metal atoms or ions, ligands are Lewis bases and donating electron pairs, central metal atoms or ions act as Lewis acids. A ligand that uses one pair of electrons to form one point of attachment to the central metal atom or ion is called a monodentate ligand. Some ligands are capable of donating more than one pair form different atoms these called polydentate. Bidentate and polydentate ligands are also called chelating agents because of their ability to hold the metal atom like a claw one example is ethylenediamine (en) abidentate ligand and ethylendiamine tetraacetate ion (EDTA) a polydentate ligand. Mixed donor ligands can participate in bi-, tri-, tetra-and higher dentate coordination

modes examples of the first three of which are show in **scheme (V)** A, B, C and D are nonmetals capable of forming coordination bonds to the central atom with significant σ-bond character. Of major importance in the stability and chemistry of mixed donor ligands are two major concepts of coordination chemistry the chelate effect and the Hard & Soft Acid – Base theory. The chelate effect aperable for all multidentate ligands is the increase in stability of a given type of complex as the number of chelate ring increases (33).

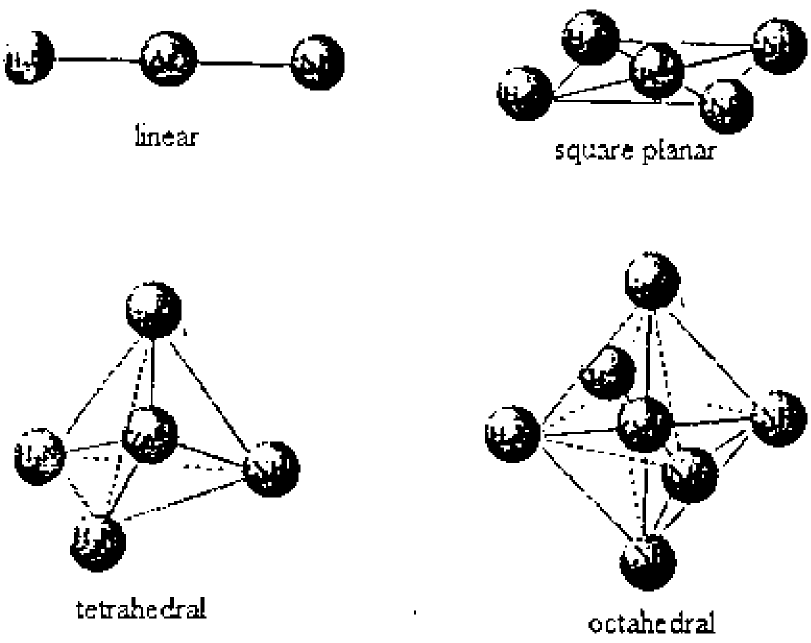


Scheme (V)

The HSAB theory is particularly applicable to mixed donor ligands because of the general tendency for "hard" nonpolarizable donors such as nitrogen and oxygen to bond to hard nonpolarizable metal ions such as the first row transition series in higher oxidation states. Likewise "soft" polarizable ligands such as sulfur, phosphorus. arsenic, selenium and tellurium have a greater tendency to bond to the low valent, more polarizable metal ions of the second and third transition series.

- **Geometry** The geometry of complex ion depends on the coordination number and the nature of the metal ion. The

$[Ag(NH_3)_2]^+$ complex ion formed by the reaction between Ag^+ ions and ammonia, the coordination number is two and has a linear geometry, other examples are $[CuCl_2]^-$ and $[Au(CN)_2]^-$. Coordination number four, there are two types of geometries with a coordination number of four. The $[Zn(NH_3)_4]^{+2}$ and $[CoCl_4]^{-2}$ ions have tetrahedral geometry, whereas the $[Pt(NH_3)_4]^{+2}$ ion has the square planar geometry. Coordination number six, all have octahedral geometry, for example of $[Ni(H_2O)_6]^{+2}$ is octahedral cation and $[Co(NH_3)_6]$ an octahedral complexes of Co(III) ion. These complex ions and their structures show below in Scheme (VI).


linear
square planar
tetrahedral
octahedral

Scheme (VI) Structure of some complex ions.
Attachment of the NH_3 molecules occurs through the lone pair electrons on the N atoms.

1.3.2. Bonding in complex ions

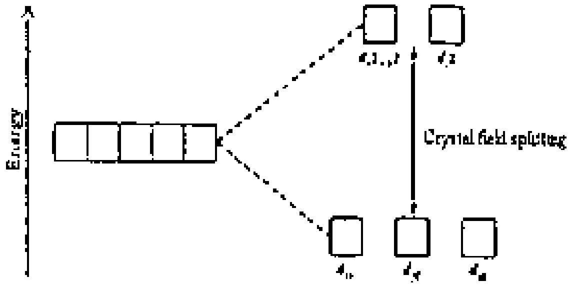
Only one theory gives a satisfactory of bonding in coordination compounds and for properties (such as color and magnetism as well as stereochemistry and bond strength) is crystal field theory. It is considering bonding in complex ion to be an electrostatic attraction between the positively central metal ion and electrons in the ligands.

1. 3.2.1 Octahedral Complexes

In octahedral complex when six ligands approach to the five d-orbitals of metal, the five d-orbitals are splits into two sets of energy levels, a higher level with two orbitals are ($d_{x^2-y^2}$ and d_{z^2}) having the same energy and other in a lower level with three equal energy which are (d_{xy}, d_{yz} and d_{xz}), **Scheme (VII)**. The energy difference between the two sets of d-orbital in the metal atom when ligands are present is called crystal filed splitting Δ_o. The magnitude of Δ_o depends on the metal and the nature of the ligands, it has direct effect on the color and magnetic properties of complex ions. The order of increasing value of Δ_o of different ligands are arranged in a spectrochemical series, which is arranged the ligands in terms of increasing abilities to split the d-orbital energy levels.

$$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < en < CN^- < CO$$

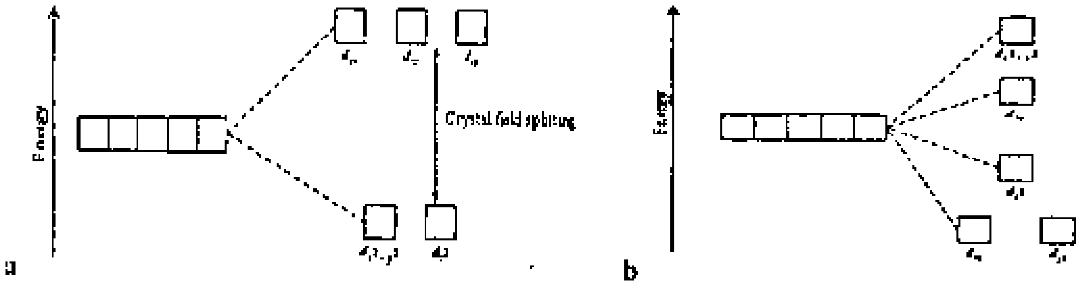
The CO and CN^- are called strong field ligands, while the halide ions and OH^- week field ligands, because they split the d-orbitils to a lesser extent.



Scheme (VII) Crystal filed splitting between d-orbital in an octahedral complex.

1. 3.2.2 Tetrahedral and Square-planar Complexes

The splitting of d-orbital energy levels of tetrahedral complex is just the reverse of that for an octahedral one. In this case the (d_{xy}, d_{yz} and d_{xz}) orbitals are more closely directed at the ligands and therefore, have higher energy than the ($d_{x^2-y^2}$ and d_{z^2}) orbitals, Scheme (IV). Most tetrahedral complexes are high-spin complexes. The crystal field splitting of square-planar complex is the most complicated. The orbital $d_{x^2-y^2}$ possesses the higher energy and the d_{xy} orbital the next highest. However relative position of the d_{z^2} and the d_{xz} and d_{yz} orbitals are lower energy but cannot determine simply by inspection and must be calculated.



Scheme (VIII) Crystal filed splitting d-orbitals in Tetrahedral and (b) square planar complexes.

1.4. Transition metals

Transition metals have incompletely filled d-subshells or ions with incompletely d filled subshells. This feature is responsible from several properties including distinctive coloring, formation of paramagnetic compounds, catalytic activity and a great tendency to form complex ions. Most transition metals are inert toward acids or react slowly because of a protective layer of oxide. The common oxidation states for each elements include (+II), (+III) or both. The first row of transition elements (from Sc to Cu) for example, their nuclear charge is increases but electrons are added to the inner 3d subshell orbitals. So the atomic radii decrease less rapidly, for the same reason electronegativity and ionization energies increase slightly. The transition elements have high melting point, good electrical conductivity, availability of electrons and metallic bonding (32).

1.4.1. Cobalt Co (II) $3d^7$

Cobalt is a hard bluish-white metal is used mostly in catalysis and alloys. The important common oxidation states of Co (II) and Co (III) possessing the electronic strictures $3d^7$ and $3d^6$ the most stable species Co (II), but Co (III) state is unstable except in the presence of molecules or anions which it can form complex ions. The most common Co(II) complexes may be either octahedral or tetrahedral, there is only small difference in stability and both types can be formed with the same ligand.

Cobalt (II) forms tetrahedral complexes more readily than any other transition metal ion. Cobalt (II) is a $3d^7$ configuration and most complexes are low-spin octahedral, the tetrahedral complexes are also common and have more intense colors than octahedral complexes.

Less commonly Co (II) forms a square planar complex with bidentate ligand such as diethylglyoxime and tetradentate ligand as porphyrin. Magnetic measurements can be used to distinguish between tetrahedral and square planar arrangements, tetrahedral complexes have three unpaired electrons and square planar has only one electron (34). The cobalt (II) ion forms octahedral complexes such as $[Co(NH_3)_6]^{-2}$ and square planar complexes such as dimethylglyoximatocoballt (II) and tetrahedral complexes such as $[CoCl_4]^{-2}$.

1.4.2. Nickel Ni (II) $3d^8$

In the pure state it resists corrosion and also used as a catalyst for hydrogenation of organic compounds that contain double bounds, the most oxidation state of nickel is (+II). Nickel (II) has form a large number of complexes. The five well known structural types are octahedral, trigonal bipyramidal, square pyramidal, tetrahedral and square planar. The maximum coordination number shown is six and with octahedral complexes are the most numerous nickel (II) also forms many five coordinate (square pyramidal and trigonal bipyramidal) and four coordinate (tetrahedral and square planar). The octahedral complexes are usually blue in color and they are paramagnetic as $3d^8$ ion which has two unpaired of electrons. In complexes with strong field ligand such as CN^- the electrons are forced to pair-up and diamagnetic square planar complexes such as $[Ni(CN)_4]^{-2}$ are formed (34). The aqua ligands in the octahedral $[Ni(H_2O)_6]^{+2}$ ion can be replaced by amines to give ions such as $[Ni(NH_3)_6]^{+2}$ and $[Ni(en)_3]^{+2}$. Their magnetic moments are in the range 2.4 to 3.4 B.M indicating that there are two unpaired electrons, several of the paramagnetic nickel (II) complexes are tetrahedral and many square planar Ni (II) complexes are diamagnetic (35). Most of the four coordinate of Ni(II) are square planar a consequence of the $3d^8$ configuration since the planar ligand set causes one of the d orbital $(d_{x^2-y^2})$ to be uniquely high in energy and the eight electrons can occupy the other four d orbital but leave this strongly antibonding. The square planar complexes of Ni (II) formed by very strong field ligands such as CN^- of $[Ni(CN)_4]^{-2}$ for example is diamagnetic.

1.4.3. Copper Cu (II) $3d^9$

The copper, sliver and gold metals have been the preferred metals for coins because they are so durable and resistant to corrosion. The metal ions are easy to reduce to the free metals which mean that metals are difficult to oxidize (32). Copper has two important oxidation states (+I) and (+II) the first oxidation state is less stable and disorientates in solution. All compounds of Cu(I) are diamagnetic and color less expect for Cu_2O which is red but the Cu(II) compounds are all paramagnetic and colored.

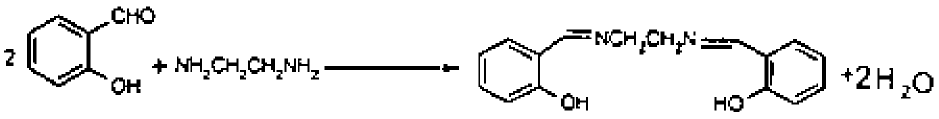
The Cu (II) state is the most stable and important, it has the electronic configuration $3d^9$ and has unpaired electron. The Cu (II) compounds are colored and paramagnetic due to d→d spectra (34). The d^9 configuration often give square planar structure with four ligand in plane and distorted octahedral structures in which two more ligand are attached by some what longer bonds above and below the plane.

Copper (II) forms many complexes with nitrogen ligands the four coordinate are usually much more stable than six coordinate. Glycine reacts with Cu (II) state to forms many complexes diglycinecopper (II) $(NH_2CH_2CO_2)_2Cu(II)$ coordinated through both oxygen and nitrogen. There are also numerous complexes with chelating oxygen donor, such as β-diketone, β-diketoesters and salicylic acid (35). Copper is one of the trace elements essential to the healthy life of many plants and animals usually occurring as a part of the prosthetic group of the oxidizing enzymes these oxidizes high molecular weight proteins containing 0.05-0.35 % of copper play a part in life's vital oxidation and reduction processes the copper undergoing cyclic changes between the Cu (I) and Cu (II) state (36).

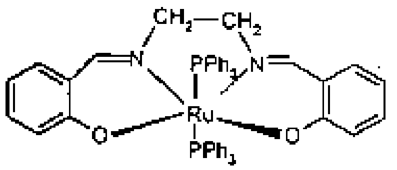
1.5. Complexes with [N, O] Schiff base ligands

Tetradentate Schiff base with 2N2O donor atom set are well known to coordination with various metal ions this has attracted many authors [37-39]. The various ligands usually contain both N and O donor atoms although purely N as well as N, S donors exist. Also complexes of transition metals (II) which involve the derivatives of salicyldehyde and diamine have gotten considerable attention. This is because of their potential as catalysts for the insertion of oxygen into an organic substrate (40, 41).

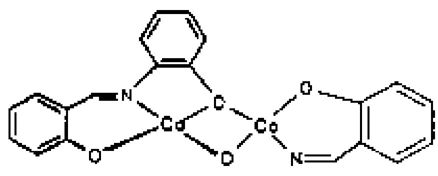
One of the best known Schiff base ligands is bis(salicyldehyde) ethylenediamine (Salen). This is an acidic (two OH groups) tetradentate (2N2O) ligand.



Other Schiff bases can be mono, di or tetra functional and can have denticities of six or more with various donor atom combinations (e.g. for pentadentate 3N2O, 2N3O, 2N2OP, 2N2OS). Complexes of un-ionized or partly ionized Schiff bases are also known (e.g., $LaCl_3salenH_2.aq$). Some representative types of complexes that illustrate the formation of not only mononuclear but of binuclear and polymeric species are (a) and (b) (42).

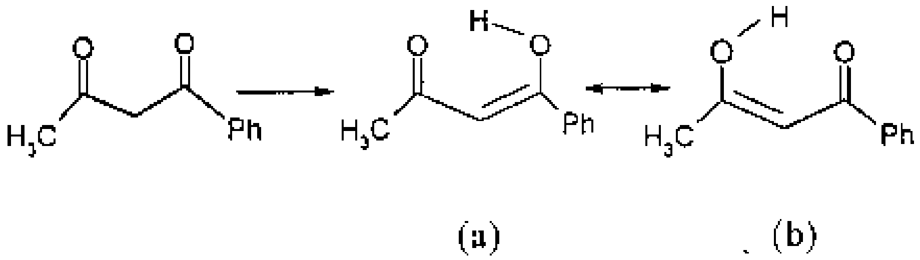


(a)



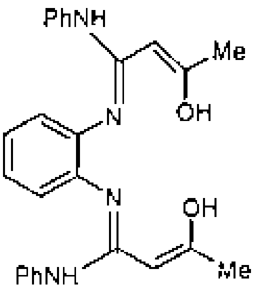
(b)

Recently a new type of unsymmetrical tetradentate Schiff base ligand was formed from the condensation between distinct aldehydes or ketones with aliphatic diamine and few examples of non-symmetric ligands derived from o-phenylenediamine have been studied (41). Benzoylacetone is a β-diketone that upon enolization forms a cis- β-keto-enol structure with an intramolecular hydrogen bond. which potentially can be either asymmetrical as in a and b (44).



New complexes of vanadium (IV) and oxovanadium (IV) with Schiff base ligands derived from β-diketones and ethanolamine o-amino-phenol have been synthesized and characterized. (45) they found that the IR spectra of the free ligands showed a strong band in the region 3270 – 3350 cm^{-1} which attributed to the intramolecular hydrogen bonding between the azomethine nitrogen and hydrogen atom of the enolic form of the β-diketon moiety.

The neutral tetradentate 2N2O type complexes of Cu (II), Ni (II), Mn (II), Zn (II) and VO (II) have been synthesized (20). They used a Schiff base formed by the condensation of o-phenylenediamine with acetoacetanilide in alcohol medium. The structure of the ligand shown in **scheme (IX)**.

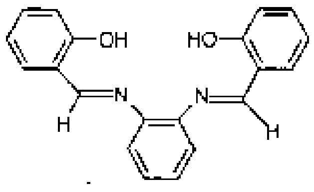


Scheme (IX)

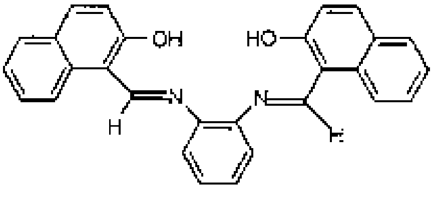
This ligand system has both nitrogen and oxygen donor sites, it coordinates to the metal ion in tetradentate manner through the enolisable carbonyl group of the acetoacetanilide moiety and azomethine nitrogen atoms of the Schiff base. The IR spectra of the free ligand showed the band at 1650 cm^{-1} of ν(C=N) this band shift to lower frequency region 1600 – 1580 cm^{-1} which is observed in all complexes which indicated nitrogen atom of azomethine group is coordinated to central metal ion, (46) also showed a broad band at 3600 – 3200 cm^{-1} of OH group indicated that the enolic carbonyl group of acetoacetanilide moiety of the ligand. The disappearances of these peaks in the spectra of all complexes indicate that chelating take place via the enolic-OH group.

The manganese complex showed abroad band at 3500 – 3100 cm^{-1} which suggests that water is coordinated to the central metal ion (46, 47).

Tetradentate Schiff base ligands with a 2N2O donor atoms and their complexes with nickel, copper and zinc have been synthesized(48) the ligands are formed by (1:2) molar ratio were condensation of o-phenylenediamine with salicylaldhyde, structure (1), 2-hydroxy-1-naphthaldyde, structure (2).



(1)



(2)

In general, he found that the ligands showed abroad band at (2800 - 2700 cm^{-1}) region which confirms the intramolecular hydrogen bonded of OH group. The phenolic v(C—O) stretching vibration, that appeared at 1298 cm^{-1} in the Schiff bases (49,50) undergo a shift towards higher frequencies by 20 to 40 wave number in the complexes. This shift confirmed the participation of oxygen in the C—O—M bond (51, 52). Also a strong band appeared at about 1613 cm^{-1} in the free ligands and their complexes. This band is attributed to the C=N stretching vibration (51). Also the complexes showed new band at low frequency region 410 - 438cm^{-1} is attributed to v(M—O) and in the region 505 - 516 cm^{-1} to v(M—N) (53) all the IR spectra suggest that the metal is bonded to the Schiff bases through the phenolic oxygen and the imino nitrogen. The electronic spectra of the ligands exhibit three main peaks at about 270, 333 and 372 nm. The first and the second peaks are attributed to benzene $\pi \rightarrow \pi^*$ and imino transitions, respectively. These bands were not significantly affected by chelation. The third band in the spectra of the ligand 372 nm is as signed to

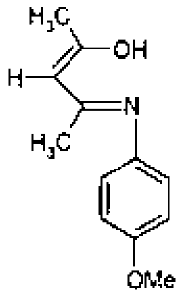
$\pi \rightarrow \pi^*$ transition. This band is shifted to a longer wave length by 28 nm along with increasing in its intensity. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N→M)⁽⁵⁴⁾.

The spectra of nickel (II) complexes consist of two bands at about 535 and 488 nm. These complexes have diamagnetic properties using a Gouy balance. The brownish red color of the complexes, its diamagnetism and the position of the electronic absorption bands of medium intensity are characteristic of low-spin square-planar Ni (II) complexes (55). The spectra of Cu(II) complexes showed two bands in the visible region at about 570 and 428 nm and assigned to $^2B_2g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2Eg$ transitions, respectively. The observed magnetic moment values of these complexes are ranged from 1.82 to 1.88 B.M. These electronic bands and paramagnetism values suggesting also a square-planar geometry around the copper (II) ion (56).

The natural tetradentate 2N2O type complexes of Cu (II), Ni (II), Co (II) and Zn (II) have been synthesized, (26) they use the Schiff base formed by the condensation of acetylacetone and p-anisidine.

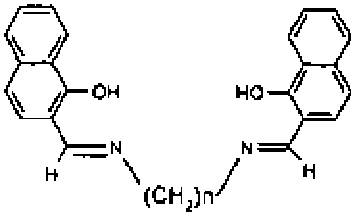
It coordinated with the metal (II) ion in a bidentate manner through the enolisable carbonyl group of acetylacetone and the azomethine nitrogen atom of p-substituted aniline of the Schiff base. Form the IR, UV-vis and H^1-NMR data they found that all complexes possesses a square-planar geometry. The IR spectrum of the Schiff base has a broad band absorption at 3190 cm^{-1} which is assigned to the enolisable of OH group of the acetylacetone moiety, the disappearance of the band in the complexes spectra in which enolic protons are completely displaced by metal (II) ions, the strong band at 1620 cm^{-1} region is assigned to the azomethine group is shifted to lower frequency in the region 1600 - 1580 cm^{-1} which indicates that the coordination takes place through the azomethine group.

The ligand spectra has no absorption at 1700 cm^{-1} which indicated that free carbonyl groups are absent and so converted to ketaimine structure. The electronic absorption spectral of the Schiff base and its Cu(II), Co(II) and Ni(II) complexes were recorded at room temperature in DMSO as solvent the electronic spectra of the ligand showed a broad band at 25706 cm^{-1} which is assigned to a centre ligand charge transfer band (INCT). The Cu(II) complex showed a band in the region 2188 cm^{-1} due to $^{2}B_{1}g(p)\rightarrow{}^{2}A_{1}g$ transition which supported square planar geometry. The Co (II) complex showed absorption in the region 16366 cm^{-1} corresponding to $^{1}B_{1}g$ (p) $\rightarrow{}^{1}B_{1}g$ transition which also supported square planar geometry. The Ni (II) complex showed absorption in the region of 20000 cm^{-1} assigned to $^{1}A_{1}g(p)\rightarrow{}^{1}B_{1}g$ transition which again suggests square planar geometry. The magnetic susceptibility measurements indicted magnetic moment of the Cu (II) complex is 1.15 B.M which shows the presence of one unpaired electron and of Ni (II) complex is zero which indicated that complex has square planar structure. The magnetic moment of the Co (II) complex is 3.58 B.M and is also indicated of square planar configuration. The structure of the Schiff base is shown below.



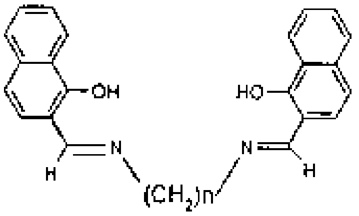
The synthesized and characterized of some new M (II), (III) complexes containing tetradentate Schiff base ligand (H_2L) ⁽⁵⁷⁾, the Schiff base derived from 2-OH-1-naphthaldehyde and aliphatic diamines $H_2N(CH_2)_nNH_2$ (n = 2,3,4 or 10). The structure and reactivity of the Mn (II) complexes were formed for n = 2, 4 or 10 but for n = 3 the pseudo-octahedral [$MnL(H_2O)$] was formed. In addition some Mn (II) complexes [$MnL(H_2O)]ClO_4$ have been obtained.

The synthesized and characterized of a series of potentially tetradentate Schiff base ligands for example N,Ṅ-ethylene bis(1-hydroxy-2-naphthylmethyleneimine) (H_2napen) in which the methylene linkage between the imine donors varies from C_2 to C_6 have been complexed to Cobalt(II) ⁽⁵⁸⁾. Two types of complex are formed $CoL(H_2O)n$ (n = 0) complex is planar n = 2 complex is pseudo-octahedral) in which the ligand binds as a dianionic tetradentate 2N2O donor and $Co(H_2L)Cl_2$ which are pseudo tetrahedral and the ligand is neutral binding through the imine group only. The structure (shown below) seems to be mainly dependent on the length of the methylene chain of the ligand.



Where n =2, 3,4,5,6

The IR spectra showed bands typical of Schiff base complexes with strong peaks in the 1650-1500 cm^{-1} region (59-61). There were generally three peaks in this region which could be assigned to v(C=N) vibration when coordinated as diamine tetradentate 2N2O species this band is shift to lower region by 15-35 wave number from that in the free ligand, (62) whilst coordination as a neutral bidentate ligand via azomethine nitrogen complexes shifts this band to higher frequencies the magnitude of this shift being only of the order of 5 - 10 cm^{-1} (63-65) and broad a absorption at 3450cm^{-1} suggest the presence of water molecules. The magnetic moment at room temperature are consistent with the structure assigned to the complexes from their electronic spectra, that the complex (1) [Co(napen)] is square planar 2.7 B.M the electronic spectra exhibited a band at 1200 nm, which is characteristic of square planar cobalt(II) species (62). The other complexes are pseudo tetrahedral or pseudo octahedral have range of magnetic moment at 4.3 - 5.3 B.M, with the exception of complex $[Co(nappn)(H_2O)_2]$ and $[Co(napbu)(H_2O)_2]H_2O$ which are showed group only. The structure (shown below) seems to be mainly dependent on the length of the methylene chain of the ligand.



