PHYSICOCHEMICAL STUDIES ON MACROCYCLIC CHELATES OF Cu (II) AND Ni (II)

A Graduate Project Presented to
the School of Graduate Studies
Addis Ababa University

In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemistry

By

Adelew Estifanos

July 2006

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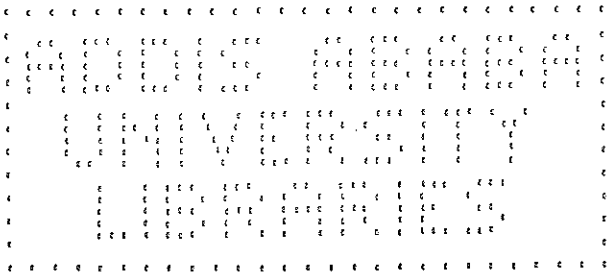


Abstract

Physicochemical studies on macrocyclic chelates of Cu (II) & Ni (II)

By Adelew Estifanos

Advisors 1. Prof. V. J. T. Raju

2. Dr. Yonas Chebude

A new macrocyclic ligand (L) and its metal complexes formulated as [$MLCl_kA$] Cl_y (M = Cu (II), Ni(II) L= Tz – ACAC - 20 & A = non chelating ligand) have been synthesized by template condensation and high dilution techniques from 4- Hydroxy- 2, 6- Bis(hydrazino)- s- triazine (HBHTz), acetylacetone and the metal chlorides.

The HBHTz was synthesized from 4- Hydroxy- 2,6- dichloro- s- triazine (DCHTz) which in turn synthesized from cyanuric chloride and phenol / NaOH mixture.

Tz – ACAC - 20 shows low affinity for nickel (II) especially under the direct (high dilution) synthesis, which can be ascribed to incompatible cavity size.

The prepared complexes were characterized by solution electronic spectra, magnetic moments, solution conductance measurements, atomic absorption spectroscopy, elemental análysis, NMR and IR spectroscopies.

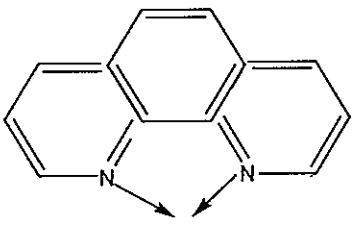
The electrical conductivity of the Ni (II) chelate indicated it to be 1: 2 electrolyte and that of Cu (II) complex to be a non electrolyte. Magnetic susceptibilities, conductance measurements & spectroscopic evidences suggest that copper complex to show an octahedral geometry whereas the Ni (II) complex to have a tetrahedral structure.

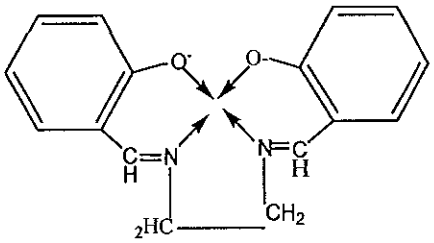
Introduction

1 .1. Chelating Ligands

Ligands can be **monodentate** (with only one donor atom) ,**polydentate or multidentate or chelating** (with more than one donor atoms) , **bridging** (that can donate more than one pair of electrons simultanously),**ambidentate**(that can attach to the central atom in two places but not both,like CN^-,which can attach at either the carbon atom or the nitrogen) ,**macrocyclic**(large ring compound with several donor atoms that can bind a Lewis acid inside the ring) ,**pi donor** (that donates electrons from a pi bond to a metal ion), they can also be sigma only or sigma and pi-interacting entities, etc[**1, 2**]

Chelating / Polydentate / ligands are an important class of ligands in complex formation that have been studied extensively. Chelating ligands are able to bind to the metal ion through multiple sites as they have free lone pairs on more than one atom. Complexes of polydentate/chelating / ligands (chelates) tend to be more stable than those of monodentatete ligand complexes as it is necessary to break all of the bonds to the central atom for displacing the ligand [**1**] .





1, 10 –phenanthroline ,phen
(A bidentate ligand)

Dianion of bis(salicylidine) ethylene diimine,salen
(a quadridentate ligand) [**2**]

Fig 1. Typical examples of chelating ligands

Many properties of chelates are determined by the nature of the chelating ligand /chelating agent / which combines with the metal ion. Thus, the size of the ring, the number of rings formed with a given metal ion, and stabilizing or interfering resonance interactions are govern the structure of the chelate.

1. 2. Chelation

Chelation (from Greek *chele*, meaning claw) is the process of reversible binding of a ligand, the chelant , chelator or chelating agent ,to a metal ion, forming a metal complex , the chelate [**2**] .

Since chelation is merely a special type of complex formation, many effects due to chelation are analogous to effects due to simple complexing [**3**].

The color of an ion may deepen, fade or change upon chelation ; a precipitating agent may dissolve when a chelating agent is added; the stability of an oxidation state of the metal ion may be appreciably altered ; or the PH of a solution of a chelating agent in water may drop when a metal ion is added (just as the PH of aqueous HCN drops when $AgNO_3$ is added ,since the formation of $Ag(CN)_2^-$ releases H^+ ions) [**4, 5**].

A typical chelate can be formed by treating aqueous $CuSO_4$ with ethylene diamine , $NH_2CH_2CH_2NH_2$. This complex is similar in appearance to the $Cu(NH_3)_4^{+2}$ complex and somewhat more stable [**3, 4**].

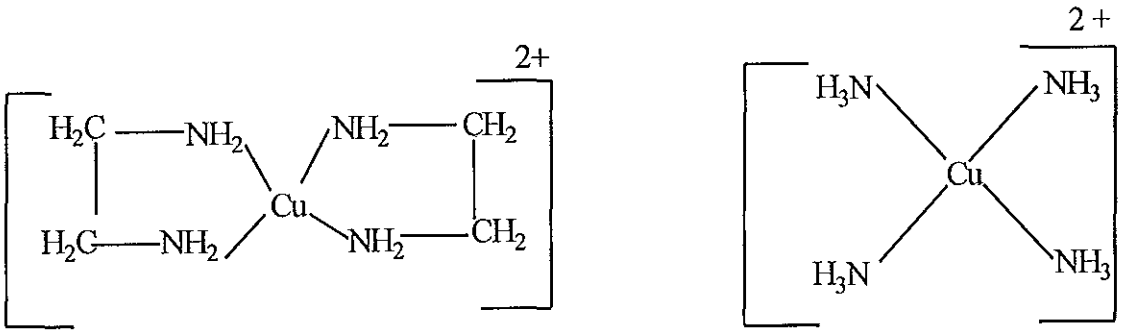


Fig. 2. Structures of Cu $(NH_2CH_2CH_2NH_2)_2^{+2}$ and Cu $(NH_3)_4^{+2}$ complexes

It has been observed that treatment of ammonia complex with ethylene diamine results in the displacement of the ammonia like

$$Co(NH_3)_6^{3+} + 3en \longrightarrow Co(en)_3^{3+} + 6\,NH_3 \quad [\,4\,]$$

The driving force of such a replacement is probably the entropy change. The equation above has four particles on the left hand side and seven on the right, so that the reaction proceeds with increase in entropy [**4, 5**].

1. 3. Macrocyclic Ligands

Macrocyclic ligands are special types of chelating agents. Coordination chemists define a macrocyclic ligand as a cyclic molecule with three or more potential donor atoms in a ring of at least nine atoms. These donor atoms are usually positioned that up on coordination preferably five or six membered chelate rings are formed with the metal ion[7].