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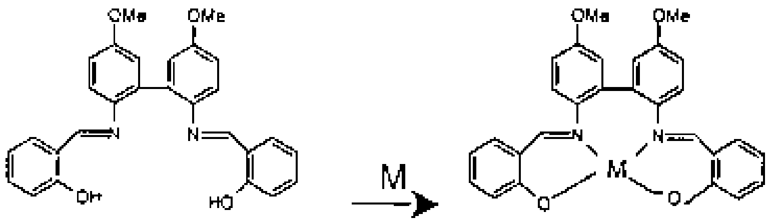
The investigation of the infrared spectra to novel Schiff base ligand derived from 2,2'-bis (p-methoxyphenylamine) and Salicylicaldehyde and it's transition metal complexes with Cu(II), Co(II) and Mn(II) have been synthesized (66).



M= Cu (II), Co (II), Mn (II).

Scheme (X)

They found disappearance of OH band of the free ligand in IR spectra of the metal complexes indicates that the OH group is deprotonated and the v(C=N) stretching mode is shifted to a lower frequency by about 29 wave numbers compared to the free ligand. These IR results indicate that the ligand is coordinated to Cu (II), Co (II) and Mn (II) via both N and O. The new IR bands appearing at 420 – 430 cm^{-1} and 541 – 560 cm^{-1} (M—O) and (M—N) vibrations respectively. According to the information data the structure proposed is shown below. It is suggested that the complexes are square planar or nearly square planar coordinated.

Metals complexes of Cu(II), Co(II), Ni(II) and Zn(II) of a new heterocyclic Schiff base derived from 1-amino-5-benzoyl-4-phenyl-1h-pyrimidine-2-on with 2-hydroxynaphthaldehyde has been synthesized (67) it has been found that the Schiff bases behave as a neutral tridentate (ONO) ligand, forming chelates with (M:2L) stoichiometry and suggested that all the complexes have octahedral structure and are non-electrolytes. The IR spectra of the ligand showed a strong band at 1633 cm^{-1} which is changed by ±10-30 cm^{-1} in the spectra of complexes, indicating coordination through azomethine nitrogen of Schiff base. The IR spectra of the complexes showed bands at 445 - 470 and 420 – 426 cm^{-1} regions which may be due to the ν(M—N) and ν(M—O) respectively (68,69). In addition, the IR spectra of all complexes showed a broad band in the region 3240 - 3350 cm^{1} due to the (OH) frequency of crystallization water (68).

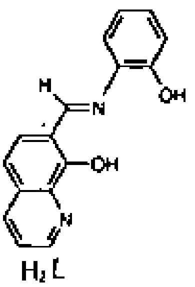
The intense band at 1288 cm^{-1} of the ligand may be assigned to phenolic stretching mode. The six coordinate [Cu $(L)_2$] complex is expected to be tetragonally distorted octahedral and this is confirmed by the characteristic absorption at 742 nm assigned to $^2Eg \rightarrow {}^2T_2g$ transition, which corresponds to the d→d transition band. The geometry of this complex may be assigned as square planar due to two absorption at 595nm and 514nm of $^2B_1g \rightarrow ^2B_2g$ and $^2B_1g \rightarrow ^2Eg$ respectively, but obtained values of the magnetic moment 1.92 B.M are typical for distorted octahedral Cu(II) chelates. $[Ni(L_2)]2H_2O$ showed d-d transitions at 595 nm (14925.3 cm^{-1}) and 765 nm (18050.5 cm^{-1}) corresponding to $^3A_2g \rightarrow ^3T_1g(F)$ and $^3A_2g \rightarrow ^3T_1g(F)$ respectively with octahedral geometry. The magnetic moment values for the Ni (II) complex of the Schiff base ligand at room temperature were found to be in the normal range 2.8-3.5 B.M (70) this complex showed magnetic moment of 3.20 B.M., the Co (II) complex has two bands at 670nm and 554nm which are assigned to $^4T_1g \rightarrow ^4A_2g$ and $4T_1g \rightarrow ^4T_1g$ (P) transition respectively indicating an octahedral configuration around Co (II) ion. The octahedral geometry of the Co (II) complex is further confirmed by the magnetic moment 4.89 B.M (71).

Some new transition metal complexes of Schiff base quinoxalin-2-carboxalidene-2-aminophenol (HQAP) have been synthesized (72) and characterized by elemental analysis, conductance, magnetic moments, electron paramagnetic resonance, IR and UV-vis techniques. They found tetrahedral structure has been assigned for the Mn (II), Co (II), Ni (II) and Cu (II) complexes and an octahedral dimeric structure of Fe (III) complex. The infrared spectra data showed that (HQAP) acts as a bidentate ligand, where the strong ν(OH) stretching band at 3379 cm^{-1} of ligand is absent in the spectra of the complexes which suggested that the phenolic oxygen atom is coordinated at the metal atom in the ionized form, the coordination of phenolic oxygen atom of the complexes is further supported by the fact that the strong band observed at 1280 cm^{-1} in the ligand of the spectrum which is attributed to the phenolic ν(C—O) stretching vibration. The ν(C=N) band of the azomethine linkage appears at 1670 cm^{-1} in the spectrum of ligand is shift to lower frequency at 1630 cm^{-1} in the spectra of the complexes indicating that the azomethine nitrogen is involved in bonding to metal atoms.

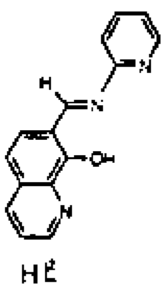
The elemental analysis and spectral data showed formation of the tetradentate Schiff base ligands with 2N2O donor set were formed by the reaction of 2-hydroxy-1-naphthaldehyde and various $H_2N(CH_2)_nNH_2$ linear aliphatic diamines (where n = 2, 3, 4, 5) these Schiff bases and their complexes with Cu(II) have been synthesized and studied (73). The molar ratio of ligand to copper was identified to be 1:1 and the IR spectra of the free ligands showed weak bands of ν(OH) around 3400 cm^{-1} which indicated that there is a hydrogen bonding in the compounds and the complexes showed no absorption bands of ν(OH) in their IR spectra. In the complexes a strong peaks have been observed at the 1631-1642 cm^{-1} region which are assignable to ν(C=N) bands, those bands shift to lower frequency about 10-20 wave numbers in the complexes spectra data relative to those of the corresponding free ligands and two absorption bands at 742-749 cm^{-1}

and 575-594 cm^{-1} in complexes are agreed to Cu—N and Cu—O bands respectively. The H^1-NMR spectra of the free ligands showed peaks at 9.1ppm and 14.1ppm are assigned to the azomethine protons and OH protons respectively.

The several new coordination compounds of copper(II), nickel(II), cobalt(II), manganese(II), Iron(II), tin(II), mercury(II), dioxouranium(VI) and Iron(III) with Schiff bases derived from 7-formyl-8-hydroxyquinoline and 2-aminophenol (H_2L^1) or 2-aminopyridine (HL^2) were synthesized (74).



H_2L



HL^2

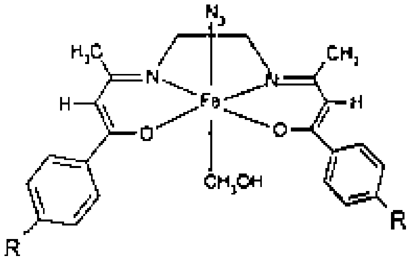
The IR and NMR studies show that the Schiff bases behaves as mono-dibasic and tridentate ligands, coordinating through the oxygen atom of the deprotonated phenolic group, the nitrogen atom of the azomethine group and pyridine. The significant change in IR spectra of the ligand (H_2L^1) upon complexing is that the increase in the azomethine ν(C=N) frequency to higher frequencies by 10-20 wave numbers suggested coordination through the nitrogen of the azomethine group (75). In the ν(OH) water region the IR spectra showed one or two strong sharp bands between 3465 and 3330 cm^{-1} attributed to coordination water (76,77).

In the spectra of other complexes of H_2L^1 and HL^2 a broad absorption at 3500-3100cm^{-1} is observed which indicated lattice water (77, 78). The appearance of some new bands at 450, 365 and 260 cm^{-1} is probably due to the formation of ν(M—O) and ν(M—N) and ν(M—Cl) respectively developed through complexation (79).

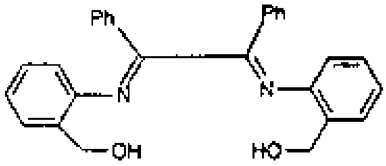
The electronic spectra of $[CuL^1]_2.2H_2O$ complex has a magnetic moment at 1.62B.M and showed three bands at 13680 cm^{-1}, 14895 and 19365cm^{-1}which assigned to $^2B_1g \rightarrow {}^2B_2g$, $2B_1g \rightarrow {}^2A_2g$ and $2B_1g \rightarrow {}^2Eg$ transitions, these are indicated the square planar geometry around two Cu(II) ion (76). The $[CuL^2(H_2O)_2Cl]$ complex has 1.92 B.M and one electronic absorption band at 13280cm^{-1} which assigned to $^2Eg \rightarrow {}^2T_2g$ transition due to octahedral geometry (76). The electronic spectra of Co(II) complex $[CoL^1(H_2O)_2]_2$, has magnetic moment value equal to 4.82 B.M. There are also three bands at 8510, 18510 and 21275 cm^{-1}, which are assigned to $^4T_1g \rightarrow {}^4T_2g$ (F), $^4T_1g \rightarrow {}^4A_2g$ (F) and $^4T_1g \rightarrow {}^4T_1g$ (F) which indicating an octahedral geometry of the complex (74). The $[NiL^1\ (H_2O)_2]_2H_2O$ complex has three bands at 9100, 14810 and 21750 cm^{-1} due to $^3A_2g \rightarrow {}^3T_2g(F)$, $^3A_2g \rightarrow {}^3T_1g(F)$ $^3A_2g \rightarrow {}^3T_1g(P)$,which corresponding to octahedral geometry of Ni(II) ion (79).

New complexes $[Pb_3(salen)_2](ClO_4)_2$ and [Pb(saltren)] have been synthesized (80). The interaction of lead (II) salts with Schiff bases N,N-bis(salicylidene)ethane-1,2-diamine (H_2Saltren) and tris[2-(N-salicylideneamino)ethyl]amino (H_3Saltren) were formed.

The Iron (III) complexes [Fe(4-R-benzen)(CH_3OH)N_3] has the structure shown below, were have been synthesized [81] where (4-R-benzen) are tetradentate open chin 2N2O Schiff base N, N-ethylene-bis(4-R-benzoyl acetoneiminato) ligands (where R= H, Cl, Br, OCH_3, CH_3).



Neutral complexes of Cu (II), Ni (II), Co (II), Mn (II), VO (II) and Zn (II) have been synthesized [82] from the Schiff base derived from benzyl and 2-aminobenzylalchol. They found all complexes exhibit square planar geometry except the Mn (II) and VO (II) chelate which showed an octahedral environment and the VO (II) chelate existed as square-pyramidal geometry. This ligand system coordinates with the metal ion in a tetradentate manner through the hydroxyl groups and azomethine nitrogen atoms of the Schiff base. The structure of the Schiff base is given below and their complexes.



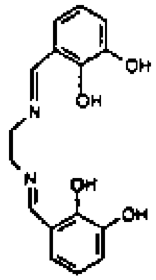
Structure of Schiff base ligand

In order to study the binding mode of the Schiff base to the metal in the complexes the IR spectrum of the free ligand was compared with the spectra of the complexes. IR spectrum of the ligand showed its characteristic of a v(C=N) bands in the region 1640-1620 cm^{-1}, which are also shifted to lower frequencies in the spectra of all the complexes (1600-1580 cm^{-1}). The IR spectra of the metal chelates also showed some new bands in the region 480 – 450 $cm^{-1}$and 400 – 350 cm^{-1}, which are probably due to the formation of (M—O) and (M—N) bands respectively (83). The weak broad band in the region 3250 – 3450 cm^{-1} assignable to intramolecular hydrogen bonded of OH groups, this band after the deprotonation of the OH group on complexation is disappeared. The manganese complex showed a strong broad band in the region 3200 - 3600 cm^{-1}, that value reinforced to the presence of water molecules coordinated to the metal ion. Thermal analysis showed that the manganese complexes losses two water molecules at 170 C° which suggests presence of two molecules water coordinated to the central metal ion which is further confirmed from its characteristic IR spectrum and the low conductance values of the chelates supported the non-electrolytic nature of the metal complexes.

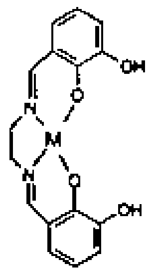
The electronic spectrum of the ligand in cyanomethane (MeCN) solution showed absorption at 31250 cm^{-1}. The UV-vis spectrum of copper in cyanomethane solution displays a broad $^2B_1g \rightarrow ^2A_1g$ (11628 cm^{-1}) and a well defined shoulder $^2B_1g \rightarrow ^2B_2g$ (23529 cm^{-1}), which strongly favors the square planar geometry around the metal ion (84, 85). The broadness of the band can be taken as an indication of distortion from perfect planar symmetry. The further supported by the magnetic susceptibility value 1.72 B.M. The nickel complex is a diamagnetic suggesting a square planar structure and electronic spectra showed a band at 1515 cm^{-1} assigned as $^1A_1g \rightarrow {}^1B_1g$ transition, which also indicates square planar geometry$^{(86, 87)}$.

The cobalt complex in chloroform showed a band at 1600 cm^{-1} assigned as $^1A_1g \rightarrow {}^1B_1g$ transition which confirmed the square planar coordination $^{(88-90)}$, the magnetic susceptibility value 3.86 B.M also supported the square planar structure of the complex.

Crystal structure of mononuclear Cu(II) and Ni(II) complexes [$M(H_2L^A)$] where H_4L^A ligand prepared by the condensation of 2,3-dihydroxy benzaldehyde with ethylenediamine have been studied $^{(91)}$ the physicochemical data suggest the metal ion is in the inner 2N2O and the [$Cu(H_2L^A)$] showed that the square planar configuration. The IR spectra of the ligand showed a strong v(C=N) peak at 1640cm^{-1} and two v(OH) at 3400cm^{-1} (sharp) and broad band 3270-3259 cm^{-1}. By the reaction with Cu (II), Ni (II), the complexes appeared v(C=N) lies at 1631 cm^{-1} shift to lower frequencies of about 10-15 wave numbers in a complexes, with respect to the free ligand and their complexes a single sharp and strong band due to the v (OH) occurs at 3387 and 3399 cm^{-1} with complex of Cu (II) and Ni (II) respectively.



Structure of lignd H_4L^A

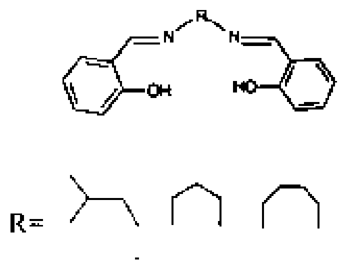


[M (H_2L^A)] complexes of

M=Cu (II), Ni (II)

Mono and poly nuclear neutral complexes have been synthesized and investigated (92) obtained by electrochemical reaction of zinc or cadmium anodes with potentially hexadentate ligands H_4L^n (n =1-3). This ligands were prepared by 2:1 molar ratio condensation of 3-hydroxysalicylaldehyde and 1,2-diaminopropane, 1,3-diaminopropane or 1,4-diaminobutane respectively. They can act as 2N2O dianionic in mononuclear complexes or 2N4O tetranionic in polynuclear complexes where metal ions are held together by μ-phenoxo bridges.

The IR spectra of the ligands and complexes were compared of their spectra in the range 1650-1200 cm^{-1} indicates that the ligands are coordinated via N and O atoms. The ν(C—N) and ν(C—O) modes are present as two very strong bands at about 1640 and 1250 cm^{-1} respectively. The sharp band due to phenolic OH groups appears at about 3220 cm^{-1} for the ligands. This band is disappeared on complexation and a very broad band at about 3400 cm^{-1} which is associated with coordination or solvated water molecules is now present. Also the presence of a sharp band corresponding to the remaining hydroxyl groups would be expected for mononuclear complexes but it is obscure by the presence of water molecules bands.



H_4L^1 H_4L^2 H_4L^3

The complexes of copper(II) with Schiff bases derived from 3-amino and 2-aminopyridine and its derivatives with salicylaldehyde and o-hydroxynaphthaldehyde have been synthesized (93). The compounds have been characterized by elemental analysis, IR and electronic absorption spectra and differential thermal analysis. The data showed formation of two different types of compound with 1:1 and 1:2 metal- ligand stoichiometries and different thermal properties. In the ligand spectra noted a strong band at 1540 cm^{-1}which assigned to ν(C=N) this band shift to lower frequency region in the complexes, which indicated the formation of a coordination bond between the nitrogen of the azomethine group and the metal ion. The IR spectra of ligand showed the band at 1285-1274 $\text{cm}^{-1}$for the salicylaldehyde Schiff bases and 1319-1300 cm^{-1} for the naphtaldehyde analogue, which is assigned to ν(C—O). This band shifted to higher frequency in spectra of complexes at 1290-1390 cm^{-1} region, which assigned to suggesting its involvement in chelating with metal ion.

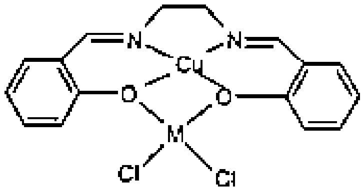
The ON-NO donor Schiff base , N,N-bis(benzoin)benzidine were synthesized (94) and formed complexes with cobalt(II), nickel(II), copper(II), manganese(II), zinc(II), cadmium(II) and mercury(II) with it. The cobalt (II) complex is a blue monomer of tetrahedral configuration, the nickel (II) and manganese (II) complexes are dimer and octahedral. A tetra nuclear square planar chloro bridged structure is proposed of the copper (II) complex. A dimeric penta coordinated square pyramidal configuration is assigned to Zn(II) and a binuclear tetrahedral stereochemistry is suggested for the cadmium(II) and mercury(II) on the basis of analytical conductance, magnetic susceptibility, molecular weight, IR, electronic spectra, TGA and DTA data.

New Schiff base chelates of Cu (II), Co (II), Ni (II) and Zn (II) derived from benzil-2,4-dinitrophenylhydrazone with aniline were have synthesis (95). The IR spectra of the free ligand has the important absorptions band in the region 1605-1630 cm^{-1} assigned to (C=N), shift to lower frequency 1580-1590 cm^{-1} after complexation indicating the coordination of azomethine nitrogen to metal ions. In the spectra of the broad band at 3400 cm^{-1} indicating the presence of coordinated water. The electronic spectra of the Cu (II) complex showed only broad band at 16638cm^{-1} assigned to $^2E_1g \rightarrow {}^2T_2g$ transition, which is in conformity with octahedral geometry (96). The electronic spectra of Co(II) complex showed a transitions at 17856 and 21734 cm^{-1} assigned to $^4T_1g(F) \rightarrow {}^4A_2g(F)$ and

$^4T_1g(F) \rightarrow {}^4T_1g(P)$ transition respectively, indicated an octahedral geometry of Co(II) ion (97). The appearance of a band at 19240 cm^{-1} due to ^3A_2g (F) → ^3T_1g (P) transition favors an octahedral geometry for Ni (II) complex (98). The absence of any band below 10,000 cm^{-1} eliminates the possibility of a tetrahedral environment in this complex. The magnetic moment value of Cu (II) complex is 1.9 B.M which suggests a distorted octahedral geometry (99,100) around the metal ion. The magnetic moment of Co (II) complex is 4.8 B.M which suggests the high spin six coordinated octahedral arrangement, (101,102) of ligand molecule around the metal ion. The Ni (II) complex has of 2.8 B.M indicating a spin frees octahedral (103,104).

A study and synthesis of the complexes $[M(ppn)_2]x_2$ (where M = Cu(II), Ni(II), Co(II) and ppn =1,3-diaminopropane) with formaldehyde and ethylenediamine in methanol (105). The complexes were characterized by elemental analysis, IR, EPR, electronic spectral data, magnetic moments and conductance measurements. The electronic spectra and magnetic moment of Cu (II) complex showed the absorption at 15974 cm^{-1} assigned to $^2Eg \rightarrow {}^2T_2g$ transition indicated the complex has octahedral geometry. The absorption at 33003 cm^{-1} may be due to ligand to metal charge transfer (LMCT) which is a characteristic of copper (II) complex with amines. The observed magnetic moment value is 2.01 B.M, which corresponded to an octahedral structure for the Cu(II) ion (42). The electronic spectrum of the Ni(II) complex is compatible with an octahedral geometry. These absorption bands were observed for the violet Ni(II) complex at 11325, 18416 and 29154 cm^{-1} corresponding to $^3A_2g(F) \rightarrow ^3T_1g(p)$, $^3A_2g(F) \rightarrow ^3T_1g(F)$ and $^3A_2g(F) \rightarrow ^3T_1g(F)$ transition respectively. On the basis of spectral bands an octahedral geometry is therefore proposed for the Ni (II) ion. This value at room temperature of magnetic moment of 3.7 B.M, which is consistent with an octahedral field.

A new series of oxygen bridged complexes show below, is reported with special emphasis on copper (II) were synthesized (106). Most of these complexes can be shown to discrete dimeric molecules. Both homo and hetero nuclear dimmers can be prepared in a large number of cases by forming a complex of metal M with tetradentate Salicylaldiamine, L. The lather ML then acts as a bidentate in complexing with a metal halide MX_2 or $M'X_2$ to which it coordinated through its two phenolic oxygen. The Schiff complexes used as ligands of copper (II) and nickel (II) .All of the homonuclear complexes of copper (II) showed antiferromagnetic interaction.



M= Cu (II), Ni (II), Hg (II) and Zn (II).

Homo and hetero dinuclear complexes with a new Schiff base ligand with N_2SO_4 donor have been synthesized (107). The complexes have been characterized by elemental analysis, IR and electronic spectral. The homo dinuclear Cu (II) complex exhibit very low magnetic moment 0.8 B.M per copper centre. The subnormal magnetic moment indicated that the copper centers are strongly antiferromagnetically coupled (108-110). This is not present in monocopper derivatives and is obviously due to the absence of unpaired spin in the second metal ions of the complexes. The IR spectra of most complexes appear broad medium bands at 3440cm^{-1} corresponding to coordinated water.

Cobalt (II) nickel(II) and copper(II) complexes of type ML_2Cl_2 where L is Schiff base formed by condensation of 2-thiophene-Carboxaldehyde and propylamine or ethylamine (TNAP) and (TNAE) respectively, have been synthesized (111). They found from the elemental analysis suggests the stoichiometry to be 1:2 (M:L). The molar conductance of the complexes in DMF (10^{-3} M) are in the range7.8-22.5 $\Omega^{-1}cm^2mol^{-1}$ indicating their non-electrolytic nature except in the $[Ni(TNAP)_2]Cl_2$ compound which is an 1:2 electrolyte ($\Lambda = 130.2\ \Omega^{-1}\ cm^2\ mol^{-1}$). Magnetic susceptibility data coupled with electronic spectra of the Cu(II) complexes exhibit only one broad asymmetric band at 11760-16670 cm^{-1} region and the effective magnetic moments 1.92 and 1.93 B.M suggest a distorted octahedral geometry(112). The spectrum of $Ni(TNAP)_2Cl_2$ complex has absorption bands at 17300 and 9650 cm^{-1} assigned to the transitions $^3T_1(F) \rightarrow {}^3T_1(P)$ and $^3T_1(F) \rightarrow {}^3A_2$. These transitions are characteristic to the tetrahedral environment around the Ni^{2+} ion. The value of magnetic moment 3.52 B.M, confirmed the structure. The electronic spectrum of the Ni $(TNAE)_2Cl_2$ could be assigned assuming that the stereochemistry pseudo octahedral and the magnetic moment 3.02 B.M lie in the region expected for an octahedral complexes.

Chapter (II)

Experimental

2.1. Materials and reagents

All materials and reagents used in this study were laboratory pure chemical they include.

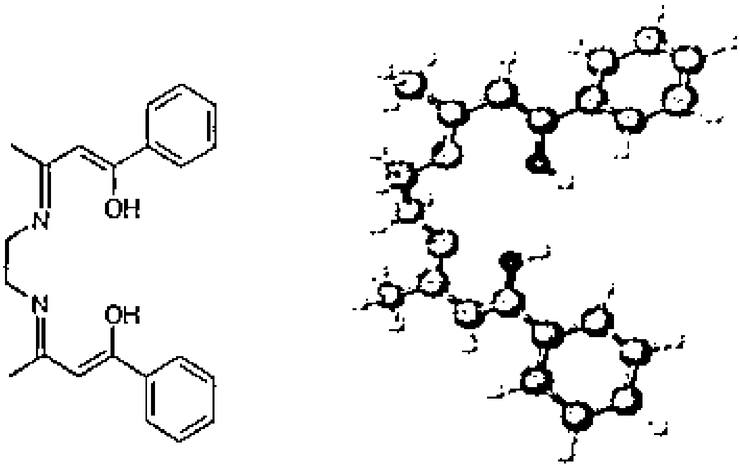
Materials and reagents	The company
Benzoin	ALDRSCH
Benzoylacetone	RIEDEL-DE HAENAG
Ethylenediamine	ALDRSCH
o-phenylenediamine	MERCK.Schuchardt
1,6-hexandiamine	ALDRSCH
Ethanol	Carblo erba regenti
Acetone	Panreac
Petroleum either 60 – 80 C°	NICE
Chloroform	Riedel-dehaen
Dimethylformamide	Carblo erba regenti
Cobalt chloride $CoCl_2.6H_2O$	Carblo erba regenti
Nickel chloride $NiCl_2.6H_2O$	Euro star Scientific limited
Copper chloride $CuCl_2.2H_2O$	T.Baker Lab Chemicals INDIA

2.2. The synthesis of the Schiff base ligands

The synthesis of Schiff base ligands was performed by the following methods. The amines were dissolved in absolute ethanol (40 ml) the ethanolic solution of amines was refluxed with ketone. The reaction molar ratio was 1:2 (amine to ketone). A few drops of pipiridine as condensing agent are added. After refluxing the mixture for about 5hrs, solid crude was formed which is filtered off and recrystallized, dried over $CaCl_2$. This method was based on the previous methods reported for the preparation Schiff base ligands (20, 26).

2.2.1. The synthesis of (H_2L^1) ligand

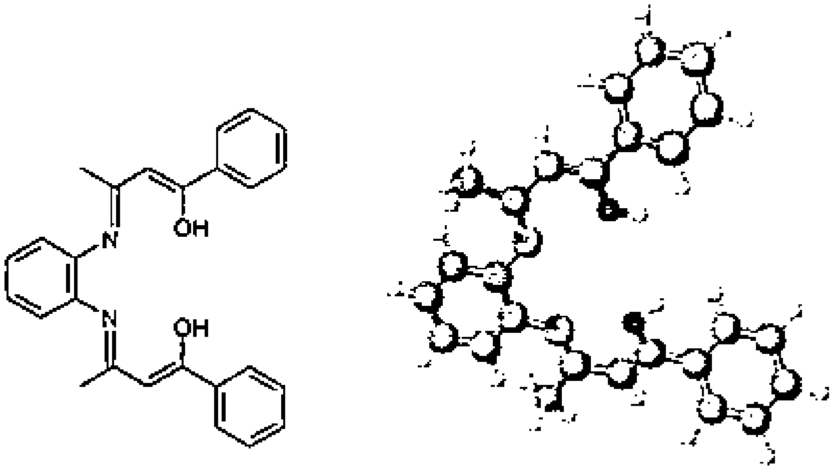
The Schiff base ligand (H_2L^1) was prepared by the condensation of Benzoylacetone (1.8 g, 0.05 mole) with ethylenediamine (1.5 ml, 0.025 mole) in absolute ethanol (40 ml). A few drops of pipiridine as catalyst agent is added. The ethanolic mixture is refluxed for 5hrs. On cooling the product is collected as white crystals by filtration. The product were recrystallized from hot ethanol and dried over anhydrous $CaCl_2$.



Structure of (H_2L^1) ligand

2.2.2. The synthesis of (H_2L^2) ligand

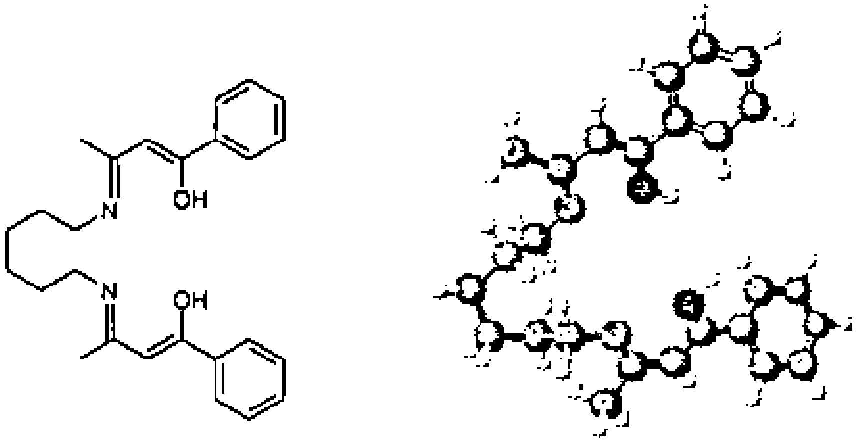
The Schiff base H_2L^2 ligand was prepared by condensation of o-phenylenediamine (1.08 g, 0.01 mole) with benzoylacetone (3.24 g 0.02 mole) in 40 ml absolute ethanol. The mixture was refluxed for about 5hrs in presence of few drops of piperidne are added. After 5h the volume of the solution was reduced to one-third and 10 ml of petroleum ether (60 - 80C°) is added and keep away in air to evaporate. The yellow solid crude product is collected and recrystallized from hot ethanol and dried over anhydrous $CaCl_2$.



Structure of (H_2L^2) ligand

2.2.3. The synthesis of (H_2L^3) ligand

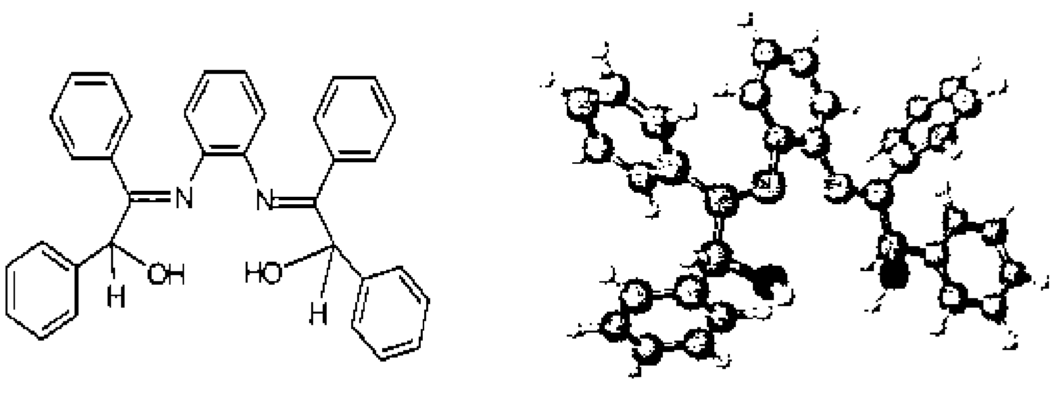
An ethanolic solution (40 ml) of 1,6-hexandiamine (2.32 g, 0.02mole) is mixed with also an ethanolic solution of benzoylacetone (6.5 g, 0.04 mole). A few drops of piperidine as condensing agent are added. The mixture is refluxed for about 5hrs. On cooling a pale yellow crystals were formed which was filtered and recrystallized from hot ethanol and dried over anhydrous $CaCl_2$.



Structure of (H_2L^3) ligand

2.2.4. The synthesis of (H_2L^4) ligand

The ligand is synthesized by dissolving o-phenylenediamine (1.08 g, 0.01 mole) in absolute ethanol (40 ml). An ethanolic solution of benzoin (4.24 g 0.02 mole) is added to the o-phenylenediamine solution. A few drops of pipiridine as condensing agents is introduced to the mixture. The mixture was refluxed for 5hrs, a pale orange color solid is formed on cooling, which is filtered and recrystallized from hot ethanol and dried in over anhydrous $CaCl_2$.



Structure of (H_2L^4) ligand.

2.3. The synthesis of Complexes

Schiff bases complexes under investigation were synthesized by two methods. The first method, a suitable ligand is dissolved in (20 ml) ethanol and added to a metal salt ethanolic solution (20 ml). The reaction molar ratio is (1:1) or (1L: 2M). The mixture is refluxed for 10hrs; the volume of the mixture is reduced to one-third. On cooling a crude product is formed, which is collected by filtration and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The second method is a solid state reaction, a suitable ligand and metal salt is melted together by (1L: 2M) molar ratio to give solid crude product. The crude is washed several times with ethanol and dried over anhydrous $CaCl_2$. Both routes gave identical products but the first route gave higher yields than the other.

The synthesis of $[NiL^1(H_2O)_2]$ by reaction of the ligand H_2L^1 (1.00 g, 0.002 mole) in 40 ml ethanol with $NiCl_2.6H_2O$ (0.53 g, 0.002 mole) in ethanol (20 ml) by (1:1) molar ratio. The two solutions are mixed and refluxed for 10hrs. The crude product is separated by filtration and washed several times with ethanol until the filtrate becomes clear. The obtained complex was dried over anhydrous $CaCl_2$.

The synthesis of $[Cu_2L^1Cl_2]8H_2O$ by adding (20 ml) warm absolute ethanolic solution of H_2L^1 (1.00 g, 0.002 mole) to an absolute ethanol (20 ml) of $CuCl_2.2H_2O$ (0.48 g, 0.002 mole) by (1:1) molar ratio.

The mixture was stirred and refluxed for about 10hrs .The solid product formed is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$

The synthesis of $[Ni_2L^1Cl_2]4H_2O$ by mixed (20 ml) ethanolic solution of H_2L^1 (0.89 g, 0.002 mole) with another ethanolic solution of $NiCl_2.6H_2O$ (1.21 g, 0.004 mole). The obtained mixture was refluxed for about 10hrs. After that the volume of the solution was reduced to one third and cooled at room temperature. The product formed was filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The $[Cu_2L^1(H_2O)_2](OH)_2$ can be prepared by addition of (1.00 g 0.0028 mole) of the ligand H_2L^1 is dissolved in absolute ethanol (20 ml). Another ethanolic solution of $CuCl_2.2H_2O$ (0.97 g, 0.0056 mole) is made. The two ethanolic solutions are mixed and refluxed for 10hrs. After refluxing the volume of the solution was reduced to one third, and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The $[Co_2L^2Cl_4(H_2O)_2]7H_2O$ complex synthesis by mixed (20ml) ethanolic solution of H_2L^2 (1.00 g, 0.002 mole) with another ethanolic solution (20ml) of $CoCl_2.6H_2O$ (0.7 g, 0.002 mole). The two ethanolic solutions are mixed and refluxed for 10hrs. After refluxing the volumes of the solution is reduced to one third and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The synthesis of [Ni $(H_2L^2)Cl_2$] by mixed (20 ml) ethanolic solution of H_2L^2 (1.00 g, 0.002 mole) is mixed with another ethanolic solution (20 ml) of $NiCl_2.6H_2O$ (0.6 g, 0.002 mole). The two ethanolic solutions are mixed and refluxed for 10hrs. After refluxing the volume of the solution is reduced to one third, and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The $[Cu_2L^2Cl_2]4H_2O$ complex can be formed by mixed (0.86 g, 0.005 mole) of the salt of $CuCl_2.2H_2O$ in the solid phase with (1.00 g, 0.0025 mole) of solid H_2L^2 ligand. The solid mixture is putted in a sealed inert container. The entire container is heated on hot plate until the powders of starting materials are melting together and their colors were changed. The crude product were collected and washed several times with acetone until the filtrate becomes clear. The product solid dried over anhydrous $CaCl_2$.

The synthesis of [Cu $(H_2L^3)Cl_2]2H_2O$ complex by mixed (20 ml) ethanolic solution of H_2L^3 (1.00 g, 0.002 mole) with another ethanolic solution (20 ml) of $CuCl_2.2H_2O$ (0.42 g, 0.002 mole). The two ethanolic solutions are mixed and refluxed for 10hrs. After refluxing the volumes of the solution is reduced to one third and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The [Ni $(H_2L^3)Cl_2]4H_2O$ complex can be synthesized by reaction (20 ml) ethanolic solution of H_2L^3 (1.00 g, 0.002 mole) with another ethanolic solution (20 ml) of $NiCl_2.6H_2O$ (0.68 g and 0.002 mole). The two ethanolic solutions are mixed and refluxed for 10hrs. After refluxing the volumes of the solution is reduced to one third and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The formation of [Co_2 $(H_2L^3)(H_2O)_8]4Cl$ by addition of(20 ml) ethanolic solution of H_2L^3 (1.00 g, 0.002 mole) to another ethanolic solution (20 ml) of $CoCl_2.6H_2O$ (1.185 g and 0.004 mole) and refluxed for 10hrs. After refluxing the volumes of the solution is reduced to one third and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and deride over anhydrous $CaCl_2$.

The [Ni_2 (H_2L^3) $(H_2O)_8]4Cl.C_2H_5OH$ complex prepared by reaction of (20 ml) ethanolic solution of H_2L^3 (1.00 g, 0.002 mole) with another ethanolic solution (20 ml) of $NiCl_2.6H_2O$ (1.185 g and 0.004 mole) and refluxed for 10hrs. After refluxing the volumes of the solution is reduced to one third and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and deride over anhydrous $CaCl_2$.

The synthesis of $[Cu_2L^3(H_2O)_4]2Cl$ by reaction $CuCl_2.2H_2O$ (0.85 g, 0.004 mole) is preformed by the mixing with the solid ligand of H_2L^3 (1.00 g, 0.002 mole) in solid state reaction by heating the mixture in inert container, over a hot plate until the powder of starting material are melting together and their colors are changed ,the product compound were collected and washed several times with acetone until the filtrate becomes clear . The obtained complex was dried over anhydrous $CaCl_2$.

The formation of $[Co(H_2L^4)Cl_2]4H_2O$complex by addition (20 ml) absolute ethanol solution of the ligand H_2L^4 (1.00 g 0.002 mole) to another ethanolic solution (20 ml) of $CoCl_2.6H_2O$ (0.50 g, 0.002 mole) . The mixture is refluxed for 10hrs, after refluxing the volume of the solution was reduced to one third, and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The preparation of $[Ni(H_2L^4) Cl_2]$ by dissolved (1.00 g, 0.002 mole) of ligand H_2L^4 in absolute ethanol (20 ml). The ethanolic solution (20 ml) of $NiCl_2.6H_2O$ (0.50 g, 0.002 mole) is made. The two ethanolic solutions are mixed and refluxed for 10hrs. After refluxing the volume of the solution was reduced to one third, and keep away to cool at room temperature.

The crude solid product is filtered and washed several times with ethanol and dried over anhydrous $CaCl_2$.

The $[CuL^4]2\frac{1}{2}H_2O$ complex can be formation by mixed (20 ml) absolute ethanol (1.00 g, 0.002 mole) of the ligand H_2L^4 with another ethanolic solution (20ml) of $CuCl_2.2H_2O$ (0.50 g, 0.002 mole). The two ethanolic solutions is mixed and refluxed for 10hrs. After refluxing the volume of the solution was reduced to one third, and keep away to cool at room temperature. The crude solid product is filtered and washed several times with ethanol and deride over anhydrous $CaCl_2$.

2.4. The studies on ligands and its metal Complexes

2.4.1. Physical techniques and spectroscopic measurements

2.4.1.1. Elemental analysis

All the Schiff base ligands and their complexes under investigation, were subjected to (C, H and N) elemental analysis which performed at analytic unit of the central laboratory of Tanta University (Egypt) and laboratories of RASCO company Libya.

2.4.1.2. Thermal analysis

The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the Schiff base complexes were carried out using shimadzu DT-30 thermal analysis with heating rate of 10 C° / min at analytical unit of the central laboratory of Tanta university (Egypt).

2.4.1.3. Melting point

The melting point of ligands and their complexes were measured in capillary tubes Philip Haris, Shenston-England, serial NO.B/A-211, at chemistry department. Faculty of Science, Al-Tahadi University (Seirt).

2.4.1.4. Conductivity measurement

The molar conductance values of prepared Schiff base complexes under investigation were calculated by measuring in (10^{-3} M) in DMF or Chloroform solution by using digited conductivity meter CMD 650, at Chemistry Department, Faculty of science, University of Garyounis (UOG).

2.4.1.5. Magnetic moment measurements

The magnetic moment measurements of complexes under investigation were determined by using a modified Goy type magnetic balance Herts SG8 SHJ, England, at Tanta University.

2.4.1.6 Infrared spectra

The IR spectra of the Schiff base ligands and their complexes under investigation were recorded using a Perkin-Elmer 1430 spectrophotometer using KBr Discs, at Menofia University, Shibin El-Kom (Egypt).

2.4.1.7 Electronic spectra

In 10^{-3} M solution of Schiff base ligands and their complexes were prepared by dissolving the accurate weight of the compound in 25 cm^3 of DMF or $CHCl_3$. The spectra of the obtained solutions were scanned within the visible and ultraviolet using measured using a 640S UV-vis spectrophotometer using 1cm matched silica cells, at Chemistry Department, Faculty of science, University of Garyounis (UOG).

Chapter (III)

Results and discussion

3. Results and discussion

3.1. The studies on ligands

The Schiff base ligands under investigation were formed by the condensation reaction of Benzoylacetone with Ethylenediamine, o-phenylenediamine and 1,6-hexanediamine to obtained H_2L^1= [$C_{22}H_{24}N_2O_2$], H_2L^2= [$C_{26}H_{24}N_2O_2$] and H_2L^3= [$C_{26}H_{32}N_2O_2$] respectively. The fourth Schiff base ligand H_2L^4= [$C_{34}H_{28}N_2O_2$] formed by the condensation of o-phenylenediamine with Benzoin. The Schiff base ligands were subjected to elemental analysis, Infrared and Electronic spectroscopy to identify their structures.

3.1.1 Elemental analysis of the ligands

Physical characteristics and elemental analysis of C, H and N of the ligands are listed in Table (1). The results of C, H and N percentage are in good agreements for the ligands and correlated well with the calculated.

3.1.2. Infrared spectra of the ligands

The important IR absorption frequencies of the prepared Schiff bases compounds along with their assignments are given in Table (2) and Figures (1-4). The IR spectra of the ligands (H_2L^1 to H_2L^4) showed that the characteristic bands of the starting materials has been vanished namely, the band at 1700 cm^{-1} are observed for those free carbonyl groups and the two bands at 3350– 3450 cm^{-1} for primary amines. The disappearance of those bands is an indication for the formation of a Schiff base ligand. Thus a complete condensation has been occurred and the ketimine structure is appeared. These results are in excellent agreement with the results reported previously (26,114).

In addition, the strong bands at the region (1690– 1580 cm^{-1}) has been noted which assigned to the azomethine group (C=N) present in the Schiff base ligands (20, 72, 82).

The ligands showed a broad band at 3200– 3600 cm^{-1} region which due to the ν (O—H) stretching band which is assigned to the enolisable (OH) group of the Benzoylacetone moiety (20, 26). The breadth of this band indicates the presence of hydrogen bonding. Another bands of ν(C—O) stretching is appeared at the 1000– 1200 cm^{-1} region. The IR spectra of these ligands have a clear absorption bands at 1500-1564 cm^{-1} attributed to the ν(C=C) stretching of the enolic ring of the β-diketone. Our results are in conformity with the previous results (20, 93,113,114,115).

The IR spectrum of ligand H_2L^1 = [N, Ǹ-bis (benzoylacetone) ethylenediamine] $C_{22}H_{24}N_2O_2$; showed a strong absorption band at1604cm^{-1} which is assigned to the ν(C=N) azomethine group (95, 20). The broad band at 3424 $cm^{-1}$is due to the hydroxyl group of enolisation of the carbonyl of Benzoylaceton (73, 26). In addition, the absorption band at the 1292 cm^{-1} is due to the ν(C—O) stretching. Moreover, the absorption band at the 1564 cm^{-1} is assigned to the ν(C=C) stretching vibration (93,113).

The Schiff base H_2L^2= [N, Ń-bis (benzoylacetone)-o-phenylene-diamine] $C_{26}H_{24}N_2O_2$. The ligand spectrum had a strong band at about 1576 cm^{-1} which is assigned to the ν(C=N) stretching mode.(26,58) The absence of any measurable absorption in the IR region characteristic of (OH) around 3404 cm^{-1} has been attributed to the existence of intermolecular hydrogen bonding (20,95). Also the broad band at 1315 cm^{-1} which is attributed to the existence of the ν(C—O) stretching band. The absorption band in the region 1526 cm^{-1} is assigned to the ν(C=C) vibration (93,113,114).

The IR spectrum of H_2L^3 = [N, Ń– bis (benzoylacetone) 1,6-hexanediamine] $C_{26}H_{32}N_2O_2$. The imine structure of this ligand is clearly indicated by the intense and sharp band of ν(C=N) which located at the region 1592 cm^{-1} (26, 58). The broad band at 3429 cm^{-1} is due to hydrogen bonding of (OH) group (73, 95). Moreover two bands at 1564 cm^{-1} and 1291cm^{-1} regions which are assigned to the bands of ν(C=C) and ν(C—O)respectively (93,113,114).

The infrared spectrum of the ligand H_2L^4= [N, Ń-bis- (Benzoin)-o-phenylenediamine] $C_{34}H_{28}N_2O_2$. A strong band at 1673 cm^{-1} is assigned to ν(C=N) azomethine group stretching (72).

Also a weak broad band at the region 3415 cm^{-1} which is assign to the ν(OH) group vibration (20,82,95). Finally a band at 1261 cm^{-1} is attributed to the existence of ν(C—O) (93,113,114).

3.1.3 Electronic absorption spectra of ligands

The electronic spectral data of the compounds in chloroform are presented in Table (3). The absorption band assigned to $\pi - \pi^*$ transitions, in the electronic spectra of the Schiff base ligands (H_2L^1 to H_2L^4) is assigned to the aromatic ring or azomethine group (48). These transitions are also found in the electronic spectra of the complexes, but they are shifted towards lower frequencies, confirming the coordination of the ligand to the metallic ions (54).

3.2. The studies on complexes

In this section, we focus our attention on the analysis of the entire complexes, the analysis is included the elemental analysis, molar conductivity, thermal analysis, magnetic susceptibility, IR and UV-vis spectra.

3.2.1 Elemental analysis

The results of elemental analyses of the complexes under investigation are listed in Table (4). The results of C, H and N percentage are in accordance with the composition suggested for the most complexes and also indicated the complexes correspond to the general (M:L) or (2M:L) molar ratio.

3.2.2 Molar conductivity

The molar conductance for the complexes measured in 10^{-3} M solution in DMF or chloroform as solvents at room temperature (29- 31C°). The molar conductivity was applied to help in the investigation of the geometrical structures of the complexes. The molar conductivity values are given in Table (4). Some complexes showed a lower molar conductivity values in the range 0.03-44.37 Scm^2mol^{-1} which indicated their non-electrolytic nature (111, 25). Other complexes found to be a higher electrolyte with the values 68.97,156, 493 and 770 Scm^2mol^{-1}; this result is demonstrated that the complexes have a binuclear nature (74, 76,111,116,117).

3.2.3 Thermal analysis

Thermal methods of analysis open a new possibility for the investigation of metal complexes. They include differential thermal analysis (DTA and thermogravimetric analysis (TGA). The DTA and TGA results are given in Figures (20- 26). The Thermal analysis data are collected in Table (5).

3.2.3.1 The DTA and TGA of $[Cu_2L^1(H_2O)_2](OH)_2$ and $[Cu_2L^2Cl_2]4H_2O$

The DTA of $[Cu_2L^2Cl_2]4H_2O$ complex showed the endothermic peak at 21-70 C° indicated to loss of hydration water (Figure 21). This peak did not appear for the other complex $[Cu_2L^1(H_2O)_2](OH)_2$. In addition the different position of melting points and partial decomposition of the two complexes, at 225 C° for complex $[Cu_2L^1(H_2O)_2]$ $(OH)_2$ may be due to decomposition of partial organic ligand with two coordinated water molecules (Figure 20) and at 283 C° of complex $[Cu_2L^2Cl_2]4H_2O$ due to partial organic ligand, which indicated the difference of organic ligands for them. The final endothermic peak of two complexes at region >300C° may be due to loses weight which assigned to formation of metal oxide (82). The thermo gram of complex $[Cu_2L^2Cl_2]4H_2O$ confirmed the lost of weight at temperature range 28-142C° corresponding to loss of hydrated water molecules (82) (Figure 22) which is assigned to (Calc.5.7%) corresponding to $2H_2O$ (found 6.03%) which confirmed from the endothermic peak at temperature range 21-70C° in the DTA curve (Figure 21). In addition the peak at 144-300 C° range, this may be due to weight lost of partial organic ligand with two water molecules.

For the $[Cu_2L^2Cl_2]4H_2O$ the weight lost at the 300-338C° may be due to the (Calc. 10.00%) corresponding to Cl_2 (found 12.14%). In addition to the final peak in the temperature ranging at 486-573C° which corresponding to $2Cu(OH)_2$ lost (Calc. 29.32%; found 28.04%), which is indicating the binuclear nature of the complex (Figure 22).

3.2.3.2 The DTA and TGA of $[Co_2L^2Cl_4(H_2O)_2]7H_2O$ Complex

As shown in Figures (23, 24), the DTA analysis of this complex showed two endothermic peak at 183-230 C°, which assigned to loss of two coordination water molecules (20,25,82). The broad endothermic peak at 260-390C° assigned to decomposition of organic partial of Schiff base ligand. The endothermic peak at 552-697C° regions is due to the decomposition of complex and indicated the formation of metal oxide (Figure 23). The TGA of $[Co_2L^2 Cl_4 (H_2O)_2]$. curve showed the loss of weight at 27-198C° range due to lost of two coordinated water molecules corresponding to (Calc.4.6% ; found 3.87%) (Figure 24), which confirmed from the two endothermic peak of DTA. In addition the peak at the temperature ranging 199-259C°, is may be due to the weight lost of $(Co_2 + H_2O)$ molecules, corresponding (Calc.7.9%; found 7.59%). The peak at 259-391C°, is assigned to the formation of metal oxide 2CoO (82) corresponding to (Calc.19.21%; found 18.6%). The final peak at 392-651C° which is assigned to the lost of partial organic ligand, corresponding to (Calc.40.67%; found 42.75%).