The macrocyclic cavity size is deterimined by the number of atoms in the macrocyclic ring. The cavity is also affected by the backbone rigidity, and by the nature and hybridization of the donor atoms [5].

Macrocyclic molecules are more stable than those with unidentate ligands of similar strength (or similar donor atoms) [7]

A macrocycle has donor atoms arranged in more fixed positions and thus there is less of an entropic effect in the binding energy of macrocycles than monodentate or bidentate ligands with an equal number of donor atoms **[8, 9]**.

Based on donor atoms type , macrocyclic ligands may be classified as aza(N-donors), oxa(O-donors) , phospha(P –donors) , thia(S- donors), arsa(As- donors), and mixed donors **[10,11**].

Schiff base macrocycles – the corner stone macrocycles to the growth of supramolecular chemistry [12, 13,14]

Macrocycles containing Schiff base linkages have provided the corner stones upon which supramolecular chemistry has been built (Fig. 2) .The earliest example of a synthetic macrocyclic ligand containing an imine linkage stems was from the work of curtis and was derived from the mixed aldol condensation of acetone with nickel (II) ethylenediamine complexes. In 1964 Curry and Busch reported the iron (II) – templated condensation of 2, 6- diacetylpyridine with triethylenetetraamine to give iron (III) complexes of a pentaazadiimino macrocycle, Jager showed that the reaction of β- ketoiminato complexes with 1,2-diminoethane gave metal complexes of a tetraazadiimino macrocycle. In all of the examples the product was recovered as a metal complex and no macrocycle was obtained in the absence of a metal ion. The requirement for a metal to be present in the reaction forming the macrocycle became known as the template effect.

The fourth corner stone was added by Pedersen with his discovery of the cyclic , or 'crown', polyethers.

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

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BY

ADELEW ESTIFANOS

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE

Approved by the Examining Board:

Prof. V. J. T. Raju _____

Dr. Yonas Chebude _____

Dedicated to my child Amanuel Adelew

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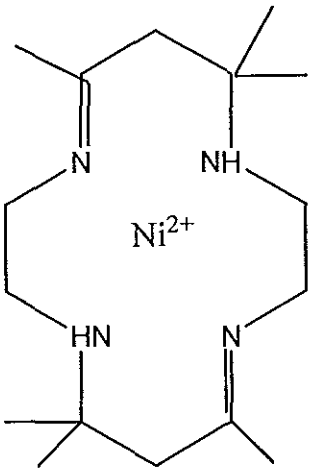
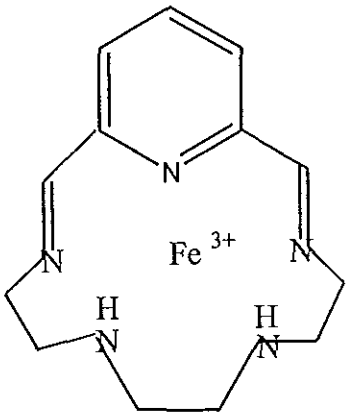


A. Curtis



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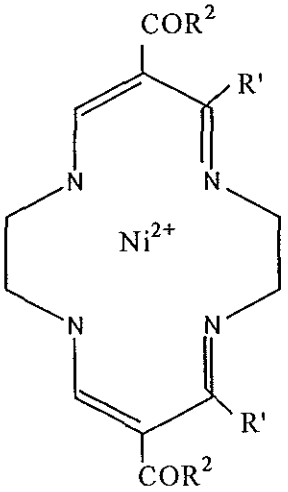
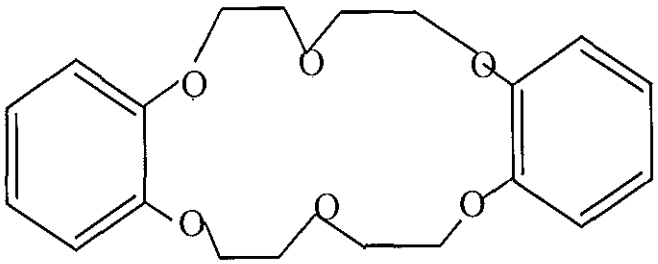


C. Jager



D. Pedersen

Fig.3. The cornerstone macrocycles [14]

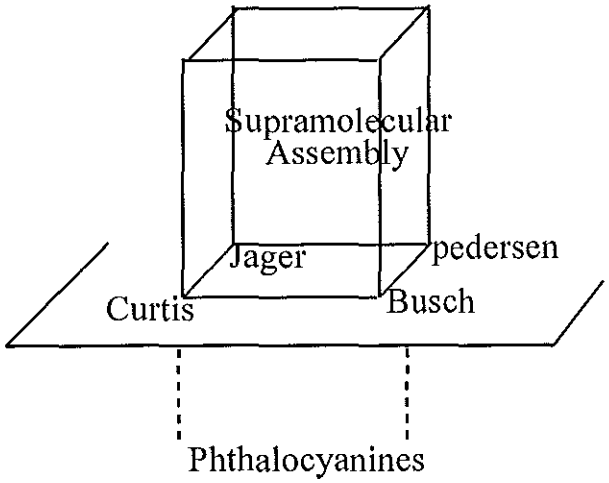


Fig. 4. The growth of supramolecular chemistry [**14**].

1. 3. 1 Macrocyclic effect

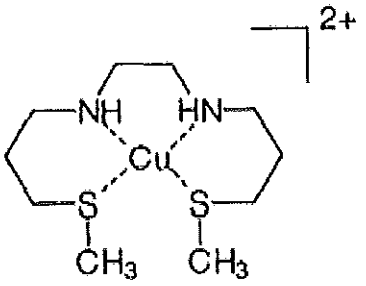
The increased thermodynamic and kinetic stability of macrocyclic complexes over their linear analogs having the same number of chelate rings is known as the macrocyclic effect **[8]**. The kinetic macrocyclic effect refers to the slow kinetics of dissociation of macrocyclic compounds as compared to the open chain analogs .It is the rate at which demetallation of the complex occurs [9]. The macrocyclic effect in essence is a specific case of the chelation effect. A macrocyclic chelating ligand forms more stable complexes than a noncyclic chelating ligand having the same number and type of donor atoms. Additional stability of the macrocyclic system is usually considerably greater than would occur for the presence of an additional chelate ring [**1 ,8**]

Stability follows the order:

Macrocyclic chelator > non cyclic (multidentate)chelator > monodentate (non chelator) [**1**]

The origins of the macrocyclic effect have engenedered much debate for individual systems .It is variable from system to system [**8**] .

For example, the changes in stability constants for Cu (II) complexes are different for the different systems [9].