3.2.3.3 The DTA and TGA of [Cu (H_2L^3)Cl_2]$2H_2O$ Complex

The DTA results showed the exothermic peak at 50-180C° range, which is assigned to the dehydration of water molecules,(82) shown in Table (5) and Figure (25). The endothermic peak around 260-348C° range may be due to the decomposition partial of organic compound of the ligand. The final endothermic peak at 482-608C° is due to the formation of metal oxide. The TGA of this complex curve shown in Figure(26) and Table (5) showed a weight lost at the temperature ranging 145-264C°, which assigned to the loss of 2½H_2O molecules, due to (Calc.7.83%) corresponding to (Found 9.85%) which confirmed form the exothermic peak of Figure(25) in DTA curve. Moreover the peak at temperature range 265-337C°, which may be due to the formation of the metal hydroxide (Calc. 16.9%) corresponding to $Cu(OH)_2$ (Found 19.9%). The final peak at 338-620C°, is may be attributed to the decomposition of organic ligand.

3.2.4 Infrared spectra of the complexes

The IR spectra of diagnostic importance of the complexes are given in Table (6) and Figures (5-19). The solid state IR spectra of complexes compared with those of ligands indicated that the ν(C=N) stretching vibration band at region 1531-1664cm^{-1}is shifted to lower frequencies in most complexes as excepted. In contrast there are three complexes shifted to higher frequencies, which indicated that the ligands coordinated to the metal ions through nitrogen atom of the azomethine group (11, 12). The presence of sharp band corresponding to the remaining hydroxyl group at 3400cm^{-1} but it is obscured by the presence of water molecules bands. This was appeared for the most complexes and a very broad band at about 3100-3500cm^{-1} region, which is associated with coordinated or solvent water molecules, is present (77, 78,47, 46). The other bands are at 1323-1427cm^{-1} region assigned to the v(C—O), which are shifted to a higher frequency after complexation with central metal ions, (93,113,115) compared to the free ligands in which was noted at 1261-1315cm^{-1}. In addition the two bands at 729-511 and 531-442cm^{-1}, is attributed to the v(M—O) and v(M—N) respectively (113,79). Moreover new bands appeared in some complexes in the 220- 290cm^{-1}regions which is assigned to v(M—Cl) vibration, which indicated the formation of (M —Cl) coordinated bond (113).

The IR spectrum of the [NiL^1(H$_2$O)$_2$] Complex showed a band at 1585 cm^{-1} assigned to the stretching vibration of the v(C=N) group, which is shifted to lower frequency by 19 cm^{-1} compared with the free ligand, which indicates that chelating take place through the azomethine group.

A comparison between the IR spectra of free ligand and its nickel complex is that the bond at 1362 cm^{-1} is shift to higher frequency by 70cm^{-1} in the spectrum of the v(C—O) complex indicating the formation at a (C—O—M) bond (48,51,52,92,72). The spectra showed a broad band at 3062-3525 cm^{-1} which suggested that the water is coordinated to the central metal ion (46, 47).

Finally new bands in the region 560 and 495 cm^{-1} which are due to the formation M—O and M—N bonds respectively (113).

IR spectrum of the $[Cu_2L^1Cl_2]8H_2O$ complex exhibit a strong band at 1568 cm^{-1} which is assigned to the ν(C=N) stretching, because this band is shifted to lower frequency by 36 cm^{-1}compared to free ligand, indicating that the ligand coordinated to the metal ion through nitrogen atom of the azomethine group and probably dianionic form (20,46,91,95). The broad band around 3425 cm^{-1}indicating the presence of coordinated or lattice water in the complex (77, 78). The spectrum reversals a weak band at 1399 cm^{-1} which is attributed to ν(C—O) vibration, again this band is shifted to higher value compared to the free ligand due to formation (C—O—M) bond (48, 51, 52).

In addition three new bands in the regions 527,466 and 221cm^{-1} were emerge, which are probably due to the formation of (Cu—O), (Cu—N) and (Cu—Cl) bond respectively (79). The IR spectrum data of the $[Ni_2L^1Cl_2]4H_2O$ complex showed a strong absorption band at the region 1585 cm^{-1} assign to the ν(C=N) stretching, which is shifted to lower frequency by 19 cm^{-1} in comparison with the free ligand, indicating the involvement of this group in complexation with metal ion through nitrogen atom of azomethine group (95. 75). The free ligand band at 1292 cm^{-1} is shifted to a higher frequency on complexaion to 1356 cm^{-1}. This band shift enhance the formation of (C—O—M) bond. Moreover, there is a broad band at 3384 cm^{-1}whch is assign to the water molecules (67, 70). Also the new bands at the regions 561, 495 and 289 cm^{-1} attributed to v(Ni—O), v(Ni—N) and v(Ni—Cl) bonds stretching vibration respectively (79, 113).

The IR spectrum data of the $[Cu_2L^1(H_2O)_2](OH)_2$ complex display a sharp band at 1567 cm^{-1} corresponded to the presence of v(C=N) vibration, this band is lowered by 47 cm^{-1} (58, 62) than its original position in the free ligand indicated the azomethine group is coordinated to central metal ion through the nitrogen atom (20, 46). The band at 1323 cm^{-1}, which is due to the v(C—O) vibration was shifted to higher position compared to the free ligand (49, 50), which indicates the formation of (C—O—M) bond (48, 51, 52).

The absorption band at 3448 cm^{-1} is due to stretching vibration of (OH) group in water molecules and this aqua complex exhibit two strong bands at 3228 and 3298 cm^{-1}stretching vibration (74,76,77) attributed to v(OH). Two new bands around 526 and 468 cm^{-1} are assigned to the (Cu—O) and (Cu—N) stretching, respectively (79, 83, 113).

The IR spectrum of the $[Co_2L^2Cl_3(H_2O)_2]7H_2O$ Complex showed a peak at about 1555 cm^{-1} which is assign to the v(C=N) stretching frequency. This band is shift to lower frequency by 21 cm^{-1} (73,74,75) compared with the free ligand which indicates that chelating takes place through the nitrogen atom of azomethine group. The spectra of the complex exhibited the presence of a band at 1405cm^{-1} which is due to the v(C—O) vibration. This vibration is shifted to higher frequency which is suggesting the formation of (C—O—M) bond (48, 51, 52). The broad band at 3367 cm^{-1} is attributed to the presence of (OH) group of water molecules. The coordination mode of ligand is further supported by the appearance of new bands in the range of 518, 466 and 290 cm^{-1} indicating the formation of (M—O), (M—N) and (M—Cl) bonds respectively (74, 79).

The IR spectrum data of the $[Ni(H_2L^2)Cl_2]$ complex showed a strong band in the 1558 cm^{-1} which is shifted to lower frequency by 18 cm^{-1} in comparison to the free ligand, which is suggested the coordinated bond formed through the nitrogen atom of azomethine group (26,28,75). The very intense band at 1399 cm^{-1} is due to ν(C—O) stretching vibration which is shift to higher frequency in comparison to the free ligand. This shift confirmed the participation of oxygen in the (C—O—M) bond (48, 51, 52) .The IR spectra exhibit the presence of ν (OH) as a broad band at 3431 cm^{-1}. Also new bands are observed in the 587, 531and 220 cm^{-1}due to ν(Ni—O), ν(Ni—N) and ν(Ni—Cl) respectively (79, 83, 113).

The IR spectrum of the $[Cu_2L^2Cl_2]4H_2O$ complex showed a strong band at 1531 cm^{-1}, this band attributed to the ν(C=N) stretching vibration, which is shifted to lower frequency in comparison to the free ligand which enhance the involvement of azomethine group in coordination (20,26).

Strong broad band absorption at about 3100-3500 cm^{-1}region, is confirmed the presence of water molecules coordinated to center metal ion (46, 47). The free ligand band at 1291cm^{-1} is shifted to a higher frequency on complexaion to 1399cm^{-1}.

This band shift enhance the formation of (C—O—M) bond (48, 51, 52). The complex bands at 511,464 and 221 cm^{-1} regions were attributed to ν(Ni—O), ν(Ni—N) and ν(Ni—Cl) stretching vibrations respectively (74,79).

The [Cu(H_2L^3)Cl_2]$2H_2O$ complex spectrum showed a strong absorption band at 1552 cm^{-1} which is assigned to ν(C=N), this band is shifted to lower frequency in comparison to the free ligand, this is indicating that the coordination occurred through the nitrogen atom of azomethine group (20, 74, 75). The broad band at 3358-3444 cm^{-1}region which are assigned to the ν(OH) of crystallization water. This water content was also supported by the elemental analyses and thermal analytical (TGA, DTA). In addition the band at 1366 cm^{-1} is due to the ν(C—O) vibration (93, 113, 48). This band shifted to higher frequency suggesting its involvement in chelating with metal ion. Moreover three new bands observed at 701,457 and 266 cm^{-1} which are due to the ν(Cu—O), ν(Cu—N) and ν(Cu—Cl) respectively (48, 51, 52).

In IR spectrum of the [Ni(H_2L^3)Cl_2]$4H_2O$ complex has a band at 1605 cm^{-1} attributed to ν(C=N) stretching this band is shifted to a higher frequency in comparison with the free ligand. The shift is an indication for which the involvement of azomethine group in chelation through nitrogen atom (74, 75). Also the band at 3421 cm^{-1} is attributed to the presence of (OH) group of water molecules. In addition the complex exhibited an absorption band at 1396 cm^{-1}, which is due to the ν(C—O) vibration.

This vibration shifted to higher frequency which suggesting its involvement in the complexation (48, 93, 113). In contrast to the free ligand a new bands is observed at 725,445 and 220 cm^{-1} which are assigned formation of (M—O), (M—N) and (M—Cl) bonds respectively (79, 74, 113).

Infrared spectrum of the $[Co_2 (H_2L^3) (H_2O)_8]4Cl$ Complex showed the strong band at 1592 cm^{-1} region in IR spectra of free ligand H_2L^3 which is assigned to ν(C=N) stretching is shifted to higher frequency and observed at 1598 cm^{-1} in spectra of complex, which again indicates that the chelation takes place through the nitrogen atom of azomethine group to central metal ion (63,64,65). The complex spectra showed a sharp band at 3553 cm^{-1} which assigned to the ν(OH) stretching vibration this assigned to coordination water molecules. The IR spectra of the complex also showed a band at 1398 cm^{-1} which assigned to ν(C—O) vibration, this band been shifted to a higher frequency by 107 cm^{-1} in comparison with its position in the free ligand (113). This is an indication to (C—O—M) bond formation. Finally two bands at 714 cm^{-1} and 442cm^{-1} are emerging which is indicating the presence of coordination modes of ν(M—O) and ν(M—N) vibration respectively (79, 82, 83).

Infrared spectrum of the $[Ni_2(H_2L^3)(H_2O)_8]4Cl.C_2H_5OH$ Complex showed the significant change in the ligand H_2L^3 spectra upon complexation is that there is an increasing in the ν(C=N) azomethine group frequency. This shift to higher frequency by 7cm^{-1} in the complex spectra at 1599 cm^{-1} suggested that the coordination is taking place through the nitrogen of the azomethine group (58, 63, 64, 65). A strong band of ν(C—O) at 1398 cm^{-1} is shifted to a higher frequency in comparison to the ν(C—O) of the free ligand (93, 113). This shift indicates the participation of both oxygen atom enolisable carbonyl group of the benzoylacetone moiety in the coordination to metal ion. The complex spectra exhibited a broad band at about 3200-3600 cm^{-1}, which is associated with coordinated water or ethanol solvent molecule (20, 114). The appearance of new peaks in the complex spectra at 714 and 442 cm^{-1} are assigned to ν (M—O) and ν (M—N) respectively (82, 83).

Infrared spectrum of the $[Cu_2L^3(H_2O)_4]2Cl$ Complex the IR spectrum of the complex showed a strong absorption band at 1571 cm^{-1} which is assigned to the ν(C=N), this band is shifted to a lower frequency by 21 m^{-1} compared to the free ligand (58, 62). Also the two sharp bands observed at 3351cm^{-1} and 3450cm^{-1} attributed to the ν(OH) stretching vibration of coordinated water molecule.(95) The band of ν(C—O) is appeared at 1390 cm^{-1} which is shifted to higher frequency by 99 cm^{-1} which have been observed for the free ligand at 1291 cm^{-1} (48, 93, 113). This shift confirmed the participation of oxygen in the (C—O—M) mode (48, 51, 52). The complex showed two new bands at 657cm^{-1} and 473 cm^{-1} which are assigned to ν(M—O) and ν(M—N) vibration respectively (79,82,83).

The IR spectrum of the $[Co(H_2L^4)Cl_2]4H_2O$ complex exhibited a strong band at 1664 cm^{-1} assigned to the v(C=N) vibration, which is shifted to lower frequency by 9cm^{1} compared to the free ligand.

The shift is suggesting its involvement in the chelation to the metal ion. The v(OH) is appeared at about 3424 cm^{-1} which is indicating the presence of water molecule (58). There is an absorption at 1335 cm^{-1} attributed to the (C—O) of (C—O—M). This valued has been shifted to a higher frequency by 74 cm^{-1}, since it has been observed at 1261 cm^{-1} for the free ligand. The new bands in the region 639,464 and 259 cm^{-1} are characterized to v(Co—O), v(Co—N) and v(Co—Cl) respectively.

Infrared spectrum of the $[Ni(H_2L^4)Cl_2]$ Complex has a strong band at 1630cm^{-1} assigned to v(C=N). This band is shifted to lower frequency by 43 cm^{-1} compared to the free ligand. This shift is demonstrated the involvement of the azomethine group in coordination to Ni (II) through nitrogen atom (58, 62). The weak band at 3588 cm^{-1} is due to the v (OH) stretching vibration. A sharp band at 1334 cm^{-1} is attributed to the v(C—O) stretching vibration. This band is shift is due to the (C—O—M) bond formation (48, 51, 52, 93). Finally three are bands observed at 638,478 and 261 cm^{-1} which attributed to the presence of v (Ni—O), v(Ni—N) and v(Ni—Cl) stretching vibration respectively (74, 49, 113).

The IR spectrum of the $[Ni(H_2L^4)Cl_2]$ complex showed a medium band at 1628 cm^{-1}, which is assigned to the azomethine group. Again this band is shifted to lower frequency by 45 cm^{-1} in comparison with free ligand, which indicates that the chelation has been occurred through the nitrogen of the azomethine group (58, 62). Also the broad band at 3424 cm^{-1} assigned to ν (OH) stretching vibration, which indicates the presence of hydration water molecule (58).

The complex is exhibited a band at 1344 cm^{-1}, which is due to the ν(C—O) stretching vibration (48, 93,113). This vibration was shifted to higher frequency in comparison to the free ligand, which suggested its involvement in the chelation to the Cu(II) ion. Moreover the new bands were showed in the regions of 636 and 551 cm^{-1} which are assigned to ν(Cu—O) and ν(Cu—N) stretching vibration respectively (82, 83).

3.2.5 Electronic spectra and magnetic moment of complexes

The electronic absorption spectra and magnetic moment values are often very helpful in the evaluation of results provided by other methods of structural investigation. Information about geometry of the complexes around the Cu (II), Co (II) and Ni (II) ions was obtained from electronic spectra and from values of the magnetic moments. The assignments of the bands of the electronic spectra of the complexes are listed in Table (7). The electronic absorption spectra of the Schiff base ligands and its complexes were recorded at room temperature using (DMF) or ($CHCl_3$) as solvents.

3.2.5.1 Electronic spectra of mono-nuclear complexes

The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the position and number of electronic transition peaks. The electronic spectra of the $[NiL^1(H_2O)_2]$ complex shows bands at 11025, 17921and 22371 cm^{-1} corresponding to the $^3A_2g \rightarrow {}^3T_1g(P)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3A_2g(F) \rightarrow {}^3T_2g(F)$ transition respectively. Our results are in good agreement with those reported for an octahedral geometry around Ni (II) ion (67, 79,95,98). There is an extra band at 25906 cm^{-1} due to $\pi \rightarrow \pi^*$ transition of aromatic ring or azomethine group (48,54). The appearance of a band at 17391cm^{-1} due to ^3A_2g (F) $\rightarrow {}^3T_1g$ (F) transition favors an octahedral geometry (95,105) for the $[Ni(H_2L^2)Cl_2]$ complex, also the absence of any band below 10,000 cm^{-1} eliminated the possibility of a tetrahedral environment in the two complexes above.(95) The absorption band at 27027 cm^{-1} is due to $\pi \rightarrow \pi^*$ transitions of aromatic ring or azomethine group (48,54). The electronic spectrum of copper (II) complex $[Cu(H_2L^3)\,Cl_2]2H_2O$ showed one band at 15384 cm^{-1} which is assigned to $^2Eg \rightarrow {}^2T_2g$ transition, which is in conformity with an octahedral geometry reported previously (95,96,105).

The value of magnetic moment 1.8 B.M is due to one unpaired electron of $3d^9$ electronic configuration in an octahedral complex of Cu (II) ion (95, 99,110). The electronic spectra of the complex $[Ni(H_2L^3)Cl_2]4H_2O$ is compatible with an octahedral geometry. Three absorption bands were observed for the complex at 11049.7, 17241 and 26666.6 cm^{-1} which attributed to the $^3A_2g \rightarrow ^3T_1g$ (P), ^3A_2g (F) $\rightarrow ^3T_1g$ (F) and ^3A_2g (F) $\rightarrow$ ^3T_2g (F) transition respectively (95,105). On the basis of spectral bands an octahedral geometry is therefore proposed for the Ni (II) ion. The value of magnetic moment at room temperature is 3.1B.M, which is consistent with an octahedral field (105). The Co(II) complex [Co(H_2L^4)Cl_2] showed two bands at 14925 cm^{-1} and 18050 cm^{-1} which are assigned to $^4T_1g \rightarrow ^4A_2g$ and $^4T_1g \rightarrow ^4T_1g$(P) transitions respectively which indicates an octahedral geometry of this complex (95,97). The bands of Ni (II) complex [Ni(H_2L^4)Cl_2] was appeared at 17391cm^{-1}, which may be due to the $^3A_2g \rightarrow ^3T_1g$ transition favors an octahedral geometry, for the Ni(II)complex (95,98). The nonexistence of any band under 10,000 cm^{-1} is an indication for that the possibility of a tetrahedral geometry around Ni (II) ion in this complex is remote (95). The complex has magnetic moment value of 3.6B.M, which is compatible with an octahedral complex (105). The Cu(II) complex [CuL^4]2½H_2O has an absorption band at 24096cm^{-1} a well defined shoulder for $^2B_1g \rightarrow ^2B_2g$, which strongly favor the square planar geometry around the metal ion (82,84,85)

The absorption band at 27027 cm^{-1} assigned to $\pi - \pi^*$ transition. This further supported the magnetic susceptibility value of 1.8 B.M due to the unpaired electron in octahedral geometry of Cu (II) ion (95, 99,100).

3.2.5.2 Electronic spectra of binuclear complexes

The electronic spectra of the $[Cu_2L^1Cl_2]\ 8H_2O$ exhibited three bands at 18348.6, 23255.8 and 25974 cm^{-1}. The first two absorption bands are due to the $^2B_1g \rightarrow {}^2A_1g$ (26, 48) and $^2B_1g \rightarrow {}^2Eg$ (43, 84, 85) transition, which corresponding to the square planar geometry around two Cu(II) ions, and the third one is assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic ring or azomethine group which agreeable with the reported results (48,54).

The electronic spectra of the nickel complex $[Ni_2L^12Cl]4H_2O$, showed a band at 17699cm^{-1} is due to $^1A_1g \rightarrow {}^1B_1g$ transition, which also indicates a square planar geometry (82, 86, 87). The absence of any band below 10,000 cm^{-1} refers to no tetrahedral geometry around two metal ions (95). Moreover low magnetic moment value 1.8 B.M of the this complex due to anti-ferromagnetic interaction between magnetic filed of two Ni (II) ions. The $[Cu_2L^1(H_2O)_2](OH)_2$ complex solution displays two band at 11037 and 25706 cm^{-1} corresponding to $^2B_1g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2B_2g$ transitions respectively, which strongly favor the square planar geometry around two metal ion (82, 84, 85). The magnetic moment value at room temperature of this complex is 1.2 B.M lower than 1.7 B.M due to anti-ferromagnetic interaction between two Cu (II) ions, which indicates the formation of binuclear complex (108,109,110). The electronic spectra in DMF solution of $[Co_2(H_2L^2)4Cl\ (H_2O)]$ complex exhibit two bands at 15267 and 16393cm^{-1}, which are assigned to $^4T_1g(F)\rightarrow{}^4A_2g$ (F) and ^4T_1g (F)$\rightarrow{}^4T_1g$ (P) transitions respectively, indicate an octahedral configuration around Co(II) ion (67).

The octahedral geometry of the Co (II) complex is further confirmed by the magnetic moment 4.89 B.M (42) the lower magnetic moment value of this complex about 3.8 B.M is may be due to anti-ferromagnetic interaction between two Co (II) ions. The electronic absorption spectra of $[Cu_2L^2Cl_2]4H_2O$ showed two absorption band at 10989 and 25705cm^{-1} corresponding to $^2B_1g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2B_2g$ transitions respectively, which indicate the square planar configuration around the two Cu(II) ions (82, 84, 85). An absorption band at 26315cm^{-1} may be due to $\pi \rightarrow \pi^*$ transitions of aromatic ring or azomethine group (48, 54). In addition the lower magnetic value 1.16B.M is attributed to the anti-ferromagnetic moment interaction between two central metal ions this is an indication of the formation binuclear complex (108,109,110).

The electronic spectra of the $[Co_2(H_2L^3)(H_2O)_8]4Cl$ exhibited three bands at 15384, 16666 and 26666 cm^{-1}, The first two absorption bands, is corresponding to the ^4T_1g (F)$\rightarrow{}^4A_2g$ (F) and ^4T_1g (F)$\rightarrow{}^4T_1g$ (P) transitions respectively, indicate an octahedral configuration around Co(II) ion,(67) and the third one is assigned to the transition of $\pi \rightarrow \pi^*$ aromatic ring or azomethine group.

The spectra of the complex $[Ni_2(H_2L^3)(H_2O)_8]4Cl.C_2H_5OH$ exhibited one band at 24875 cm^{-1}, this is assigned to the ^3A_2g (F) $\rightarrow{}^3T_1g$(F) transition, the complex bands are attributed to the octahedral structure around per Ni(II) ions (119,120,121).

Other bands at 25706 cm^{-1}, may be due to the transition of $\pi \rightarrow \pi^*$ aromatic ring or azomethine group (48, 54). The magnetic moment of the complex 1.8 B.M is lower than the normal 3.8 B.M of an octahedral structure due to anti- ferromagnetic interaction between magnetic filed of two Ni(II) ions. The complex $[Cu_2L^3(H_2O)_4]2Cl$ complex showed two transition bands in the regions 18155 and 22593 cm^{-1} assigned to $^2B_1g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2B_2g$ transitions respectively, which strongly favor the square planar geometry around two metal ion (82, 84, 85). The magnetic studies of binuclear copper (II) complex, $[Cu_2L^3 (H_2O)_4]2Cl$ showed very low magnetic value 0.8 B.M per copper centre The subnormal magnetic moment indicates that the copper centers are strongly anti-ferromagnetic coupled (107,108,109,110).