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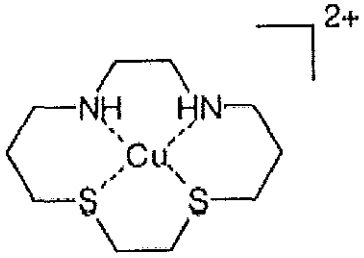
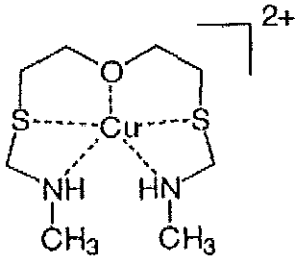
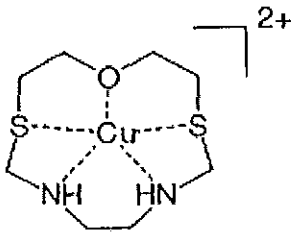


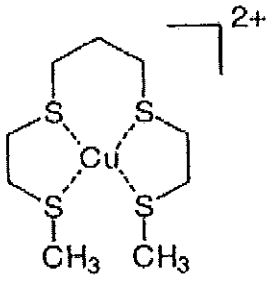
log K_{ML} = 16.0



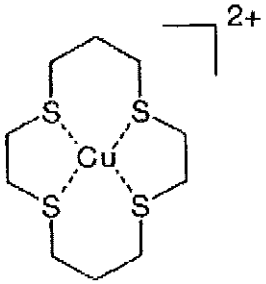
log K_{ML} = 9.2



log K_{ML} = 13.3



log K_{ML} = 9.2



log K_{ML} = 13.3

Scheme 2. Changes in stability constants for Cu (II) complexes from system to system

In the simplest situation, one may compare the formation of an open chain ligand complex and its cyclic analogue: M +L ⟶ ML (k_f)

For both ligand types the above process should be facile, although formation of the cyclic complex is expected to be somewhat slower.

However, the dissociation of the metal from the macrocyclic complex (considered to be first order) is likely to be much slower than for the open –chain analogue which can unwrap one bond at a time, for example in a series of SN_1 steps:

$ML \xrightarrow{Kd} M + L$

At equilibrium : $M + L \underset{K_f}{\overset{K_d}{\rightleftharpoons}} ML$, $K = Kf/Kd$

Hence, for the macrocyclic complex case Kd will be smaller and K will be enhanced.

Thus, the macrocyclic effect states that complexes of macrocyclic ligands are more stable than those with polydentate ligands of similar strength (or similar donor atoms),

The same can be said for multicyclic macrocycles or cryptases, being stronger complexing agents (a cryptase effect).

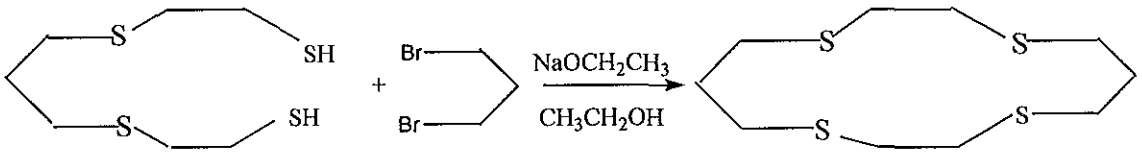
1. 3. 2 synthesis of macrocyclic ligands [13, 15, 16]

Macrocyclic ligands are generally synthesized from smaller usually linear molecules. To create a ring,either an intermolecular reaction ,where two or more molecules come together in a reaction to form a ring, or an intramolecular reaction where one molecule reacts with it self to form a ring , must occur.

Usually the following general methods are used in the preparation of macrocycles.

A. High dilution (direct) method, in which the ring closure is achieved under conditions of high dilution, high temperature and inert atmosphere.

High dilution (large amount of solvent and low concentration) favors self-condensation over linear polymerization; special procedures are developed for such reactions like slow addition of reagents to large reaction volumes using motor driven burettes. An example of such a method is given in scheme 3.



Scheme 3. Synthesis by the direct method.

Reactions may have to be performed over a long period of time (days) to ensure reasonable yields of desired products.

The concentration of unreacted reagent is kept low through out the reaction. This enhances the chance that a half cyclized products to condense with in themselves to give a fully cyclized product. Otherwise, the half cyclized products will react with more reactants to give oligomeric products [**9, 10**].

Conventional organic reactions, which are not dependent on metal ion are made to occur by the direct method.

B. The metal template (insitu) method

In this technique, the reaction takes place in the presence of metal ion, which acts as a template.

A metal ion can act as a collector of ligands as well as promoter of ligand reactivity by means of chelation and polarization effects [**6, 8**].

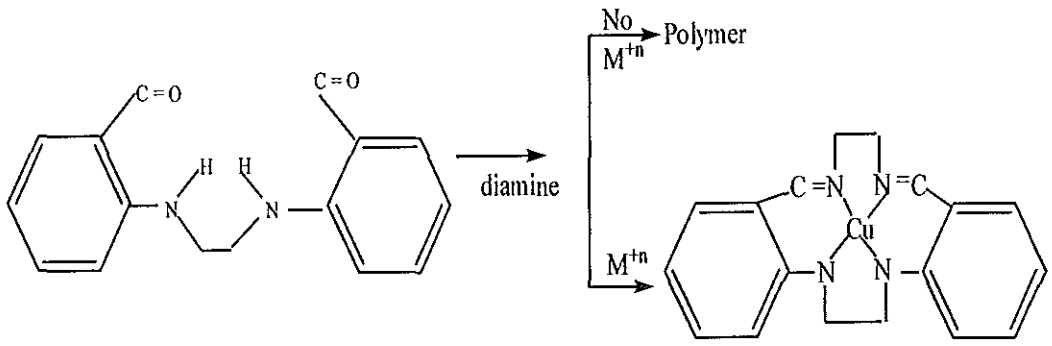
Particularly transition metal ions, with their ability to gather and dispose of ligands in a given predictable geometry can induce a " template effect "

By binding to the linear molecule, to influence its geometry, a metal "template" can accelerate either the intra molecular or the intermolecular reaction.

Thus the judious choice of a metal ion and the relative locations of donor atoms would allow a metal to control the cyclization process [**8**].

The metal template method is used to:

1. Promote nucleophilic substitution reactions on coordinated ligands, protection of coordinated ligand from side reactions and induction of strain within coordinated ligands in strain releasing reaction [**10, 11**].
2. Provide an appropriate stereochemical requirements at a collecting point for reactants, bring them into closed proximity and enhance the chance of the desired reaction to occur.



Scheme 4. Template synthesis [5]

The aim of both template and direct synthesis is to maximize yields by choosing strategies, which **inhibit the formation of competing linear polymerization reactions.**

1.3.3. Applications of macrocyclic ligands

Removal of heavy metals from aqueous solution for water purification, chelation therapy where by the use of chelating agents such as EDTA to remove heavy metals from the body, molecular switches and linear motors for constructing artificial nanoscale machinery (rotaxanes), chemical sensors, mimicry of cellular receptors , molecular recognition (recognition of peptides , small molecules) and organic light emitting diodes (OLEDS), etc. [**10**]

Historically,phthalocyanine (A porphyrin analogue) is arguably the most useful, in uses as dyes and pigments since their discovery in 1928, due to their dark blue color.

Biological macrocycles like heme, the active site in hemoglobin (the protein in blood transports oxygen) is a porphyrin containing iron.

Chlorophyll, the green photosynthetic pigment found in plants contains a chlorin ring, vitamin B_{12} contains a corrin ring.

1. 4. Characteristics of Ni (II) and Cu (II) complexes

4 .1. Ni (II) complexes

Ni (II) is the d^8 ion and is able to form stable square planar complexes as well as octahedral ones.Tetrahedral complexes are also widely observed. Ligands with large crystal field favor square planar coordination, because of the more favorable CFSE [**2, 16, 17**].

Octahedral complexes of Ni (II) involve $sp^3dx^2\text{-}y^2dz^2$ hybridization & paramagnetism from 2 unpaired electrons. They are obtained often from aqueous solution by replacement of coordinated water especially

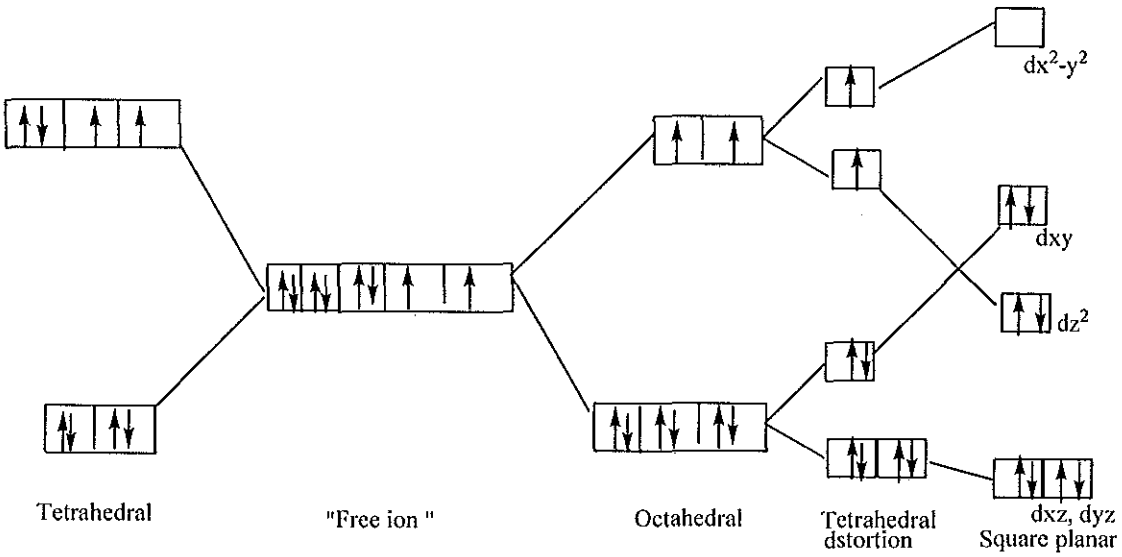


Fig. 6. The splitting of d orbitals in fields of different symmetries, and the resulting electronic configurations of the Ni (II) d^8 ion [**2**].

Providing therefore that the ligand field of sufficiently low symmetry (or sufficiently strong) to split the d orbitals enough to off set the energy required to pair up 2 electrons, then the four coordinate, square planar extreme can be energetically preferable not only to the tetrahedral but also to the 6- coordinate octahedral extreme [**12**].

Some structures are complicated by interconversions between square planar and tetrahedral, or square planar and octahedral coordination.

The salicylaldimato complexes provide such examples of all the three stereochemistries .

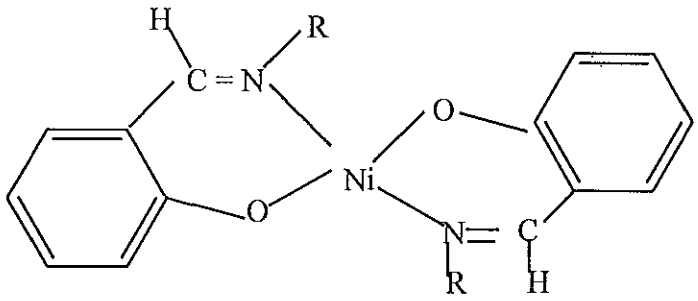


Fig. 7. Bis-(N-alkyl salicyl aldimato) nickel (II) complexes

When R= methyl or **iso butyl** ,the complex is **square planar** and when R= **isopropyl** , it is **tetrahedral** .

If the diamagnetic square planar complex is dissolved in pyridine, it becomes paramagnetic with the moment expected for an octahedral complex, and an octahedral dipyridine derivative may be isolated [**11**].

In addition, the potential of some ligands to bridge between metal centers may cause ambiguity.

Electronic spectra and magnetic properties of complexes of Ni (II) [2, 19]

Ni(II) is the only common d^8 ion and its spectroscopic and magnetic properties have accordingly been extensively studied .

A. Spectroscopic properties

In an octahedral field the splitting is the same as for the octahedral d^3ion and the same energy level diagram can be used to interpret the spectra as used for octahedral Cr^{III}. Spectra of octahedral Ni(II) usually do consist of three bands which are accordingly assigned as

$\nu_1 = {}^3T_{2g}(F) \longleftarrow {}^3A_2g = 10DQ$

$\nu_2 = {}^3T_{1g}(F) \longleftarrow {}^3A_{2g}$

$\nu_3 = {}^3T_{1g}(P) \longleftarrow {}^3A_{2g}$

Quite often there is also evidence of weak spin forbidden (i.e spin triplet ~~-sing~~let) absorptions and , in $[\ Ni(H_2O)_6\ ]^{2+}$ and $[\ Ni\ (dmso\ )_6\ ]^{2+}$,for instance , the ν_2 absorptions has a strong shoulder on it . This is ascribed to a transition to the spin singlet ^1Eg which occurs when the $^3T_1$ g (p) & $^3T_1$ g (F) terms are in close proximity.

For d^8 ions in tetrahedral fields the splitting of the free ion ground term is the inverse of its splitting in an octahedral field, so that ^3T_1g (F) lies lowest. In this case three relatively intense bands are to be expected, arising from the transitions:

$\upsilon_1 = {}^3T_2\ (F) \longleftarrow {}^3T_1(F)$: $\upsilon_2 = {}^3A_2\ (F\ ) \longleftarrow {}^3T_1\ (F)$

$\upsilon_3 = {}^3T_1(P) \longleftarrow {}^3T_1(F)$

Tetrahedral complexes of Ni (II) are characteristically intensely blue to a relatively intense absorption in the end of the spectrum. These intense spectral lines distinguish tetrahedral nickel (II) from octahedral complexes, where the absorptions are relatively weak.

The spectra of square planar d^8 complexes are usually characterized by a fairly strong band in the yellow to blue region (i.e about 600- 450nm) which is responsible for the reddish color, and another band near the ultra violet.

B. Magnetic properties [2, 4 ,21]

Magnetic moments of octahedral Ni(II) complexes are usually close to the spin-only value of 2.83 μBM .In contrast, tetrahedral complexes posses magnetic moments ≈ 4μBM due to orbital contributions, and square planar complexes such as Ni $(CN)_4^{2-}$ are diamagnetic[**5,6**].

1. 4. 2. Copper (II) complexes

Copper (II) is the most studied of all the transition metal ions . For example , in july 2003 the combined number of Cu(II) compounds on the inorganic structure data base , and the Cambridge crystallographic data base , was 13604. This is 66% more than the Ni(II) which has 8182 compounds [**22**]. Quite apart from the biological or technological relevance of Cu (II) compounds, the attractions of Cu (II) to inorganic chemistry researchers are easy to understand, given the user friendliness of Cu (II) compounds. These are commonly air – and moisture stable have informative and easy to obtain UV /Vis and EPR spectroscopic signatures, and often under go reactions in solution effectively with in time of mixing [22]. The stereochemical flexibly of Cu (II) compounds also means that they adopt a wider range of coordination geometries than any other transition metal ion[**2,14**] .

The most common coordination numbers of Cu (II) are 4, 5, and 6, but regular geometries are rare and the distinction between square planar and tetragonally distorted octahedral coordination is generally not easily made. This is due to the Jahn-Teller effect arising from the e_g pair of orbitals (dz^2 and dx^2-y^2) when a d^9 ion is subjected to an octahedral crystal field. Occasionally, this results in a compression of the octahedron, i.e " 2 + 4 " coordination (2 short and 4 long bonds)[2].

The usual result, how ever, is an elongation of the octahedron i.e " 4+2 " coordination (4 short and 2 long bonds) , as is expected if the metal's dz^2 orbital is filled and its dx^2-y^2 half filled . In its most extreme form this is equivalent to the complete loss of the axial ligands leaving a square planar complex [**15**].