TABLES & FIGURES

Table (1) *Elemental analysis data, colors and M.P of ligands*

The ligands	**M.W$_t$**	**Found (Calc.)**			**M.P C°**	**Color**
		C%	**H%**	**N%**		
H_2L^1	348	75.86 (75.40)	6.89 (7.35)	8.04 (7.96)	177	White
H_2L^2	396	78.70 (75.00)	6.06 (6.15)	7.07 (4.72)	50	Yellow
H_2L^3	404	77.22 (76.11)	7.92 (7.83)	6.93 (7.38)	100	Pale yellow
H_2L^4	496	82.25 (82.85)	5.64 (4.71)	5.60 (6.65)	90	Pale orange

Table (2) *Infrared spectra of ligands.*

Ligands	**ν (C=N) cm^{-1}**	**ν (OH) cm^{-1}**	**ν (C=C) cm^{-1}**	**ν (C—O) cm^{-1}**
H_2L^1	1604	3424	1564	1292
H_2L^2	1576	3404	1526	1315
H_2L^3	1592	3429	1564	1291
H_2L^4	1673	3415	—	1261

Table (3) *Electronic spectra of ligands*

Ligands	λ nm	ε (L.mol^{-1}cm^{-1})	ν cm^{-1}	Transitions
H_2L^1	380	2.017	26315	$\pi \rightarrow \pi^*$
H_2L^2	382	2.013	26178	$\pi \rightarrow \pi^*$
H_2L^3	385	2.102	25974	$\pi \rightarrow \pi^*$
H_2L^4	370	1.928	27027	$\pi \rightarrow \pi^*$

Table (4) *Color, molar cond., M.P and Elemental analysis of complexes*

Complex	**M.w$_t$**	**color**	**Cond. scm^{2}mol^{-1}**	**m.p C°**	**Found (calc.)**		
					C%	**H%**	**N%**
$[NiL^1(H_2O)_2\}$	440	Brown	10.17	150	59.40 (59.90)	4.64 (5.80)	7.02 (6.35)
$[Cu_2L^1Cl_2]8H_2O$	687	Brown	0.03	206	39.96 (38.42)	4.62 (4.36)	7.32 (4.07)
$[Ni_2L^1Cl_2]4H_2O$	606.7	Brown	37.97	180	43.58 (43.54)	5.53 (4.94)	5.40 (4.61)
$[Cu_2L^1(H_2O)_2](OH)_2$	543	Blue	156	180	49.50 (48.50)	3.24 (5.15)	5.12 (5.15)
$[Co_2L^2Cl_4(H_2O)_2]$ $7H_2O$	781.8	Blue	45.07	140	39.20 (39.90)	4.08 (4.86)	4.78 (3.58)
$[Ni(H_2L^2)Cl_2]$	525.7	Pale green	18.07	60	59.93 (59.34)	4.40 (4.56)	5.00 (5.32)
$[Cu_2L^2Cl_2]4H_2O$	664	Red	44.37	92	45.62 (46.98)	4.45 (4.51)	5.03 (4.21)
$[Cu(H_2L^3)Cl_2]\ 2H_2O$	574.5	Green	1.05	210	54.31 (54.30)	4.30 (6.26)	4.78 (4,87)
$[Ni(H_2L^3)Cl_2]4H_2O$	605.7	Pale green	20.87	200	50.55 (51.51)	6.98 (6.60)	4.24 (4.62)
$[Co_2(H_2L^3)(H_2O)_8]4Cl$	807.8	Dark green	68.97	143	36.99 (38.63)	5.31 (5.94)	2.75 (3.46)
$[Ni_2(H_2L^3)(H_2O)_8]4Cl$ C_2H_5OH	853.4	Olive green	493	220	39.35 (39.39)	7.06 (5.73)	2.17 (3.28)
$\{Cu_2L^3(H_2O)_4]2Cl$	672	yellow	770	150	47.40 (46.42)	4.03 (5.65)	6.19 (4.16)
$[Co(H_2L^4)Cl_2]4H_2O$	697.9	green	22.17	110	58.01 (58.46)	5.36 (5.15)	4.92 (4.01)
$[Ni(H_2L^4)Cl_2]$	625.7	Pale yellow	19.27	100	65.05 (65.20)	4.46 (4.47)	5.37 (4.47)
$[CuL^4]2\frac{1}{2}\ H_2O$	602.5	Pale yellow	20.27	250	67.80 (67.71)	3.47 (5.14)	4.39 (4.64)

Table (5) *Thermal analysis* (DTA and TGA) *of some complexes*

complex	Tmep.range C°	DTA peaks	Tmep.range C°	TGA (loss %)		Loss species
				Found	Calc.	
$[Cu_2L^1(H_2O)_2](OH)_2$	225°	Endo.	—	—	—	2(OH)
	398C°	Endo.	—	—	—	Coord.$2H_2O$
	449 C°	Endo.	—	—	—	Metal oxide
$[Cu_2L^2Cl_2]4H_2O$	21-70C°	Endo.	28-142C°	6.03%	5.7%	$2H_2O$
	238C°	Endo.	144-300C°	—	—	Organic specie+H_2O
	>300 C°	Endo.	300-338C°	12.14%	10.0 %	Cl_2
	—	—	486-573C°	28.04%	29.3%	$2Cu(OH)_2$
$[Co_2L^2Cl_4(H_2O)_2]$ $7H_2O$	183-230C°	Endo.	27-198C°	3.87%	4.6%	$2H_2O$ Coord.water
	260-390C°	Endo.	199-259C°	7.59%	7.9%	Co_2 +H_2O
	552-697 C°	Endo.	259-391C°	18.6%	19.21%	2CoO·
	—	—	392-651C°	42.75%	40.67%	Organic specie
$[Cu(H_2L^3)Cl_2]2½H_2O$	50-180C°	Exeo.	145-264C°	9.85%	7.83%	$2½H_2O$
	260-348C°	Endo.	265-337C°	19.9%	16.9%	$Cu(OH)_2$
	482-608C°	Endo.	338-620C°	—	—	Organic specie

Table (6) *Infrared bands assignments (cm^{-1}) of the complexes*

The complex	ν(C=N) cm^{-1}	ν(C-O) cm^{-1}	ν(OH) cm^{-1}	ν(M-O) cm^{-1}	ν(M-N) cm^{-1}	ν(M-Cl) cm^{-1}
$[NiL^1(H_2O)_2]$	1585	1427	3422	560	495	—
$[Cu_2L^1Cl_2]8H_2O$	1568	1399	3425	527	466	221
$[Ni_2L^1Cl_2]4H_2O$	1585	1356	3384	561	495	289
$[Cu_2L^1(H_2O)_2]$ $(OH)_2$	1567	1323	3448	526	468	—
$[Co_2L^2Cl_4(H_2O)_2]7H_2O$	1555	1405	3367	518	466	290
$[Ni(H_2L^2)Cl_2]$	1558	1399	3431	587	531	220
$[Cu_2L^2Cl_2]$ $4H_2O$	1531	1399	3447	511	464	221
$[Cu(H_2L^3)Cl_2]$ $2H_2O$	1552	1366	3444	701	457	266
$[Ni(H_2L^3)Cl_2]$ $4H_2O$	1605	1396	3421	725	445	220
$[Co_2(H_2L^3)(H_2O)_8]4Cl$	1598	1385	3553	729	420	—
$[Ni_2(H_2L^3)(H_2O)_8]4Cl.$ C_2H_5OH	1599	1398	3401	714	442	—
$[Cu_2L^3(H_2O)_4]2Cl$	1571	1390	3152	657	473	—
$[Co(H_2L^4)Cl_2]4H_2O$	1664	1335	3382	639	464	259
$[Ni(H_2L^4)Cl_2]$	1630	1334	—	638	478	261
$[CuL^4]2½$ H_2O	1628	1344	3424	636	551	—

Table (7) *Electronic Spectra and magnetic moment of the complexes*

The complex	λ nm	ε $Lmol^{-1}cm^{-1}$	ν cm^{-1}	μ_{eff} B.M	Geometry
$[NiL^1(H_2O)_2]$	907 558 447 386	0.05 0.207 2.334 2.109	11035 17921 22371 25906	—	Octahedral
$[Cu_2L^1Cl_2]8H_2O$	545 430 385	1.638 2.446 2.305	26178 23255 25974	—	Square planar
$[Ni_2L^1Cl_2]4H_2O$	565 454 385	0.392 2.456 2.121	17699 22026 25974	1.8	Square planar
$[Cu_2L^1(H_2O)_2]\ (OH)_2$	389 906	0.346 0.079	25706 11037	1.2	Square planar
$[Co_2L^2Cl_4\,(H_2O)_2]7H_2O$	610 655	0.767 1.038	16393 15267	3.8	Octahedral
$[Ni(H_2L^2)Cl_2]$	575 370	0.08 1.916	17391 27027	—	Octahedral
$[Cu_2L^2Cl_2]4H_2O$	380 395 910	2.276 2.176 0.301	26315 25316 10989	1.16	Square planar
$[Cu(H_2L^3)Cl_2]2H_2O$	650	0.176	15384	1.8	Octahedral
$[Ni(H_2L^3)Cl_2]4H_2O$	580 905 375	·0.08 0.06 1.98	17241 11049 26666	3.1	Octahedral
$[Co_2\,(H_2L^3)(H_2O)_8]4Cl$	650 600 375	0.633 0.564 2.003	15384 16666 26666	—	Octahedral
$[Ni_2(H_2L^3)\,(H_2O)_8]4Cl.$ C_2H_5OH	402 389	0.155 0.219	24875 25706	1.8	Octahedral
$[Cu_2L^3(H_2O)_4]2Cl$	442 550	2.99 0.148	22593 18155	0.8	Square planar
$[Co(H_2L^4)Cl_2]4H_2O$	605 670	0.267 0.370	16528 14925	—	Octahedral
$[Ni(H_2L^4)Cl_2]$	575	0.084	17391	3.6	Octahedral
$[CuL^4]2½\ H_2O$	370 415 440	1.952 0.343 0.316	27027 24096 22727	1.8	Square planar

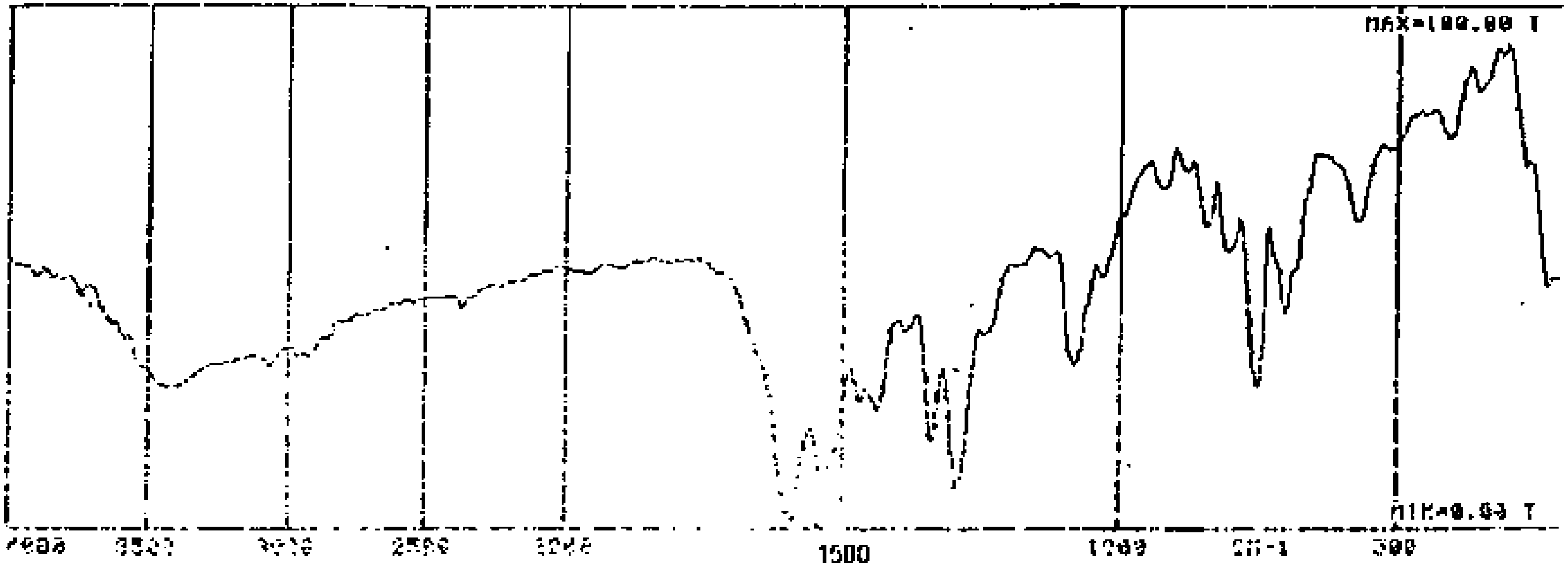


Fig. (1) IR. Spectrum of (H_2L^1) Ligand.

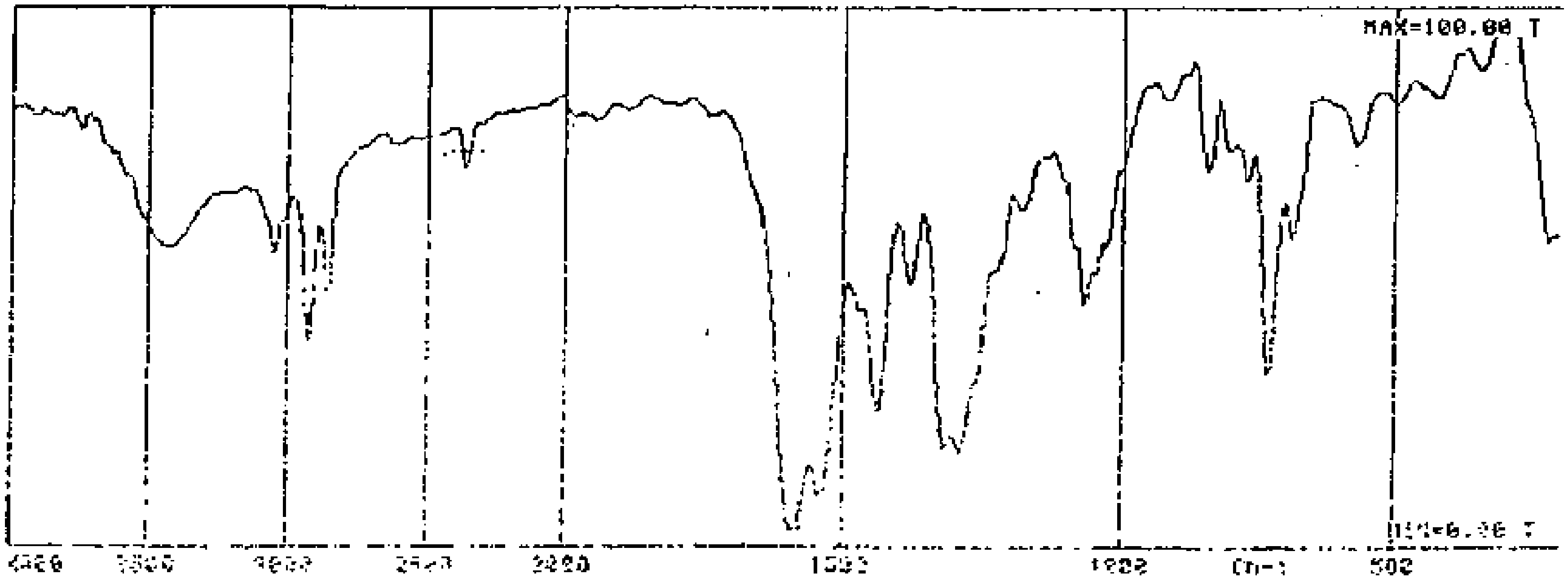


Fig. (3) I.R. Spectrum of (H_2L^3) Ligand.

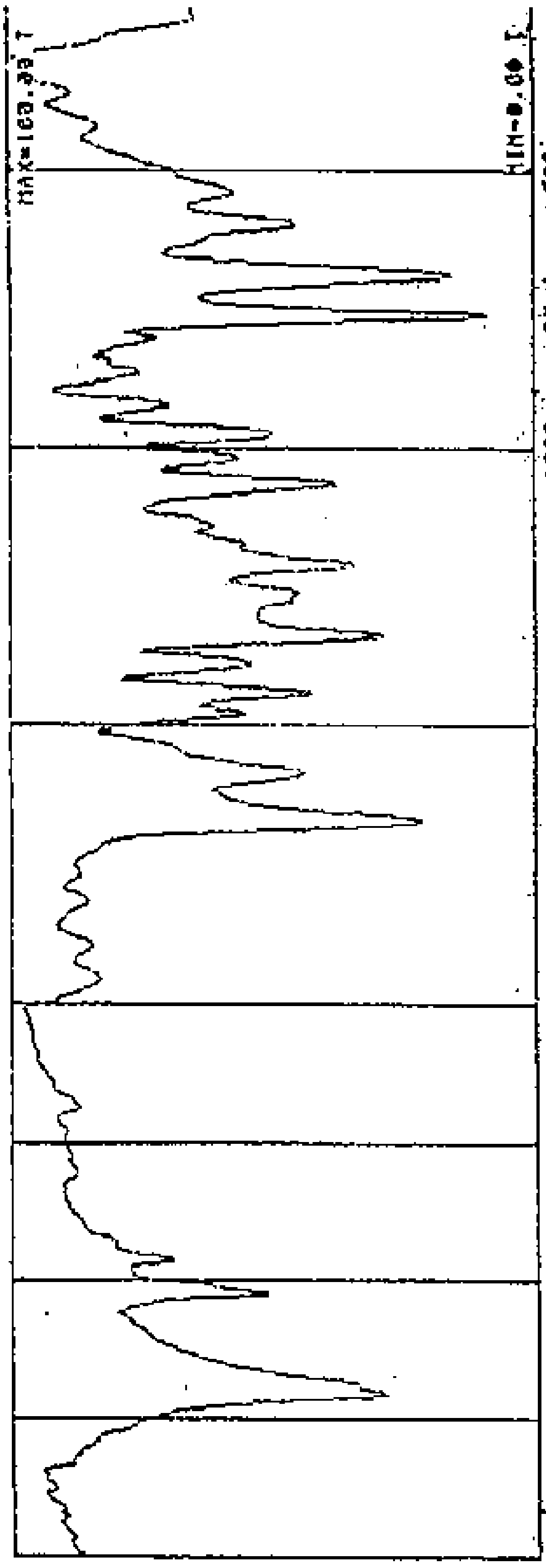


Fig. (4) IR. Spectrum of (H_2L^4) Ligand.

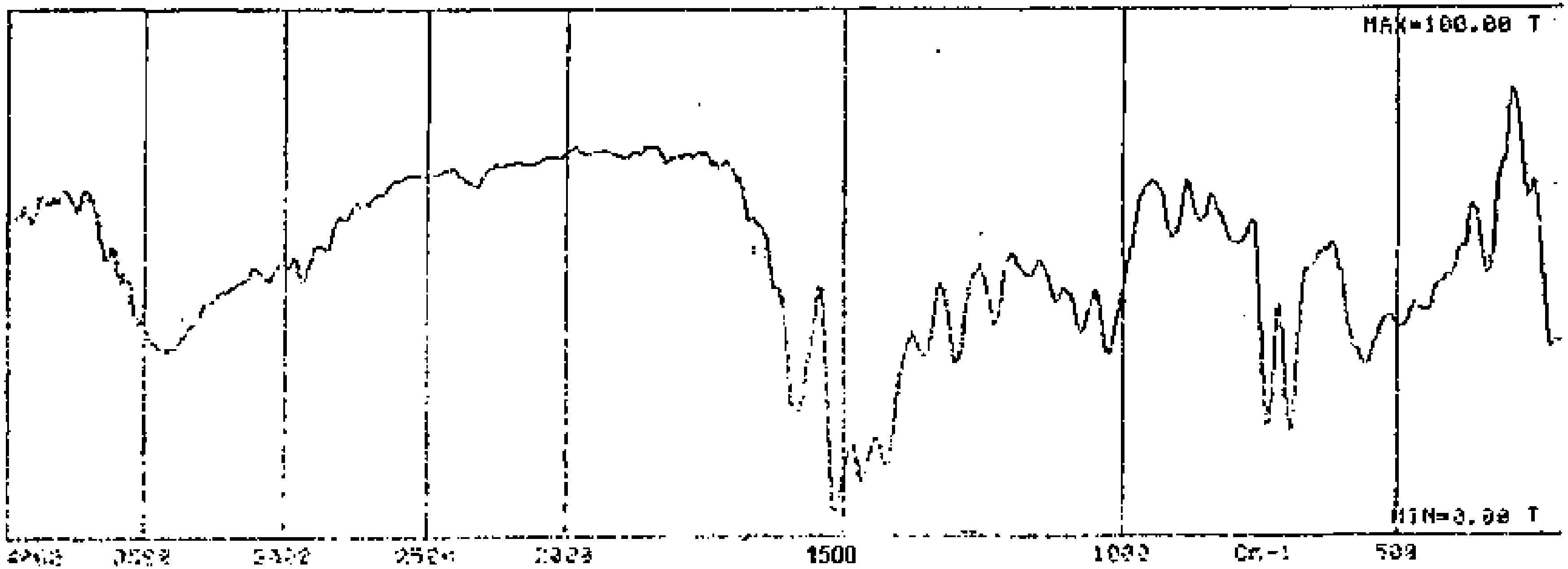


Fig (5) I.R. Spectrum of [(Ni L^1 ($H_2O)_2$] Complex.

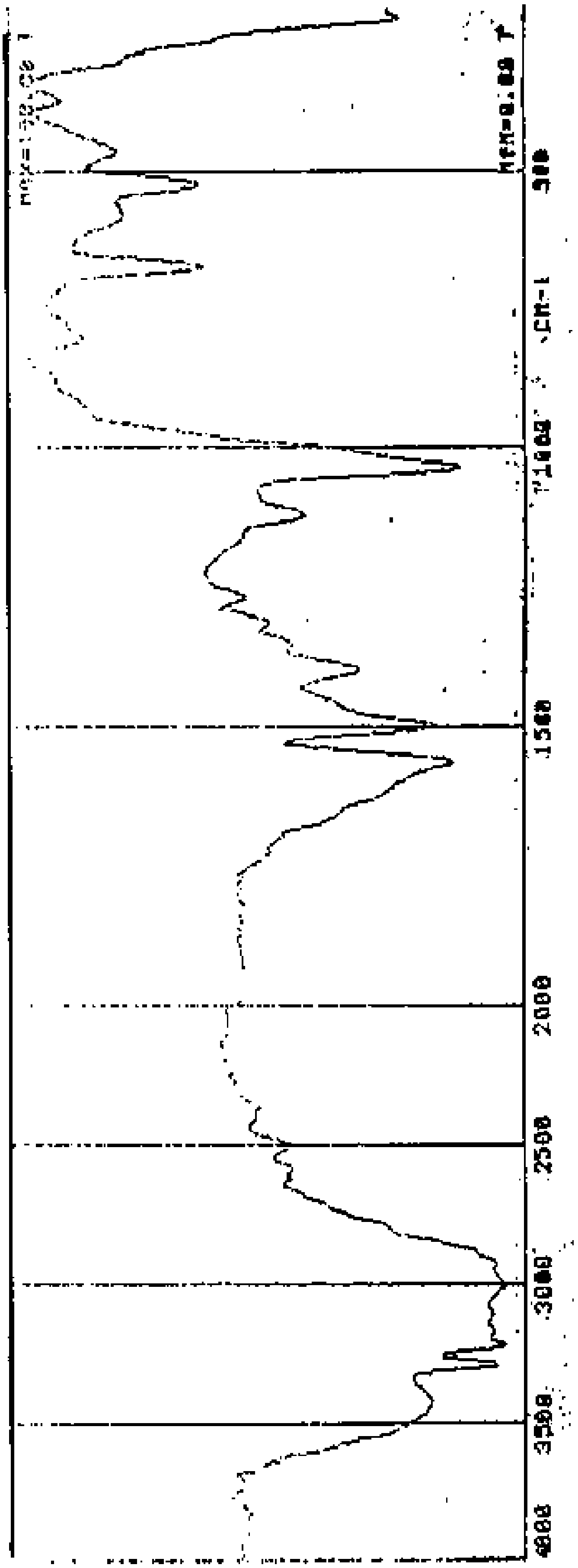


Fig (6) I.R. Spectrum of [(Cu$_2$L^1 2Cl)]8H$_2$O Complex.

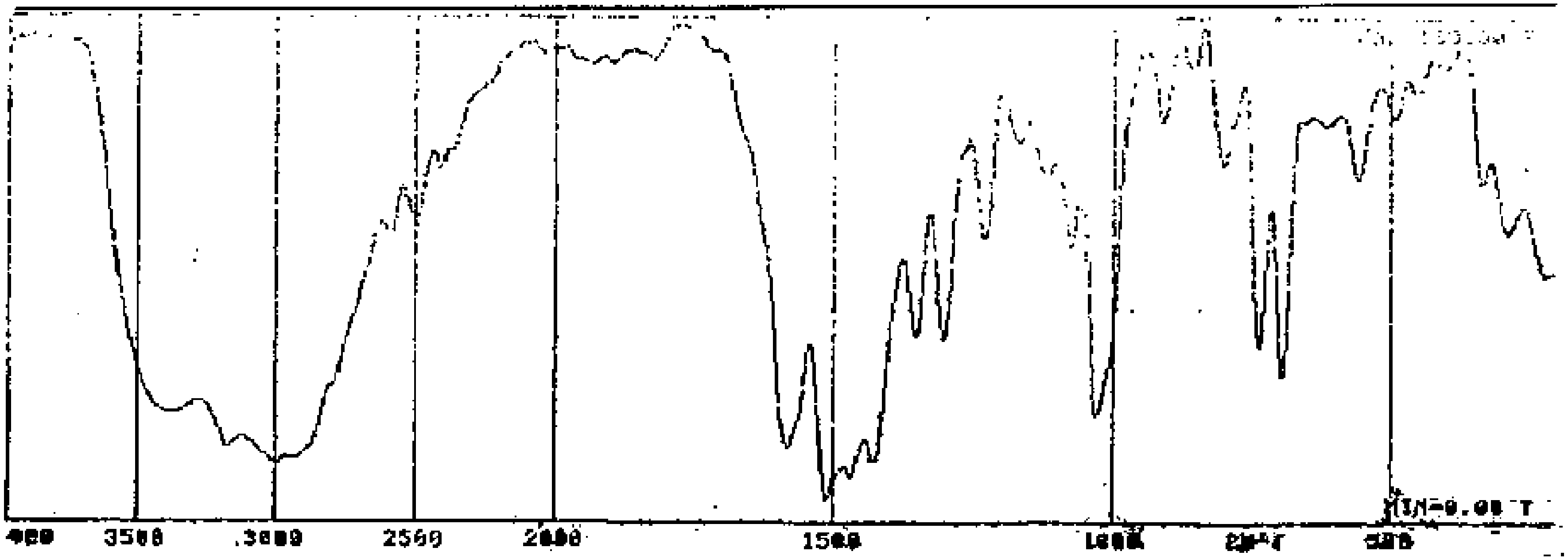


Fig (7) IR. Spectrum of [(Ni_2L^1 2Cl)]4H_2O Complex.