Elongation has the further consequence that the fifth and sixth stepwise stability constants are invariably much smaller than the first 4 for Cu(II) complexes[**2, 9**]. For instance , mixed complexes of water and ammonia are found up to $[Cu(H_2O)_2(NH_3)_4]^{2+}$, but replacement of the last two water molecules is impossible in aqueous solution and $Cu(NH_3)^{2+}_6$ can only be prepared in liquid ammonia .

Likewise,chelating N-donor ligands like en, bipy and phen show a reluctance to form triscomplxes like $Cu(H_2O)_4\ en^{2+}$ and $Cu(H_2O)_2\ en^{2+}{}_2$ [**2, 22**].

The macrocyclic N-donor, phthalocyanine, forms a square planar complex and substituted derivatives are used to produce a range of blue to green pigments which are thermally stable to over 500^0c , and are widely used in inks , paints and plastics [**16**].

Cu(II) also forms stable complexes with O-donor ligands . In addition to the hexaaquaion , the square planar β-diketonates such as [$Cu(acac)_2$] (which can be precipitated from aqueous solution and recrystallized from non-aqueous solvents) are well known, and tartarate complexes are used in Fehling's test[**16 ,17**].

A practical application of N-, O –donors of Cu(II) is the biuret test for peptides and proteins . Compounds containing peptide linkages form a violet complex when reacted in solution with a few drops of aqueous $CuSO_4$ [**10, 16**] .

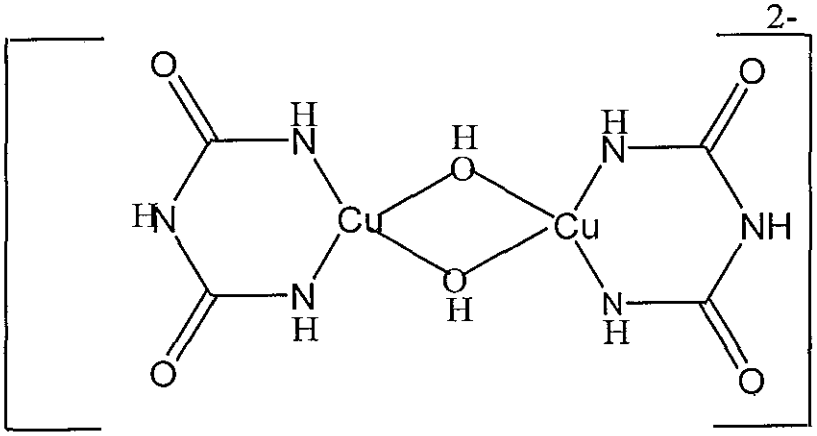


Fig 8. Binuclear copper complex formed in biuret test .

When a Cu (II) salt is treated with excess KCN at room temp., cyanogen is evolved and the copper reduced [**2**] .

$2\ Cu^{2+} + 4\ [\ CN^-\ ] \longrightarrow 2\ CuCN\ (s\ ) + C_2N_2$

Electronic spectra and magnetic properties of copper (II)

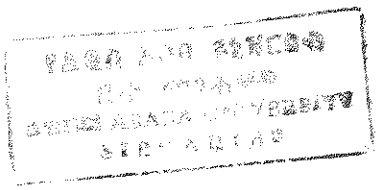
The d^9 configuration can be thought as an inversion of d^1. Thus relatively simple spectra might be expected. It is indeed true that the great majority of Cu(II) compounds are blue or green because of a

single broad band in the region 11000- 16000 cm^{-1} . How ever, as already noted, the d^9 ion is characterized by large distortions from octahedral symmetry and the band is unsymmetrical, being the result of a number of transitions which are by no means easy to assign unambiguously [**15, 14**].

The free ion ^2D ground term is expected to split in a crystal field in the same way as the ^5D term of the ^4D ion and a similar interpretation of the spectra is likewise expected.

Unfortunately this is now more difficult because of the greater overlapping of bands that occurs in the case of Cu (II).

The T ground term of the tetrahedrally coordinated ion implies an orbital contribution to the magnetic moment, and there fore a value in excess of μspin-only (1. 73BM). But the E ground term of the octahedrally coordinated ion is also expected to yield a moment [μe = μspin-only $(1 - 2\lambda)/10DQ$] in excess of 1.73BM, because of " mixing " of the excited T term in to the ground term , and the high value of λ (-850 cm^{-1}) makes the effect significant. In practice, moments of magnetically dilute compounds are in the range 1.9 – 2.2BM, with cpds whose geometry approaches octahedral having moments at the lower end,and those with geometries approaching tetrahedral having moments at the higher end, but their measurements cannot be used diagnostically with safety unless supported by other evidence.



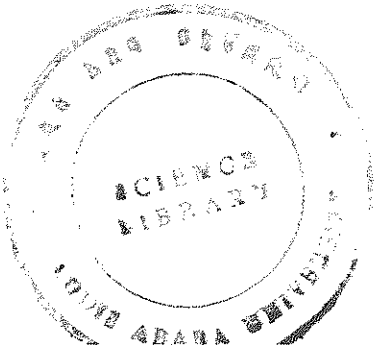
5. Literature review

Nature has exploited macrocycles – porphyrins and related systems –for an aeon but man has only used them in this century [**14**].

Until the 1960's only pthalocyanines and various isolated compounds such as 1, 4, 8, 11-tetraazacylodecane (cyclam) and the polyethers were available. The early 1960's saw the advent of a range of polyazamacrocyclic ligands, formed by metal template procedures and of Pedersen's crown ethers. These discoveries of macrocycles and their metal complexes provided the corner stone upon which supra molecular chemistry has been built [**14, 19**].

Since Pedersen reported the synthesis and cation – complexing properties of crown ethers, there has been a growing interest in macrocyclic compounds as complexing agents for neutral organic substrates, inorganic and organic cations [19].

Macrocyclic complexes have attracted considerable attention from a wide range of organic, biological, and medicinal chemistry [**23, 24 , 25, 26**] .



Applications include a wide range such as metal ion transport, catalysis of ester hydrolysis, enzyme modeling, detoxification, etc [**16, 17**].

Macrocyclic ligands are considerably attractive in the quest for new chemistry, not least because they can offer a wide varity of donor atom types, ligand charges, coordination numbers, and resultant complex geometries. Macrocyclic complexes can also exhibit enhanced stability in comparison with those of unidentate ligands.

Owining to the presence of a central cavity, macrocyclic ligands have long been employed as selective hosts for a wide range of guest molecules [**18**].

There is a learning process from nature and an opportunity to adopt the knowledge retrieved to the generation of new chemistry and potential catalysts based on metalloenzyme processes[**13, 19**] .

However, studies on the geometry around the metal center by electronic spectra and magnetic properties of the metal ions present in the active site of metallo- biomolecules are rather difficult owing to the fact that metal ions in active sites are embedded in protein polymer back bone[**19, 20**].Hence, design and synthesis of model transition metal complexes that mimic the physical properties of the active site present in the metallobiomolecules are very essential [**13, 16**].

The objective of this paper is thus to study the physicochemical characteristics of macrocyclic chelates of the two penultimate first row transition elements, Ni (II) & Cu (II) composed of schiff base ligand systems. Such study may probably contribute to the modeling (mimicking) of nature's macrocyclic chelates like metalloenzymes.

Schiff base ligand systems; Schiff bases are compounds containing an imino or methine group (R-C = N-) and are usually formed by the condensation of a primary amine with an active carbonyl compound. They are important intermediates in many chemical and enzymatic reactions, and for this reason the control of their formation & subsequent reactions by the metal ions is particular interest **[17, 19].**

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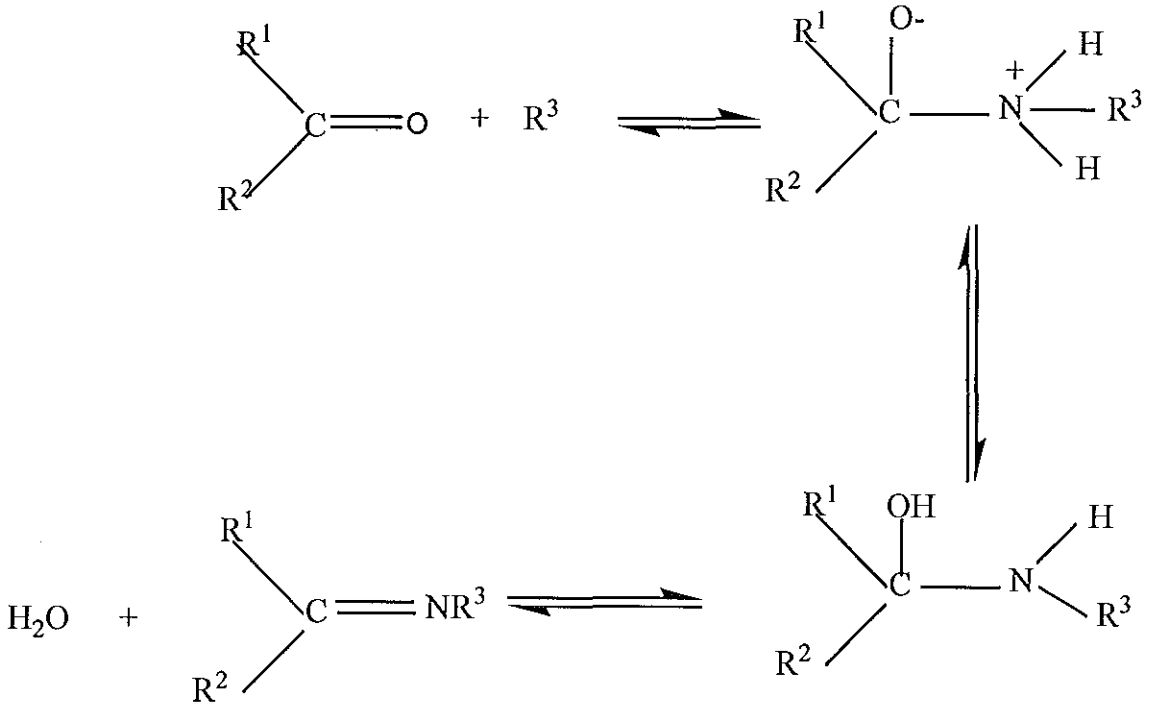


Scheme 5. **Schiff base reaction [17, 19]**

As the free ligands are not always stable the presence of metal in the reaction forming the macrocycle is important.

The extent of Schiff base formation can be controlled by choosing the described carbonyl and amine components.

4-Hydroxy- 2, 6-Bis (hydrazino)-s –triazine/ HBHTz /, synthesized in this lab. was allowed to react with acetylacetone for the macrocyclic formation. The macrocylic ligand is then treated with the metal salts to the formation of chelate compounds.Chelate formation is accomplished both by template (metal assemby) & direct method.

A. Scope of the present investigation

Literature survey reveals that chelates of macrocyclic ligands have wide range of applications.

A variety of new macrocyclics are yet to be investigated for structural studies and applications. HBHTz has been reported to behave as bidentate nitrogen donor and a number of schiff bases derived from HBHTz produce di – or mononuclear complexes[**13**].

In view of symmetric spread of chelating sequences, HBHTz is choosen for developing macrocyclic system of desired properties. It is proposed that amine groups on the HBHTz molecules can be condensed with compounds having dicarbonyl groups such as acetylacetone to generate a macrocycle with azomethine system. This condensation can be effected in the presence/ template / or absence/ direct / of the metal ions. Such procedures are well documented in literature[**6**]. The starting materials like HBHTz will be synthesized from known procedures. Macrocyclic chelates of Ni (II) & Cu (II) will be synthesized.

The products formed will be characterized on the basis of analytical (C, H, Cl, metals), thermal (melting point), spectral (NMR, IR, UV-Vis, AAS), conductance and magnetic susceptibility studies.

2. Experimental

2.1. Methods & Materials

Melting points of the starting materials and complexes were recorded using IA 9200 digital melting point apparatus. The complexes were analysed for C, N and H.

Elemental analysis for C.H, and N was carried out by Exter Analytical CE 440 EA Elemental analyzer (CE instruments), and metal analysis was carried out using Buck scientific 210 VGP atomic absorption spectrometer.

Chlorine was estimated as AgCl by titration using silver nitrate and also by gravimetric estimation of AgCl. Magnetic moments (μ) deterimined from mass susceptibility (x) measured using MSB Auto, Sherwood.

Infrared (IR) spectra were recorded using PerkinElmer spectrum BX (400- 4000cm^{-1}) KBr as reference.

Nuclear magnetic Resonance (NMR) spectra were obtained using BRUCKER ARX 400, TMS reference.

UV- VIS spectra were obtained using optical Absorption perkin Elmer (λ19) Uv/vis NIR spectrometer,in the range of 200 to 1100 nm,in methanol/ chloroform media..

Conductivity measurements were carried out using Digital Multimeter.

2.2. Chemicals

Chemicals used in this research work were cyanuric chloride , hydrated hydrazine (66.7%) solution, phenol , NaOH, HNO_3 (65%) from Riedel- deHean

The solvents were dichloromethane, acetonitrile, n-Hexane, chloroform, ethanol,DMSO and DMF also from Riedel-deheHean.

All were of analar grade and were used as received.

2.3. Analytical procedures

Chloride estimation

To 50mg of the complex, 10ml of conc. HNO_3 was added and carefully heated almost to dryness on a low flame, to completely decompose the complex. The resulting mass was dissolved in distilled water to make 50ml solution. To the clear solution, 0.1N silver nitrate was added slowly with constant stirring. White precipitate of AgCl was formed which was heated for coagulation, the precipitate was allowed to settle and filtered through a sintered glass crucible. It was washed with 0.01N HNO_3 and dried at 110^0c to a constant weight.

Metal estimation

Each metal complex solution (app.5x 10^{-4} M) was prepared by digesting the complex in 2ml of HNO_3 until no precipitate (solid) remains during dissolution .The solution was further refluxed for 30 minutes to get complete decomposition of the complexes into the free metal & the organic materials.
For sample analysis, four series of working standared metal solutions (in optimum concentration range) were prepareds by appropriate dilution of the metal stock solutions with water. After manipulating the instrumental operation procedure, calibration graph (concentration versus absorbance) for each metal element using the prepared standared was obtained.

The percentage of the metals in the complexes were determined using the relation

$$M(II)\% = \text{Concentration(ppm)} \times \frac{\text{Volume diluted to}}{\text{Mass of the sample}} \times 100$$

Magnetic susceptibility (χ)

Magnetic moments (μ) were calculated from mass susceptibility (χ) using the relation

$\mu corr.eff = 2.84 (\chi'_M T)^{1/2}$, $\chi'_M = \chi_M + \chi_M^{corr.}$, $\chi_M^{corr.}$ = diamagnetic correction.