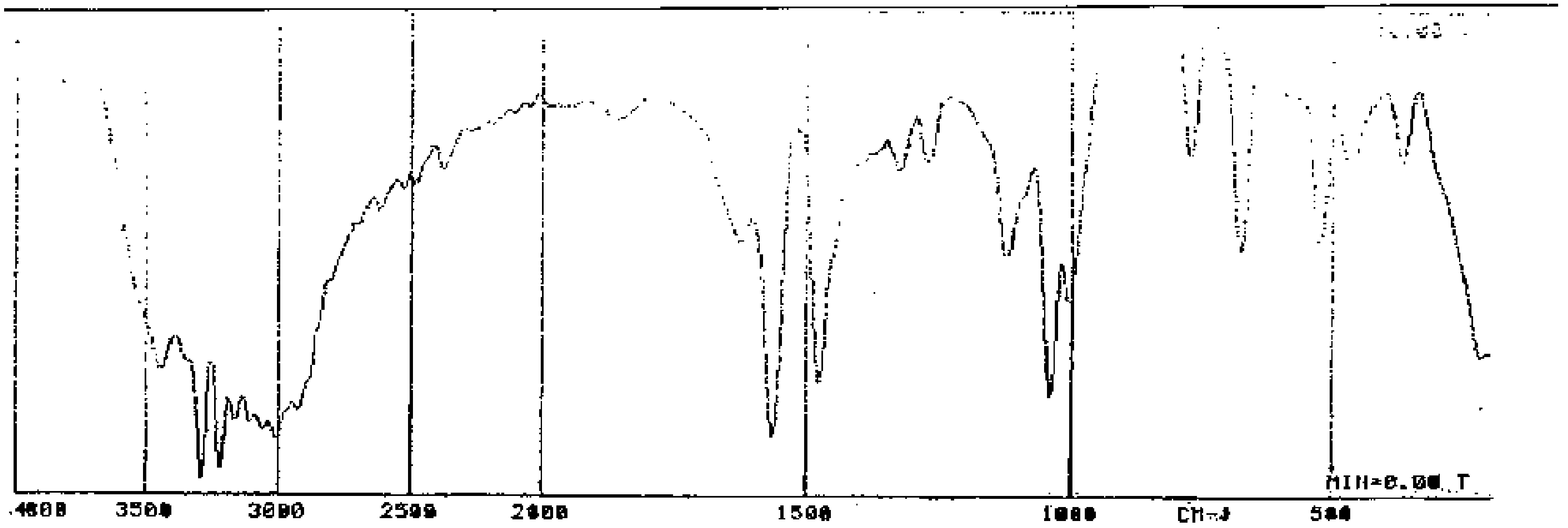


Fig (8) IR. Spectrum of $[(Cu_2L^1\ (H_2O)_2]2(OH)$ Complex.

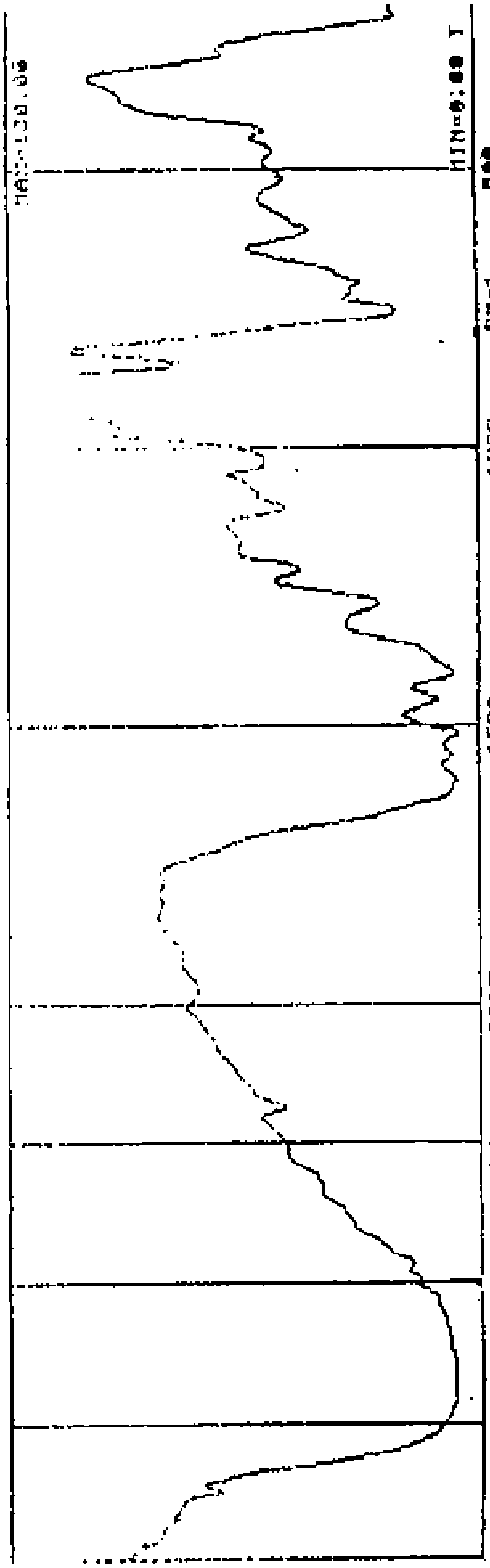


Fig (9) IR.Spectrum of [(Co$_2$L^2 4Cl (H$_2$O)$_2$]7H$_2$O Complex.

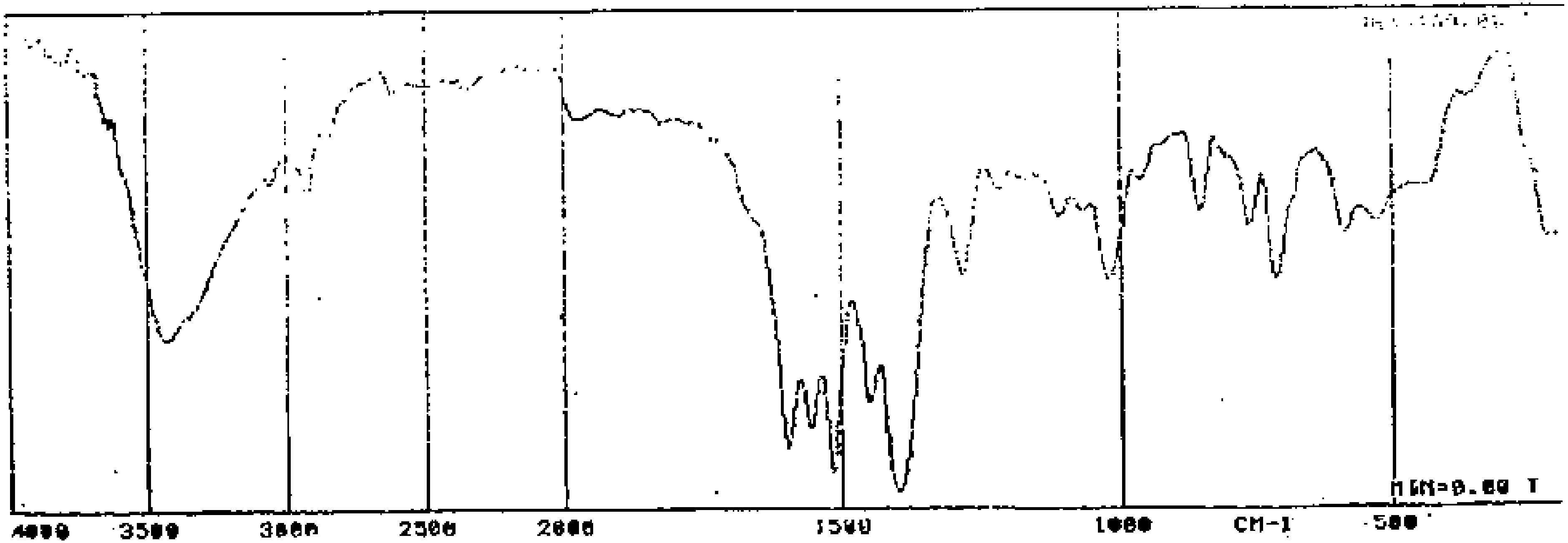


Fig (10) IR.Spectrum of [Ni (H_2L^2) 2Cl] Complex.

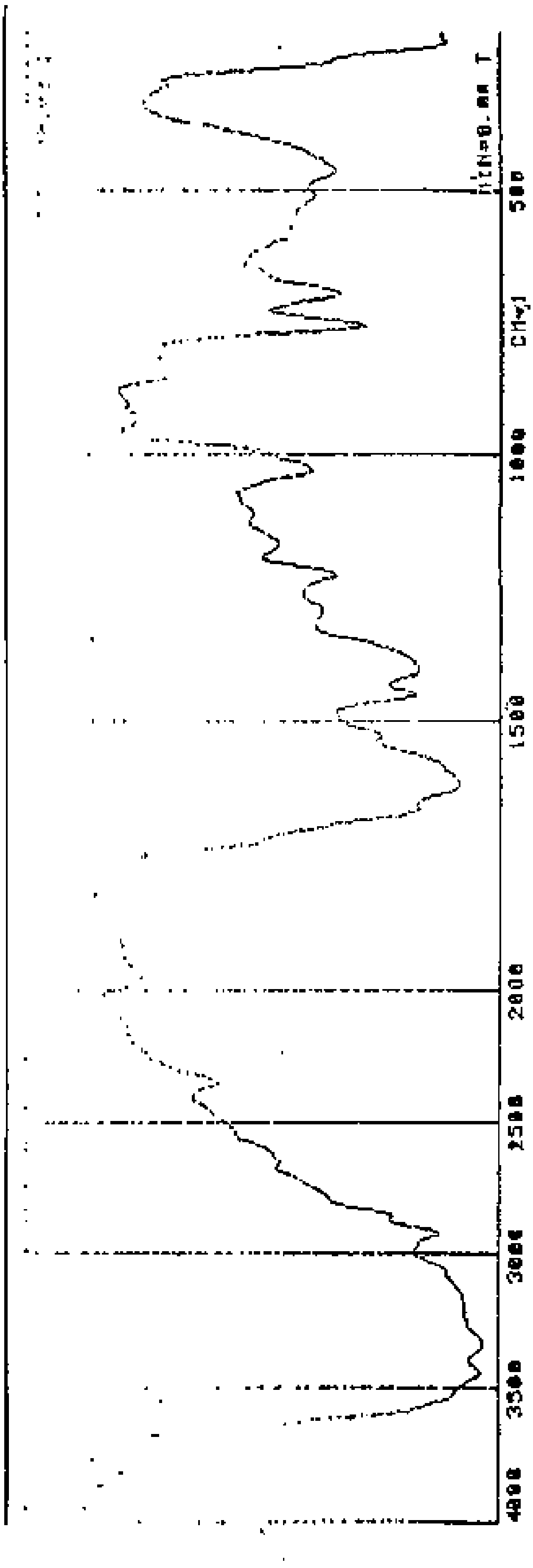


Fig (11) IR.Spectrum of [$Cu_2L^2 2Cl$]$4H_2O$ Complex.

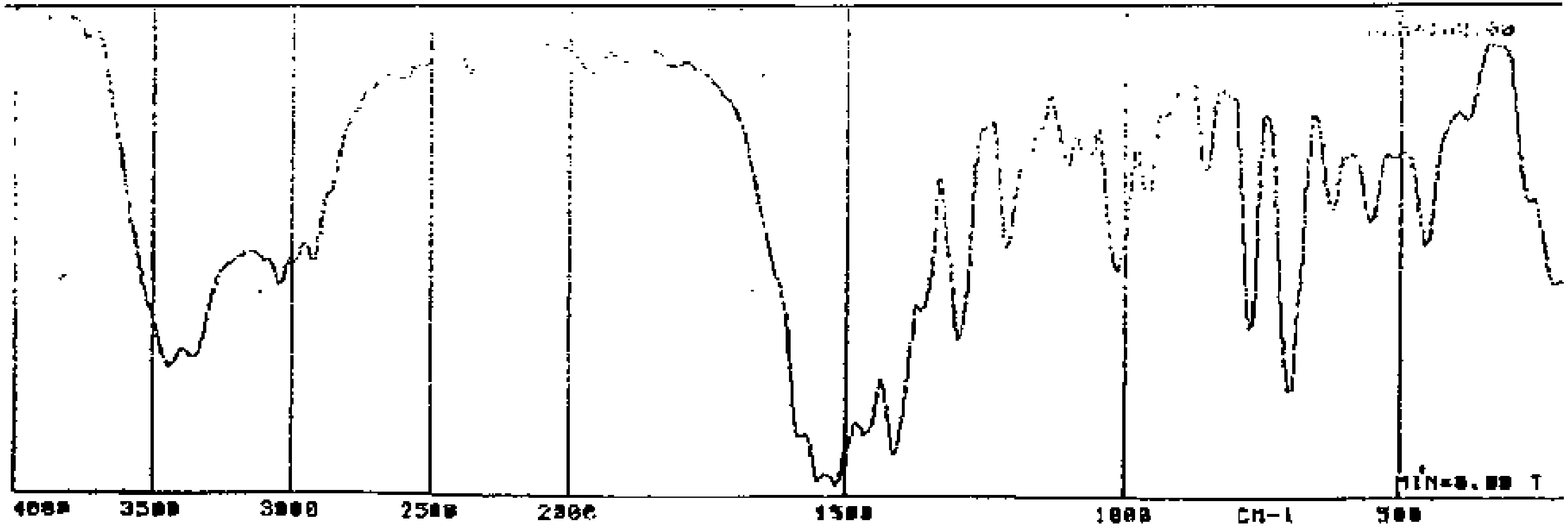


Fig (12) IR. Spectrum of $[Cu\ (H_2L^3)2Cl]2H_2O$ Complex.

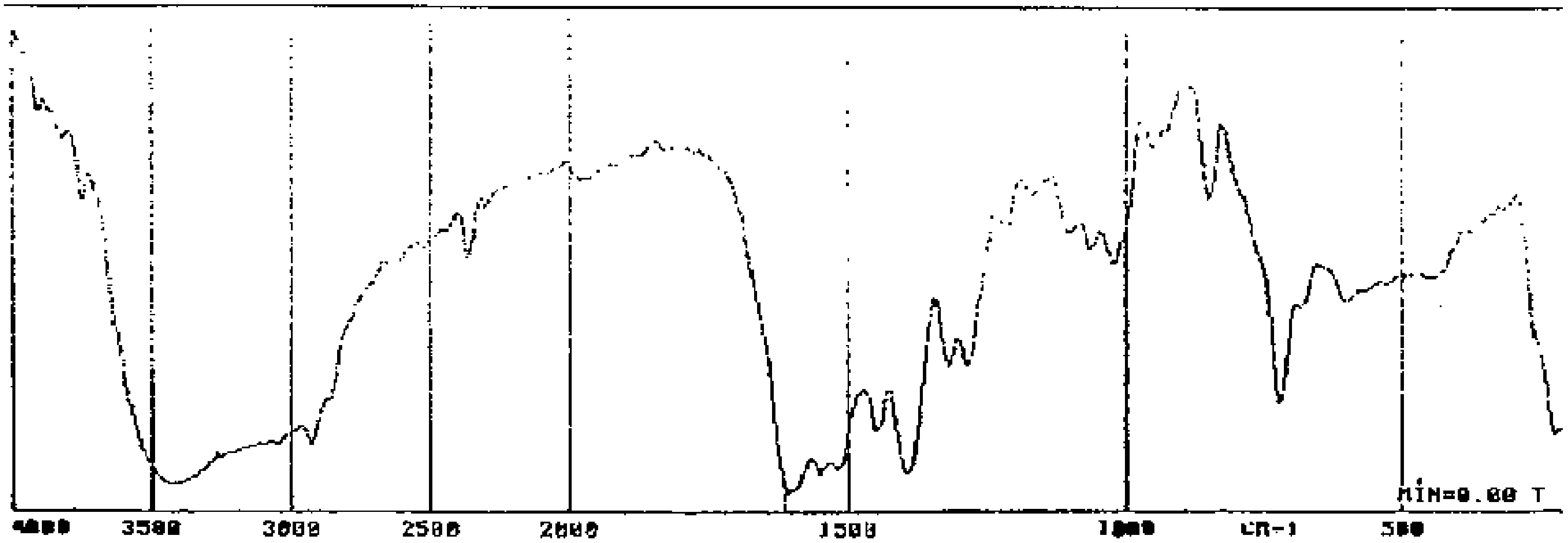


Fig (13) IR.Spectrum of [Ni (H_2L^3)2Cl]$4H_2O$ Complex.

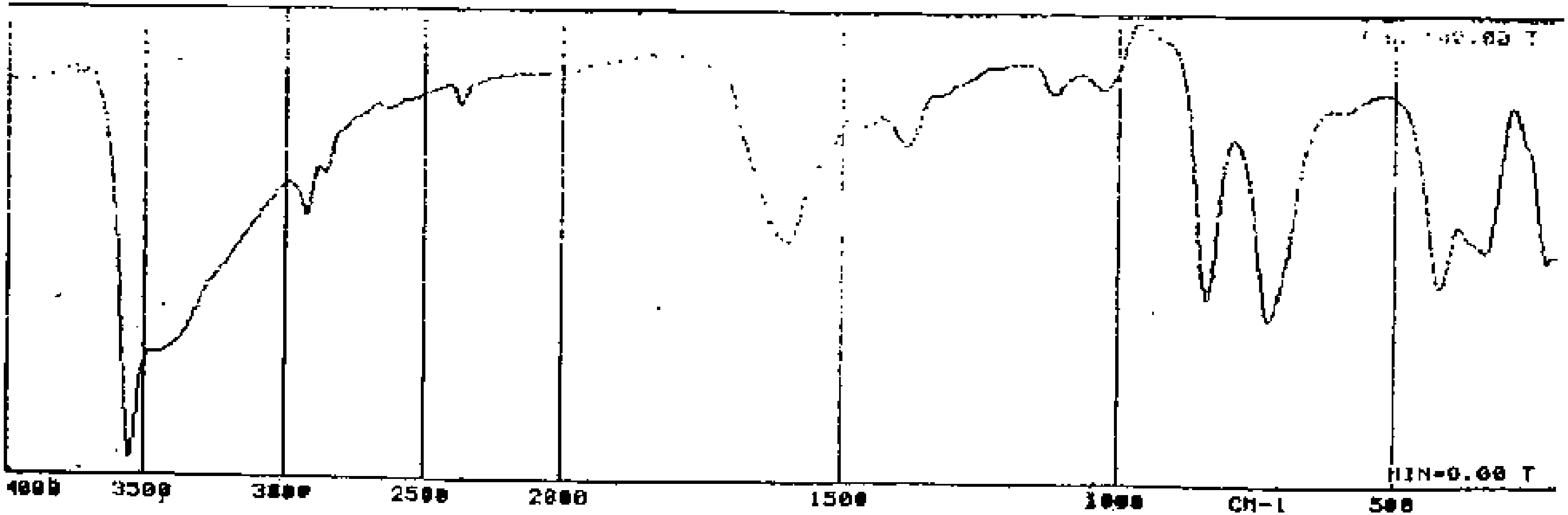


Fig (14) IR.Spectrum of $[Co_2(H_2L^3)(H_2O)_8]4Cl$ Complex.

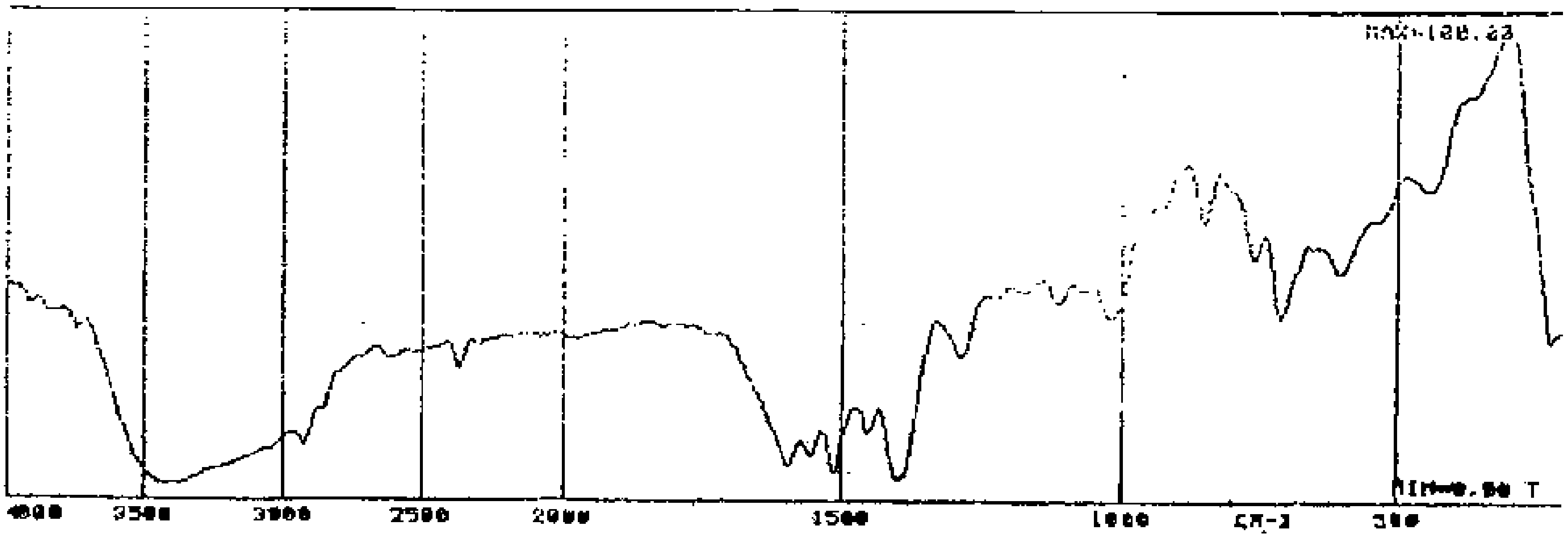


Fig (15) IR.Spectrum of $[Ni_2(H_2L^3)(H_2O)_8]4Cl.\ C_2H_5OH$ Complex.

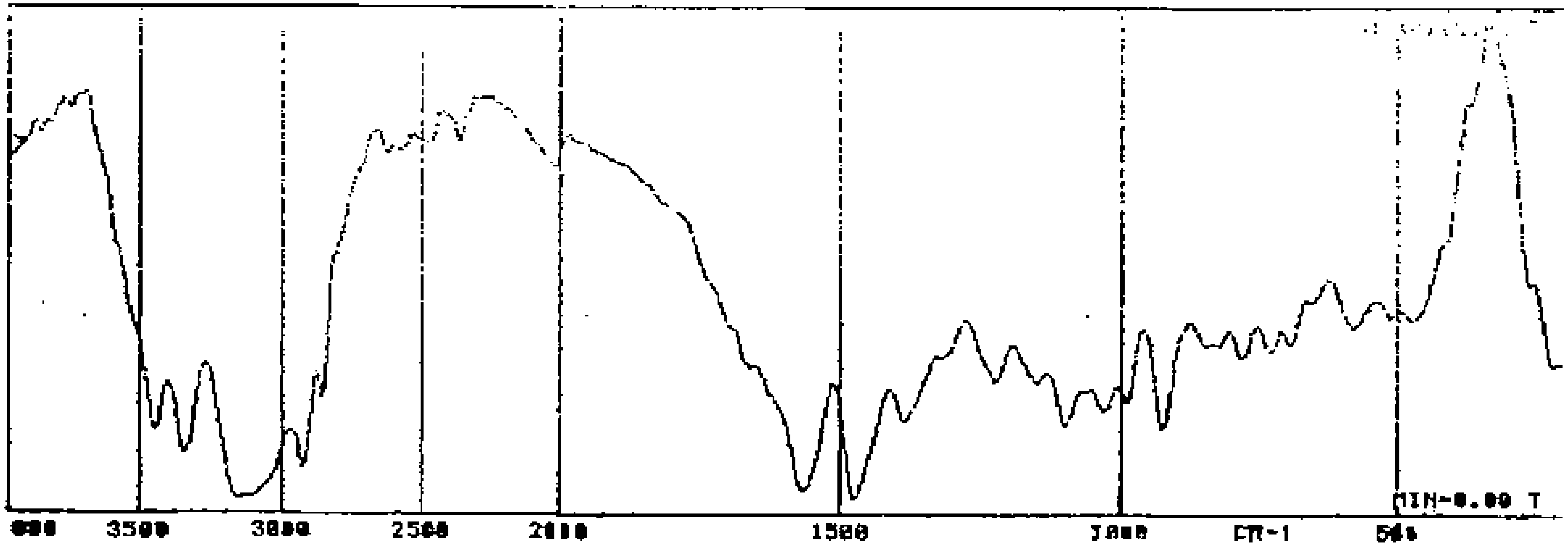


Fig (16) IR.Spectrumof $[Cu_2L^3(H_2O)_4]2Cl$ Complex.