Coductivity measurement

25ml of 1mmolar solution of each complex and metal salts (for comparison purposes) were prepared in the appropriate solvent. The conductance of each sample was deterimined using the digital multimeter. The reading was obtained interms of the microsiemens (m/S).

2. 4. Synthesis

2. 3. 1. Synthesis of the ligands

2.3. 1a. Synthesis of 4-Hydroxy- 2, 6- dichloro – s - triazine(DCHTz) [21, 27]

A suspension of cyanuric chloriode (0.75 gm, 4. 06mmol) in 40 ml dichloromethane placed in a 250ml round bottom flask equipped with a magnetic stirrer was cooled in an ice bath. A solution of phenol (0.3821gm, 4.067mmol) and sodium hydroxide (0.163gm, 4.067mmol) in 20ml of H_2O was added dropwise to the suspension over a period of 10 minutes, keeping the temprature at about 5^0c. The reaction mixture was then stirred for 3hrs in the cooled water bath. The nondissolved particles were removed by filtration, followed by separation of the organic phase. The organic phase was washed with dilute sodium hydroxide solution and the solvent was removed by rotary evaporater . The white crude product obtained was dried over $CaCl_2$, recrystallized from n-hexane /chloroform(4: 1) yielded 0.65gm (66.06 %) of pure product (melting point = 110^0C- 112^0C)

2. 3. 1b. Synthesis of 4-Hydroxy- 2, 6- bis(hydrazino)- s-triazine/HBHTz /

0.9gm (3.72mmol) of 4-Hydroxy- 2, 6- dichloro- s- triazine(DCHTz) was dissolved in 50ml of ethanol in a 250 ml round bottom flask.To this solution , a solution of hydrated hydrazine (0.186gm, 3.72 mmol) was added dropwise while stirring. The reaction mixture was then refluxed with continous stirring at about 80^0C- 90^0C for 3 hours. The white product which was then filtered, washed with cold ethanol and allowed to dry over $CaCl_2$ yielded 0.6 gm, (68.9%),decomposes above 370 ^{0}C.

2.3.1c. Synthesis of the Tz- ACAC_ 20 (L) [26, 27]

0.233 gm (1mmol) of 4-phenoxy- 2, 6- bis(hydrazino)- s- triazine(HBHTz) was dissolved in a mixture of DMSO (5ml) and hot ethanol (15 ml)in a 250ml round bottom flask fitted to a condenser and equipped with a magnetic stirrer. 0.12gm (1.2mmol, 0.12ml) of acetyl acetone was added to the stirred solution of HBHTz and the mixture was refluxed for 6hrs. The white solid product was then cooled, filtered, washed, dried over $CaCl_2$ and weighed. Yield = 0.05 gm (34.5%), Mpt.=223^0C

2.3.2. Synthesis of macrocyclic chelates of Cu (II) & Ni (II) [26, 27 28]

Metal complexes of the Macrocyclic ligand (L) were synthesized both by the direct and the template method.

Direct method

For this route, the metal chlorides were converted to metal perchlorates as follows.

1% NaOH solution was added to the aqueous solution of metal chlorides to precipitate metal ions as metal hydroxides. The hydroxides were filtered and dissolved in minimum quantity of dilute $HClO_4$ solution.

Then, two parts (in mmol.) of the acidic solution of perchlorate salts were mixed with one part of the macrocyclic ligand (L) dissolved in chloroform / ethanol (1:1) mixture.

The mixture was refluxed for 8hrs in a 250ml round bottom flask in the presence of few drops of piperidine (condensing agent). Colored solid products were collected, filtered, washed with ethanol, dried over $CaCl_2$ and weighed. Yield =0.152gm (34.5% Mpt.263^0C (in the case of copper complex) .

Template method

Two parts of metal chlorides were mixed with one part of acetyl acetone in a chloroform / ethanol mixture in a 250 ml round bottom flask.

The chloride salt–acetylacetone mixture was refluxed for 30 minutes in presence of $KClO_3$ and few drops of piperidine.

After 30 minutes, HBHTz (half the molar quantity of chloride salts) was added to the salt – acetylacetone mixture. After 8hrs of refluxing, colored solid products were formed which were filtered, washed and dried. Yield = 0.103gm, 47% & Mpt 263^0C in the case of copper complex and 0.102gm, 51% & Mpt 345^0C in the case of nickel complex respectfully.

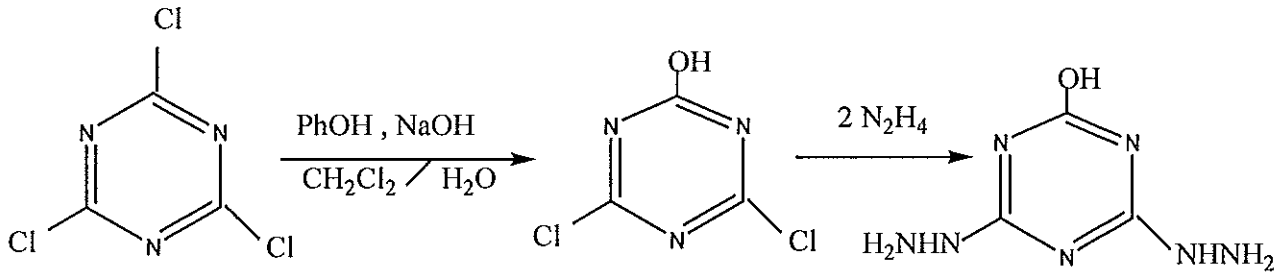
Caution : perchlorate–containing complexes are potentially explosive and appropriate precautions were taken for their preparation , handling and storage **[18]**