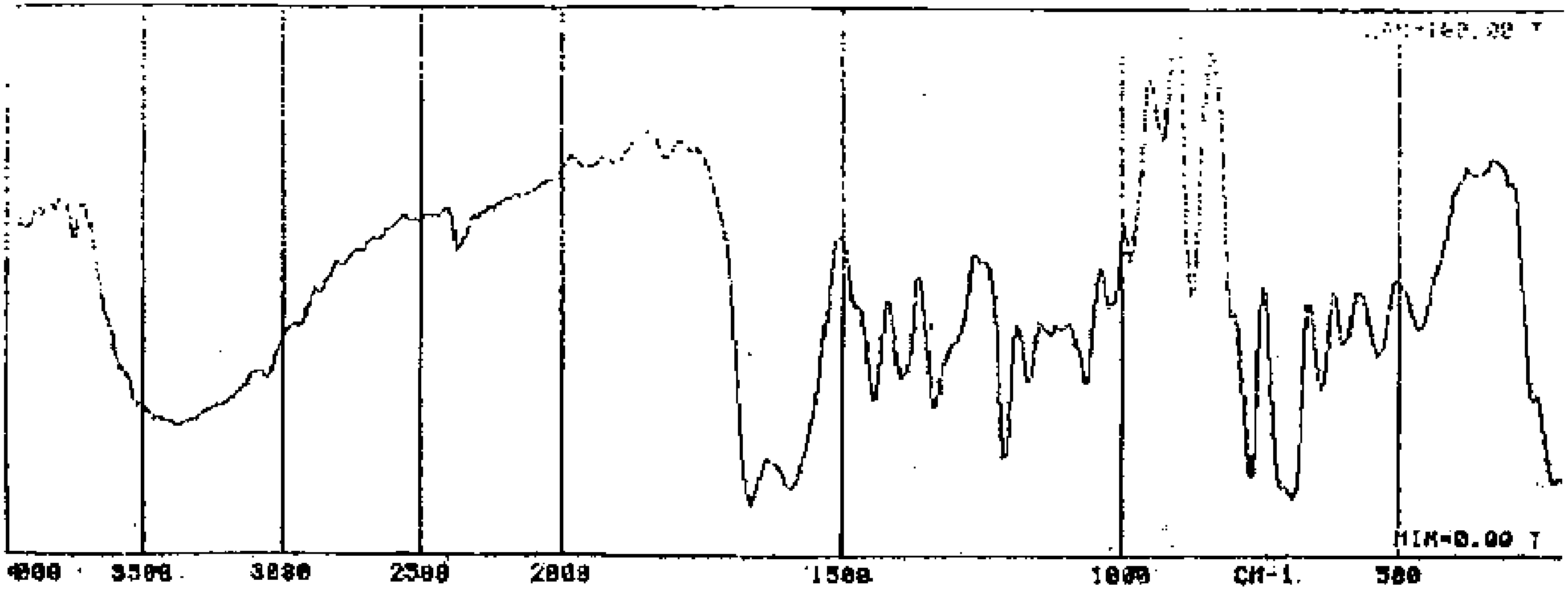


Fig (17) IR.Spectrum of [Co (H_2L^4)2Cl]4H_2O Complex.

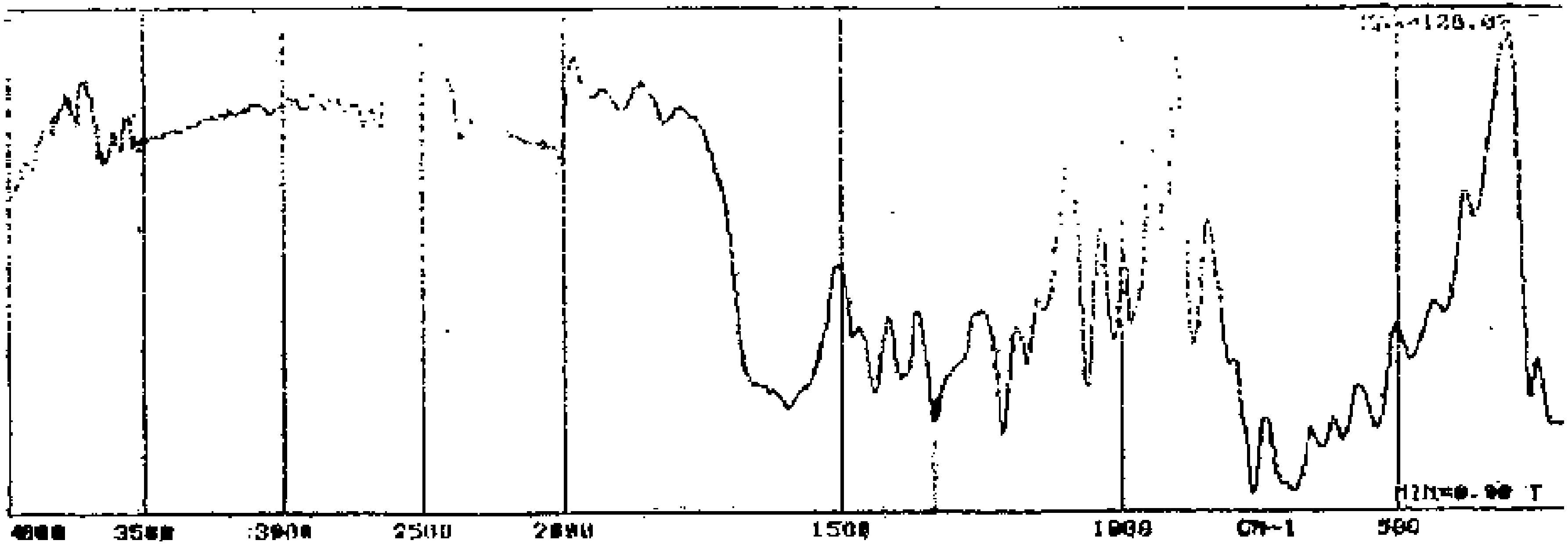


Fig (18) IR.Spectrum of [Ni (H_2L^4)2Cl] Complex.

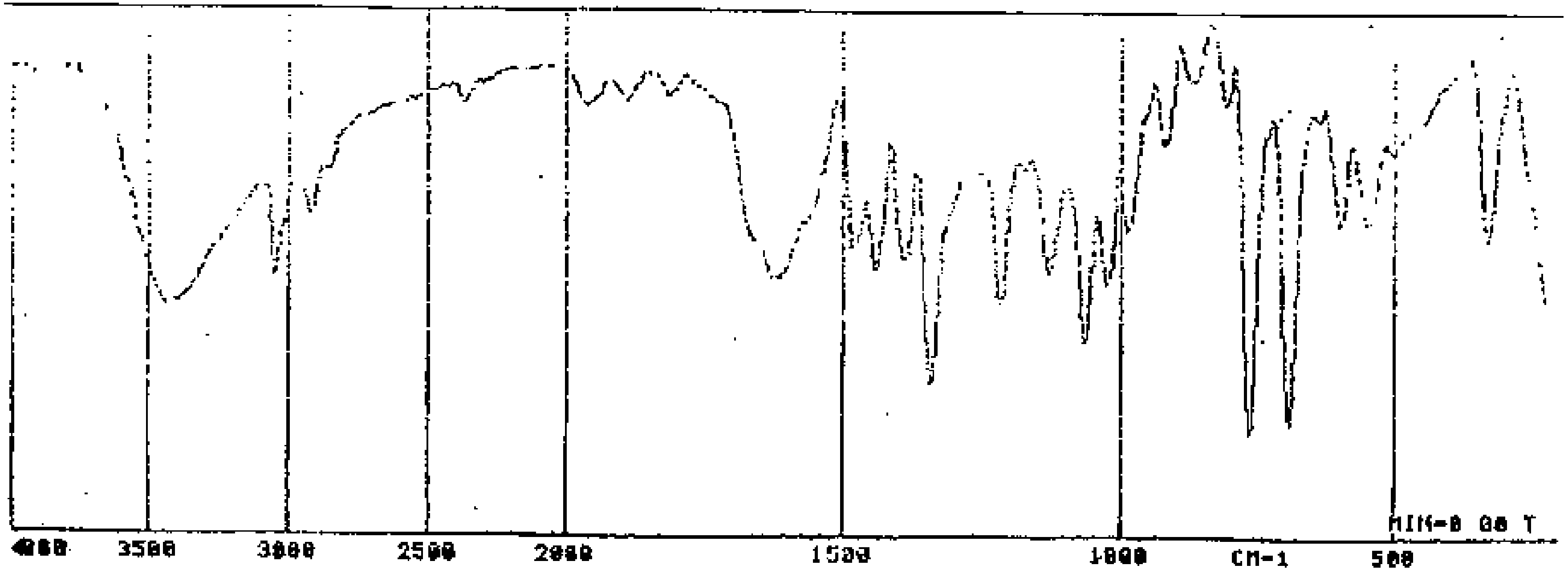


Fig (19) IR.Spectrum of [Cu L^4]2 $\frac{1}{2}$ H_2O Complex.

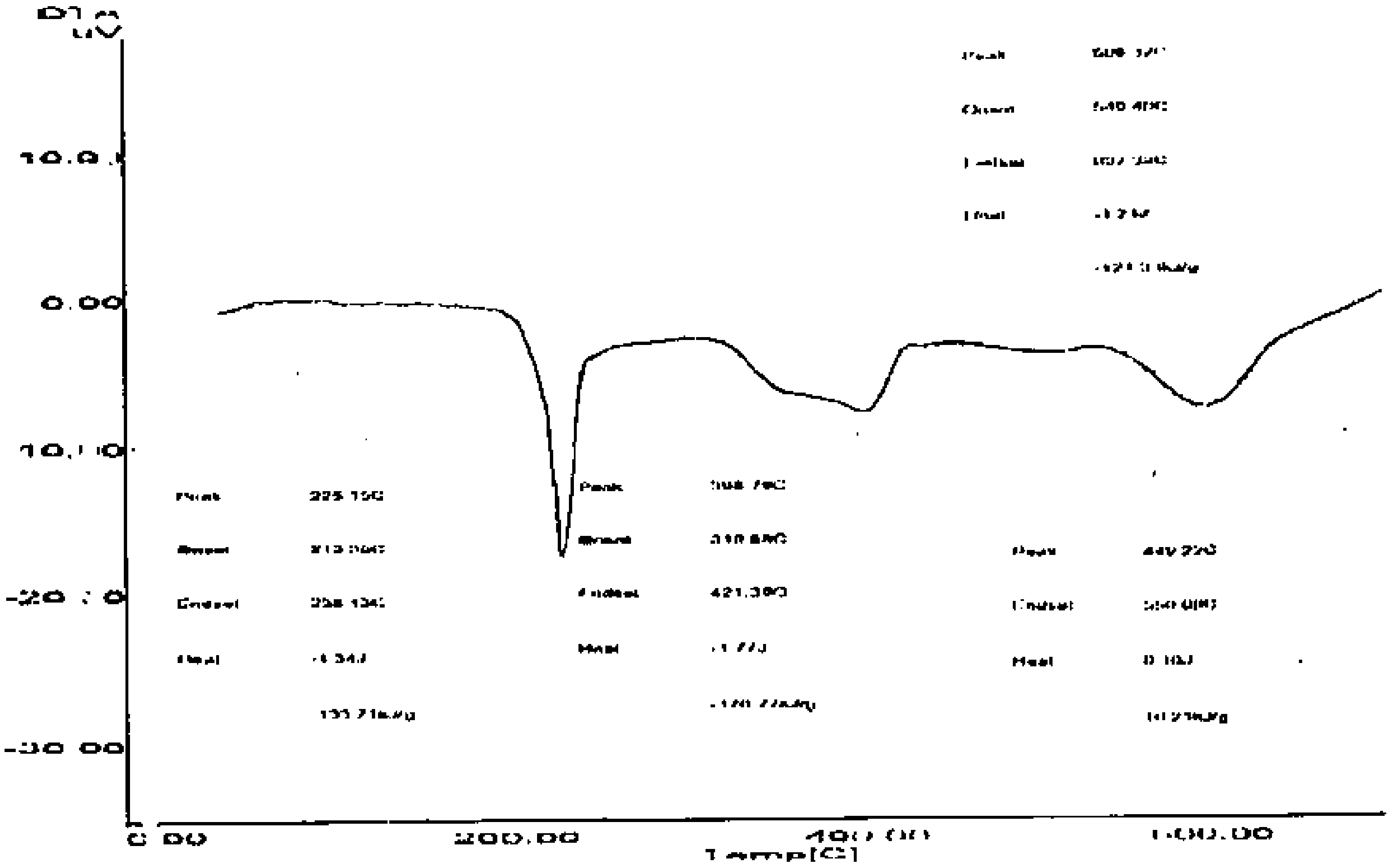


Fig (20) DTA of $[Cu_2L^1_2(H_2O)_2]2(OH)$ Complex.

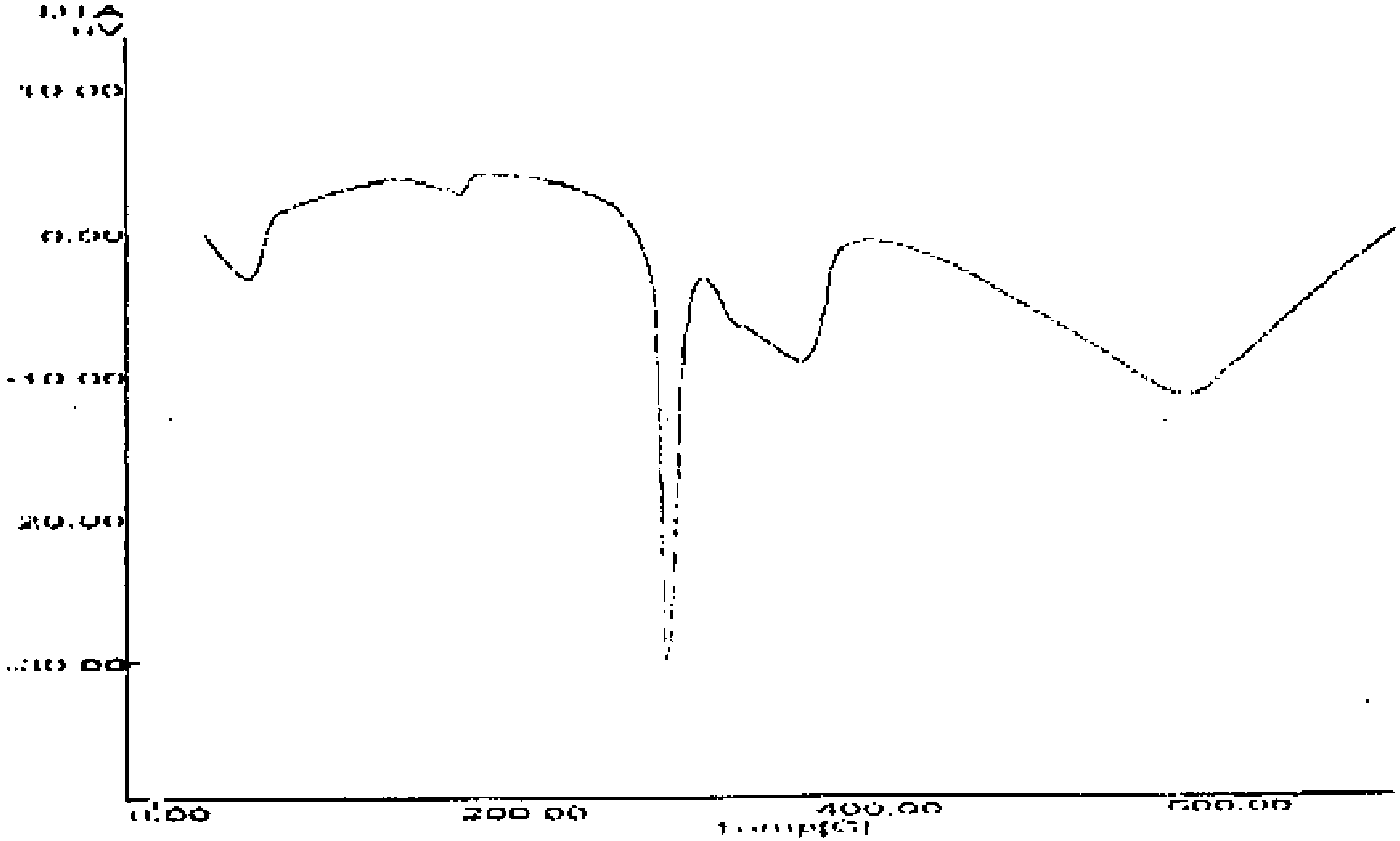


Fig (21) DTA of $[Cu_2L^4 2Cl] 4H_2O$ Complex.

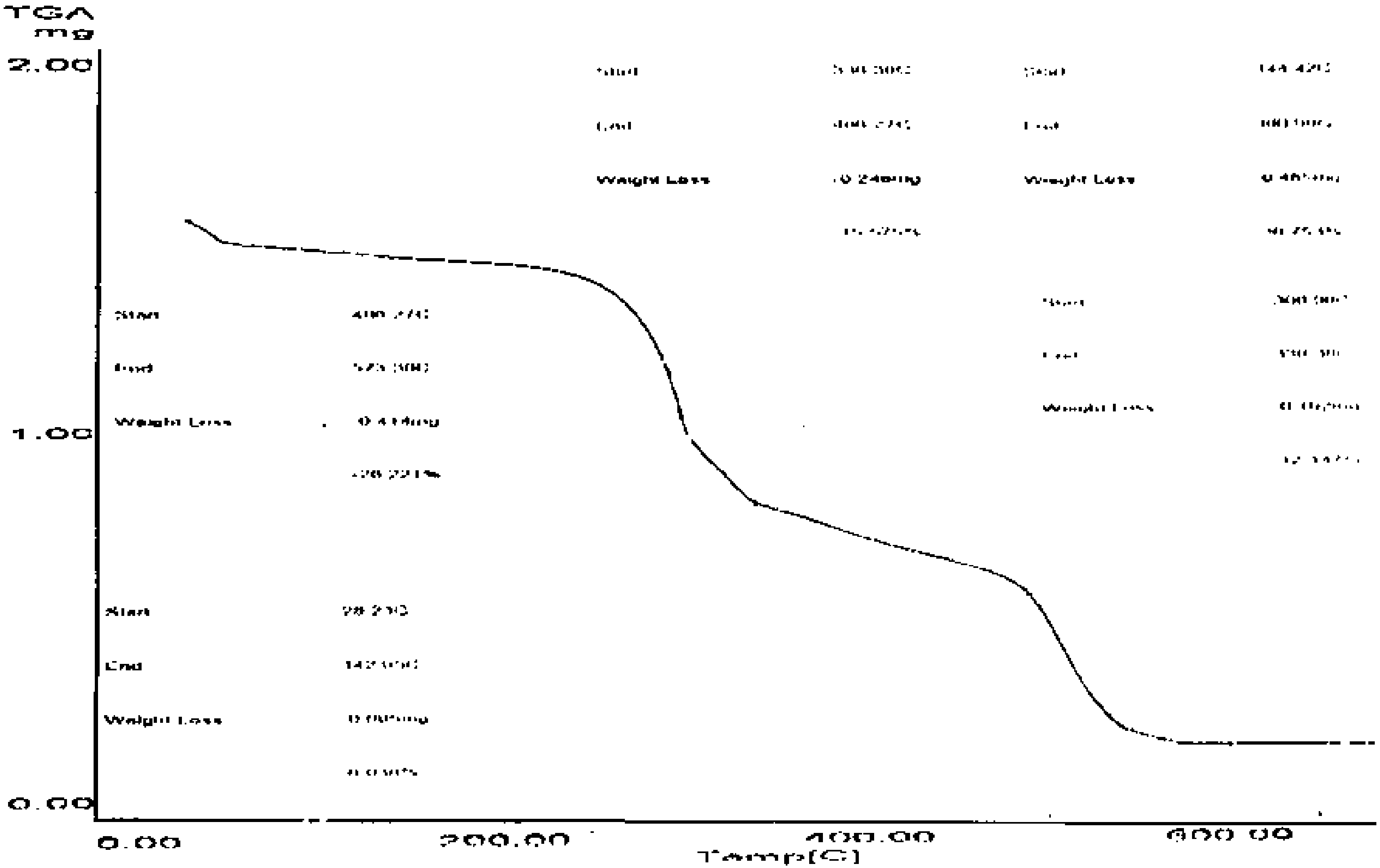


Fig (22) TGA of $[Cu_2L^2 2Cl] 4H_2O$ Complex.

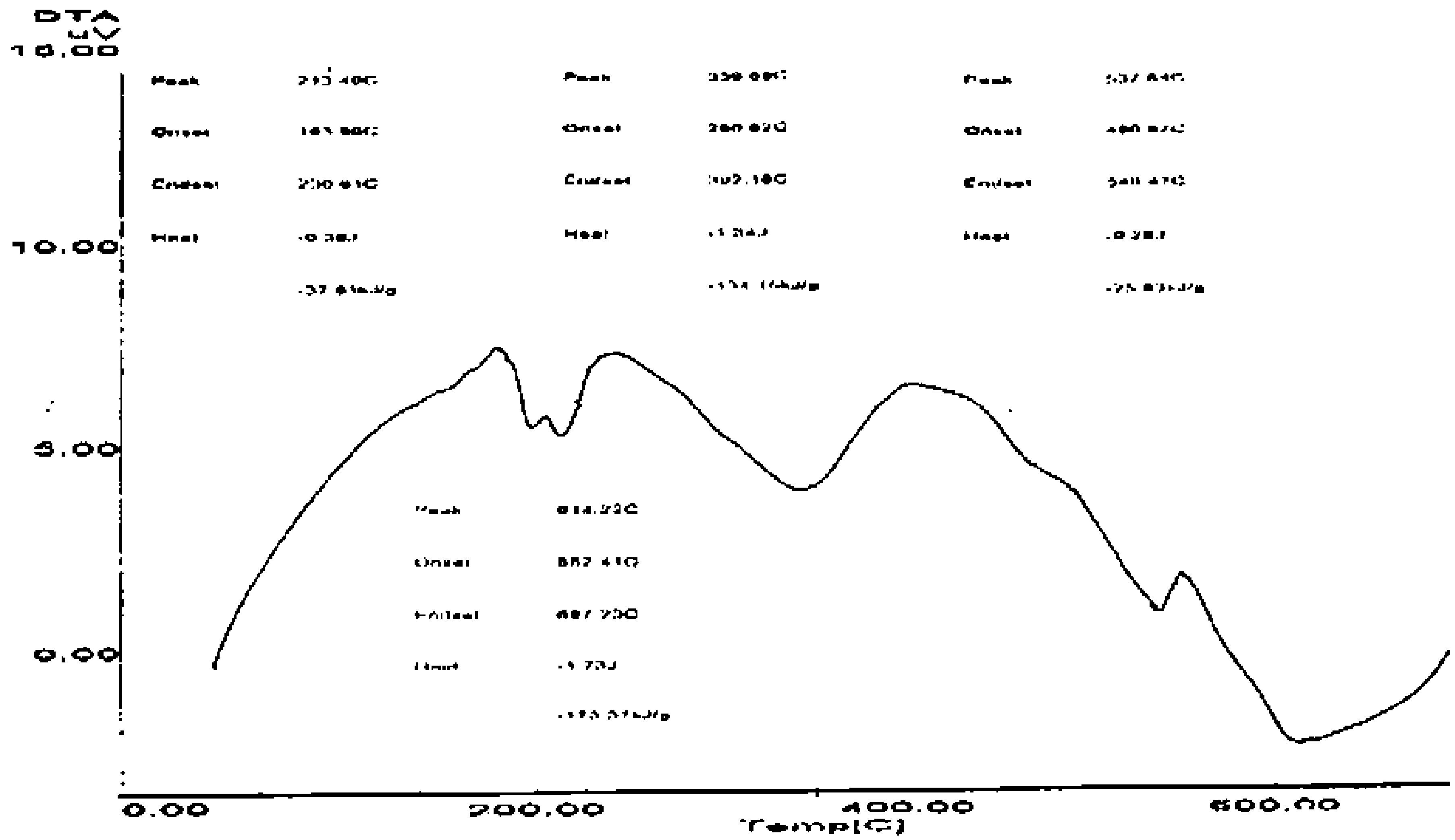


Fig. (23) DTA of $[Co_2L^{ii}4\ Cl(H_2O)_2]7H_2O$ Complex.

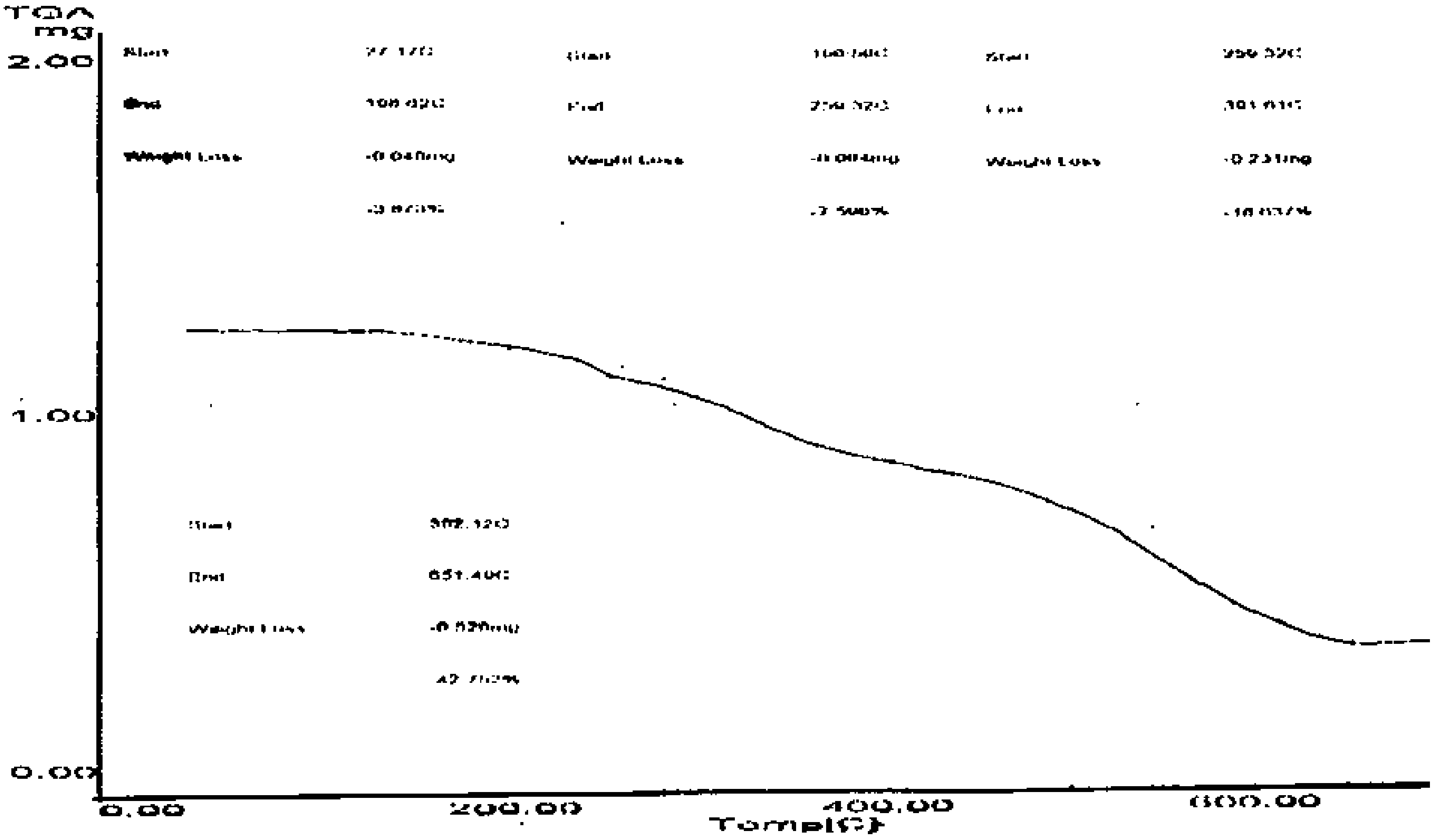


Fig. (24) TGA of $[Co_2L^2 4\ Cl(H_2O)_2]7H_2O$ Complex.

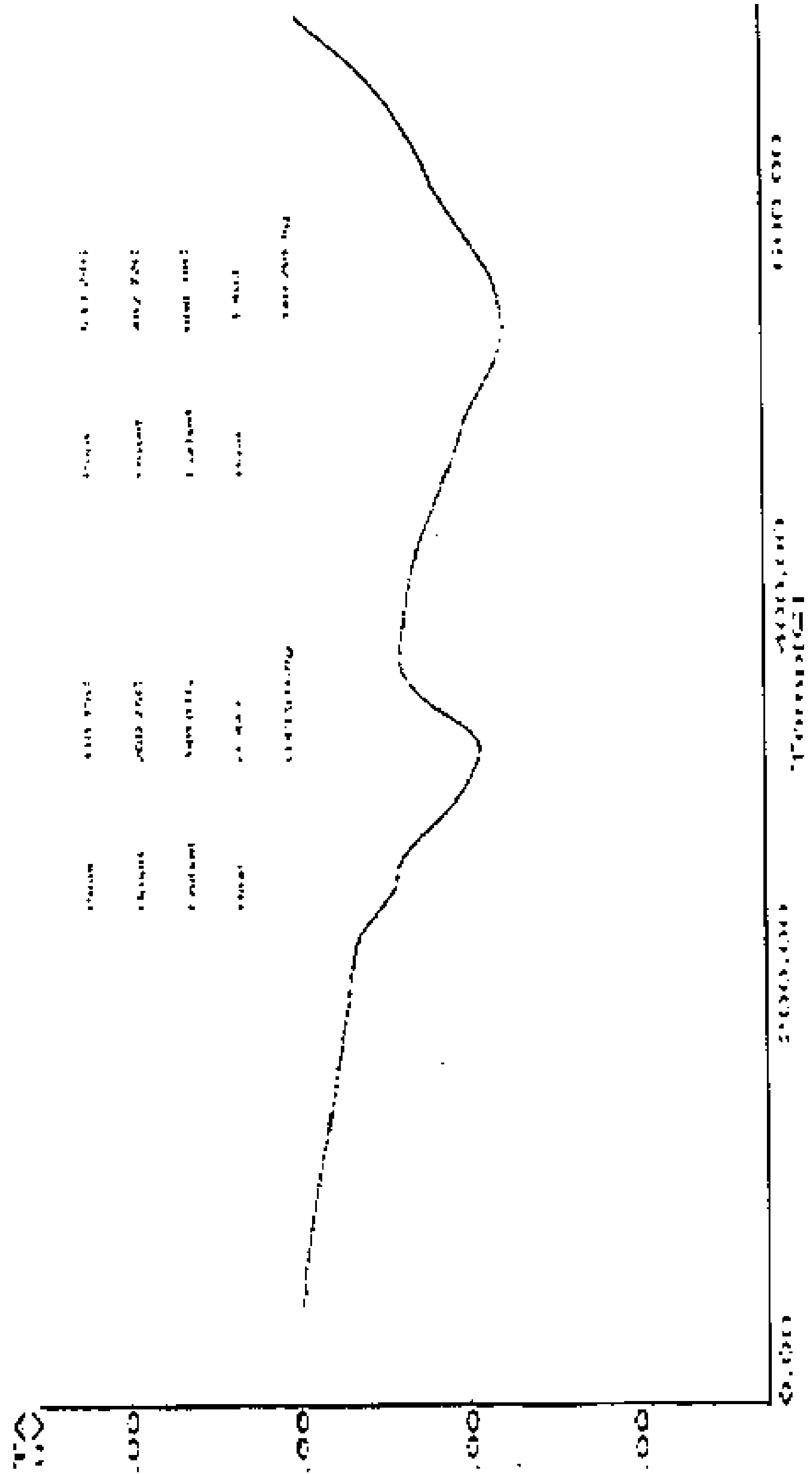


Fig (25) DTA of [Cu (H_2L^3)2Cl] $2H_2O$ Complex.

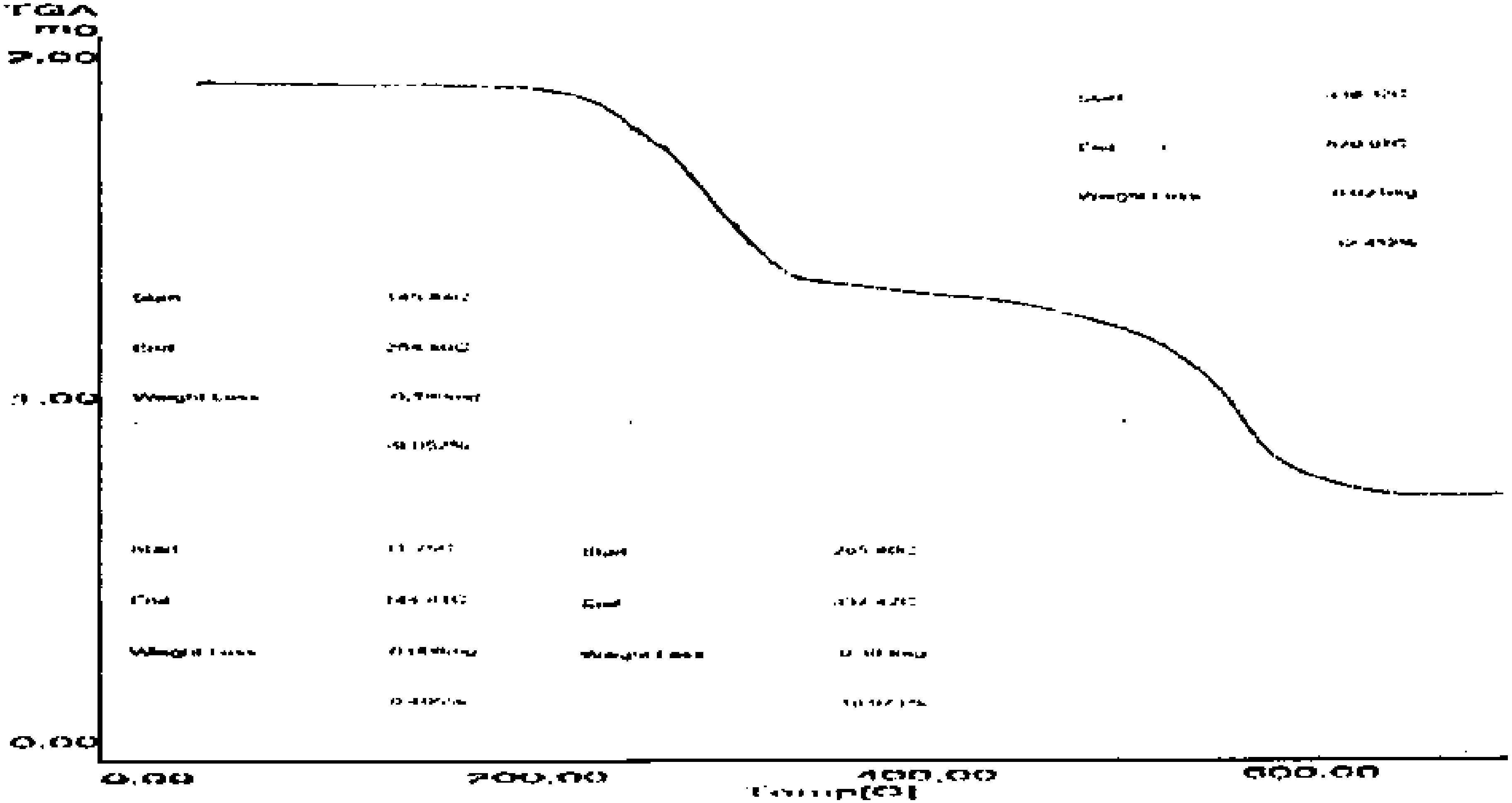
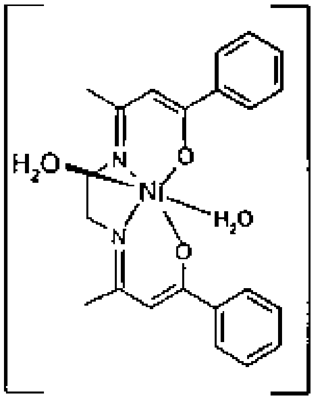


Fig (26) TGA of [Cu (H_2L^3)2Cl] $2H_2O$ Complex.

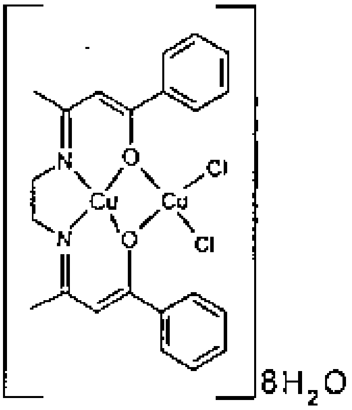
APPENDIX

The suggested geometrical structures for the complexes under investigation

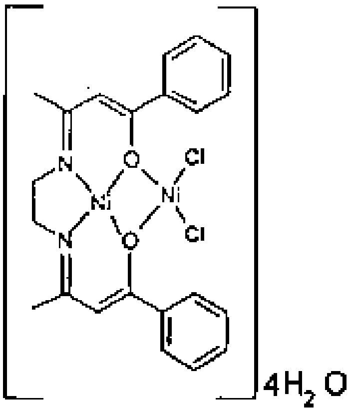
The suggested geometrical structures of complexes.



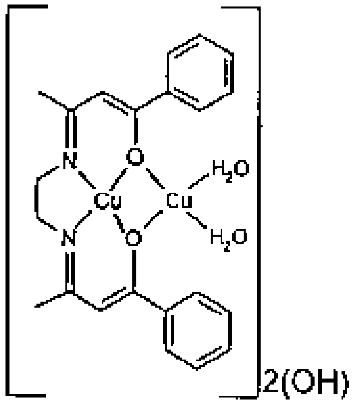
$[NiL^1(H_2O)_2]$



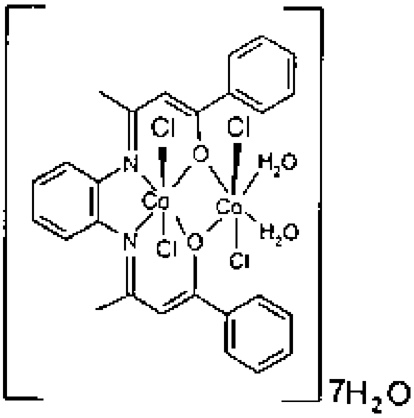
$[Cu_2L^1Cl_2]8H_2O$



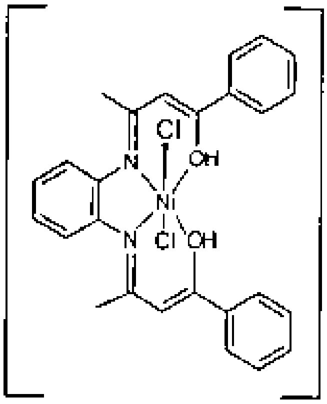
$[Ni_2L^1Cl_2]4H_2O$



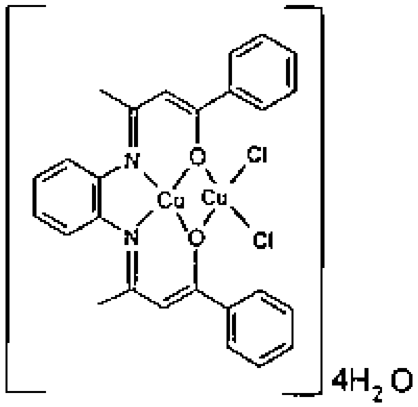
$[Cu_2L^1(H_2O)_2]2(OH)$



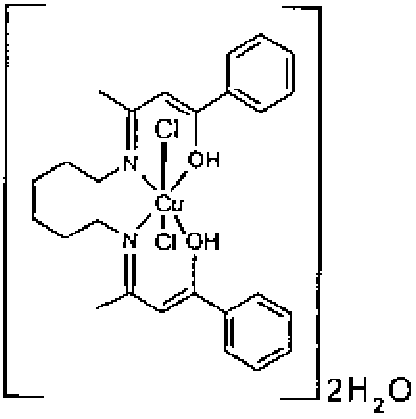
$[Co_2L^2C_4l(H_2O)_2]7H_2O$



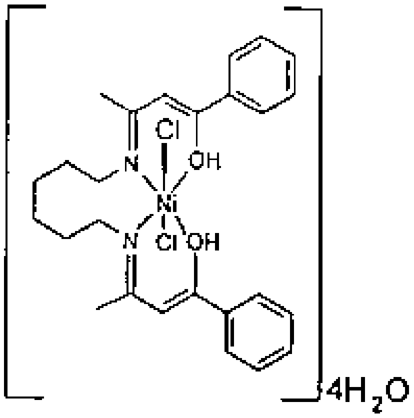
$[Ni\ (H_2L^2)Cl_2]$



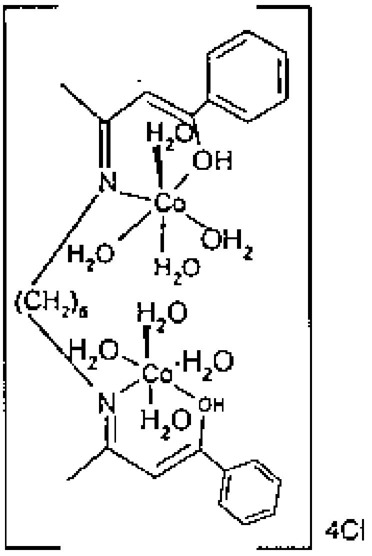
$[Cu_2L^2Cl_2]4H_2O$



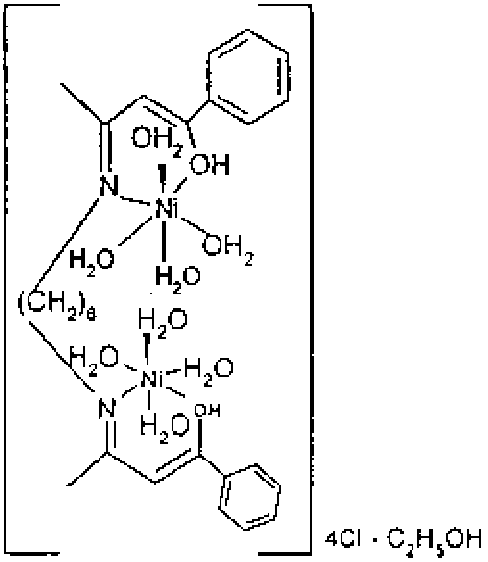
$[Cu\,(H_2L^3)Cl_2]2H_2O$



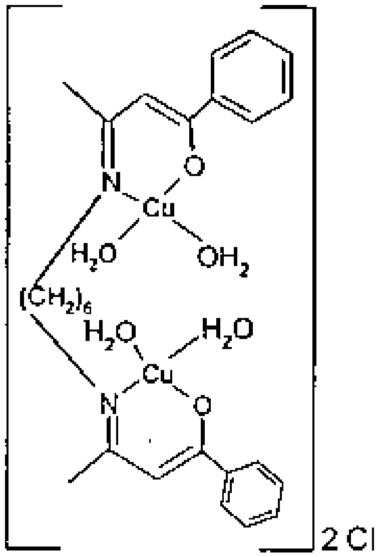
$[Ni\,(H_2L^3)Cl_2]4H_2O$



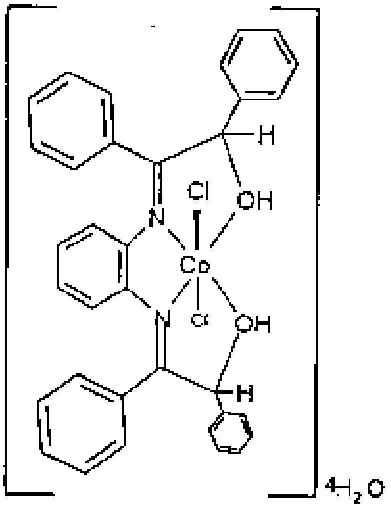
$[Co_2(H_2L^3)(H_2O)_8]4Cl$



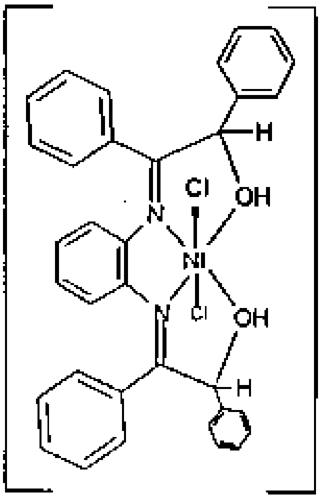
$[Ni_2(H_2L^3)(H_2O)_8]4Cl.$
C_2H_5OH



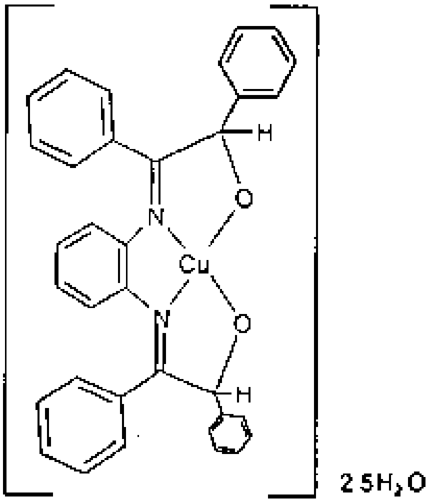
$[Cu_2L^3(H_2O)_4]2Cl$



$[Co(H_2L^4)Cl_2]4H_2O$



$[Ni(H_2L^4)Cl_2]$



$[CuL^4]2\frac{1}{2}\ H_2O$

Conclusion

The elemental analysis of C, H and N% confirmed the suggested structures for ligands and their metal complexes, which are formed in a mono- and binuclear manner. The IR supported the ligands structure and the site of chelation through the function groups investigations. In all complexes the chelation proved to be through N and O atoms as expected.

The conductivity measurements, thermal analysis gave more evidence of the shape and the complexes formations sphere. Electronic spectra and magnetic susceptibility confirmed that the complexes under investigation have octahedral or square planar geometries around the central metal atom. The complexes are formed in a mono- and binuclear mode.Cobalt complexes proved to own an octahedral structure in both modes.

The nickel complexes in mononuclear demonstrated to have an octahedral structures, whereas the binuclear nickel complexes had a square planar structure. Finally, the copper complexes in mononuclear confirmed to have an octahedral structures, while the binuclear copper complexes had a square planar structure

Further work

Previous studies on Schiff base metal complexes have showed the formation of a mono-, bi- and polynuclear metal complexes. No evidence on polynuclear metal complexes has been seen in this study. This may be due to a steric effect of large ligands, which maybe investigated by using small size ligands. We propose a pH controlled synthesis of the metal complexes, e.g. at pH=4 and pH=9.

On the preparations of metal complexes of Co (II) and Fe (II) and Cr (III), the effect of O_2 molecules (carrying the reaction under O_2 gas) may be investigated to see the oxidations ability and the protection activities of oxygen molecule. Finally, the physiological effect of Schiff base and their complexes may also be inspected by the aid of interested researcher form the biology department.

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ملخص باللغة العربية

ملخص باللغة العربية

شهد العقدين السابقين اهتمام كثير من الدراسات السابقة بدراسة كيمياء قواعد شيف و معقداتها لما لها من تطبيقات مختلفة وهامة و خاصة في المجالات البيلوجية والطبية السريرية ولذلك استخدمت كمضادات للبكتريا والفيروسات والفطريات و الأورام الخبيثة. وأوضحت بعض الدراسات أن بعض الأدوية ذات التراكيب العضوية تزداد فاعليتها أكثر عند اتحادها مع عناصر فلزية. وتمثل قواعد شيف سلاسل مختلفة من المرتبطات وذلك لسهولة تحضيرها وحساسيتها العالية نحو الذرة المركزية. وتهتم هذه الدراسة بتحضير أربعة من قواعد شيف تحتوي على أربعة مواضع منح من نوع 2N2O المشتقة من تفاعل تكاثف مركبات أمنية أولية ثنائية. {اروماتية اواليفاتية} مع مركبات كيتونية. وهي

Ethylenediamine, o-phenylenediamine, 1,6-hexanediamine. Benzoylacetone, and Benzoin.

واستخدمت هذه المركبات لاحقا للحصول على خمسة عشر معقد ذلك بتفاعل هذه المركبات مع مجموعة من العناصر الانتقالية ثنائية التكافؤ وهي

Co (II), Ni (II) and Cu (II).

وتهدف هذه الدراسة محاولة التعرف على الشكل الهندسي لخمسة عشر معقد وذلك عن طريق إجراء التحاليل الأزمة عليها وهي

Elemental analysis, Thermal analysis, Melting point Conductivity measurement, Magnetic moment measurements, Infrared spectra, Electronic spectra.

وبمناقشة نتائج هذه التحاليل ومقارنتها مع بعض الدراسات السابقة أمكن التوصل إلى الشكل الهندسي الافتراضي لهذه المركبات.

وتم تقسيم هذا البحث إلي ثلاثة فصول رئيسية وهي

الفصل الأول

تناول هذا الفصل الدراسات السابقة التي تناولت الموضوع ومقدمة عامة عن أهم طرق تحضير قواعد شيف ومعقدتها واهم تطبيقاتها البيلوجية و الكيميائية واستخدامها كمرتبطات مع العناصر الانتقالية للحصول منها على العديد من المعقدات الهامة.

الفصل الثاني

تناول الفصل الثاني من هذا البحث تحضير قواعد شيف ومعقداتها واهم الطرق التي استخدمت في هذا المجال حيث تم استخدام طريقتين للحصول على المعقدات الناتجة في الطور السائل وفي الطور الصلب وأضيفت المواد المتفاعلة بنسب متساوية مرة وأخرى بنسب مختلفة وذلك للحصول على نوعين من المعقدات أحادية وثنائية الذرة المركزية.وتم أيضا عرض أهم التحاليل التي أجريت على هذه المركبات و معقداتها.

الفصل الثالث

في هذا الفصل تم مناقشة نتائج التحاليل المختلفة المتحصل عليها ودراستها ومقارنتها مع بعض الدراسات السابقة وذلك للتوصل الى الشكل الهندسي لهذه المعقدات. وبنا على تلك التحاليل ومن خلال تلك النتائج المتحصل عليها استنتج أنه أمكن الحصول على ليجند جديدة اشتقت من تفاعل اورثوفنيلين داي امين مع البنزوين والحصول منها على ثلاث معقدات. أيضا تم الحصول على معقدات أحادية وثنائية الذرة المركزية. يتوقع الباحث أن لهذه المعقدات خواص بيلوجية لذلك يأمل أجرا عليها بعض الاختبارات البيلوجية في المستقبل.

لجماهيرية العربية الليبية الشعبية الاشتراكية العظمى
جامعة التحدي
التاريخ ....
الموافق: 26/12/2006 ف

ان الدراسة ليست غاية في حد ذاتها
و انما الغاية هي خلق الانسان النموذجي الجديد

G. S. P. L. A. J.
AL_TAHDI UNIVERSITY
الرقم الإشاري: لع.ى.ع.9.2006ف

كلية العلوم

قسم الكيمياء

عنوان البحث

تخليق وتمييز بعض معقدات العناصر الإنتقالية (II) M مع قواعد شيف

سرت / ليبيا

مقدمة من الطالب

أبوبكر عبد النبي الهادي

لجنة المناقشة : **التوقيع**

الدكتور / عبد الحكيم أبو القاسم أحمد. **(مشرف الرسالة)**

الدكتور / عبد الرحيم عبد الحميد بن عوشه. **(ممتحن خارجي)**

الدكتور / حسن عمرون عويس. **(ممتحن داخلي)**

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جامعة التحدي – كلية العلوم

قسم الكيمياء

سرت – ليبيا

تخليق وتمييز بعض معقدات العناصر الانتقالية
M(II) مع قواعد شيف

بحث مقدم كجزء من متطلبات استكمال درجة الماجستير في علم الكيمياء

إعداد

أبو بكر عبد النبي الهادي محمد

تحت إشراف

الدكتور: عبد الحكيم أبو القاسم احمد

2006 - 2005