3. Results and discussion

3.1. Reaction routes and structures of the Ligands and chelates

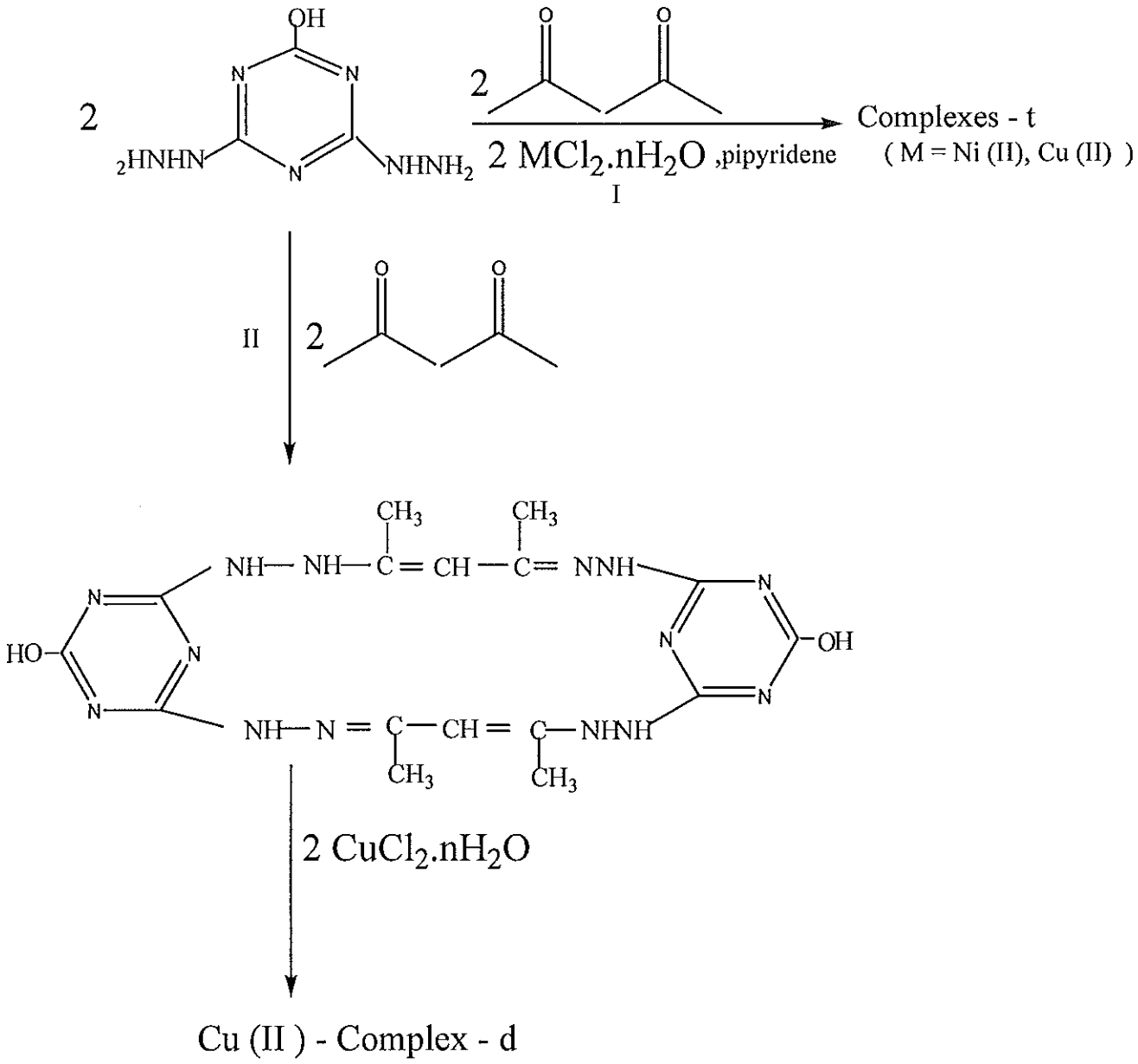
A new macrocyclic ligand (L) and its complexes formulated as [$MLCl_kA$] Cl_y (M = Cu (II), Ni(II) L= Tz – ACAC - 20 & A = non chelating ligand) have been synthesized by template condensation and high dilution techniques from HBHTz, acetylacetone and the metal salts. The HBHTz, was synthesized from 4 – hydroxy-2, 6- dichloro –s-triazine/ DCHTz / which in turn synthesized from cyanuric chloride and phenol /NaOH mixture as indicated in scheme 6.

Copper complexes (made by both template & direct synthesises) show an octahedral geometry whereas the Ni (II) complex shows a tetrahedral geometry as evidenced from analytical, conductance, and magnetic studies.The conductance data also indicated that copper complexes are non electrolytes where as nickel (II) complex-t is ionic.



Cyanuric chloride DCHTz HBHTz

Scheme 6. Preparation of 4-Hydroxy-2, 6-Bis (hydrazino)- s-triazine/ HBHTz /



Scheme 7. Synthesis of the complexes by direct- d (II) & template- t(I) methods.

3. 2. Physicochemical characteristics of the ligands

3.2. 1. 4- Hydroxy– 2, 6-dichloro – s- triazine (DCHTz)

3. 2. 1 A. Physical characteristics of DCHTz

The physical characteristics of 4- Hydroxy– 2, 6- dichloro- s- triazine is presented in table1

Table1. Physical characteristics of DCHTz

Physical property	Result
Color	White
Appearance	Crystalline
Solubility	Aetonitrile, chloroform
Melting point (^{0}C)	105 - 109
Yield	66%

3. 2. 1 B. IR spectra of DCHTz

The IR spectra of DCHTz is characterized by sharp bands at 1536 cm^{-1}, 1190 cm^{-1}, 1484 cm^{-1}, 869 cm^{-1}, 800cm^{-1}, which are assignable to the stretching frequencies of sym-triazine ring stretching ,ν(C-O) (heteroaromatic ring breathing), C – N – C Ring bend and sym-triazine oop bending respectively. Weak broad band at 3448cm^{-1} is assigned to the stretching frequency of ν (O-H). Observed IR bands of DCHTz together with the above ones are listed in table 2.

Table 2. Observed IR bands of DCHTz

Cpd	ν(O-H)	Ring stretching	ν(C-O)	ν_{O-H},in plane deformation	sym-triazine oop bending	νC - Cl	ν(C-N) (aromatic)	C-N-C Ring bend
DCHTz	3448	1536	1190	1484	800	693	1158	869

The IR spectrum of DCHTz is consistent with its structure and thus confirms its formation.

3. 2. 2. 4- Hydroxy – 2, 6-Bis (hydrazino)- s –triazine / HBHTz /

3. 2. 2 A. Physical characteristics of HBHTz.

. Physical characteristics of HBHTz are presented in table 1.

Table 3. Physical characteristics of HBHTz

.Physical property	Result
color	white
appearance	crystalline
Solubility	Sparingly soluble in DMSO,suspension in hot ethanol
Melting point	Decomposes above 370^0C
Yield	82%

3. 2. 2B. Spectroscopic studies

HBHTz is characterized also on the basis of IR and NMR spectral studies.

IR spectra

The most important bands in the IR spectra of HBHTz are listed in table 2. The IR spectrum of HBHTz is characterized mainly by strong bands at 3307,1572 and 1511 cm^{-1}, which are assignable, respectively, to the stretching frequencies of N-H (primary amine), sym-triazine ring stretching and C= N(aromatic) groups, [**28, 29**].

It also exhibits medium bands at 1075 & 935 cm^{-1}, which correspond to the stretching frequencies of C-N (exocyclic) and N-H wagging respectively.

Table 4.Important IR bands of HBHT

Cpd	υ(N - H)	Ring stretching	υ(C= N), aromatic	υ (C-O)	υ(C - N) (exocyclic)	υ(N-H) wagging
HBHTz	3308	1572	1511	1212	1075	935

The IR spectrum of HBHTz is thus consistent with the proposed structure.

NMR Spectra

The ^{1}HNMR and ^{13}CNMR spectra of HBHTz have been recorded in d_6-DMSO solution using TMS as internal standard. In spite of the fact that some characteristic peaks are obscured due to less solubility of the HBHTz in most of the common solvents, a bit structural information can be obtained from its NMR spectra.

In the ^{1}HNMR spectrum signals at $\delta = 3$ & $\delta = 4$ may be assigned to the N- H_2 & N-H protons respectively. The presence of N-H groups can also be ascertained from the IR spectra of HBHTz that confirms the formation of HBHTz from its precursor, DCHTz.

In ^{13}CNMR peaks at $\delta = 167.8$, $\delta = 167.4$, $\delta = 164.4$ may correspond to the quaternary carbons in the heteroaromatic ring (triazine moiety).

3. 2. 3. Tz – ACAC - 20 (L)

3. 2. 3A. Physical characteristics

The physical characteristics of the macrocyclic ligand are presented in table 5

Table 5. Physical characteristics of the ligand (L)

Physical property	Result
Color	White
Appearance	Powdery
Solubility	Ethanol, chloroform
Melting point	223^{0}c

3.2.3B. Spectroscopic results

IR Spectra

Evidence for the formation of the Tz – ACAC - 20 (L) can be obtained from the IR spectrum of the HBHTz.

The IR data of the Tz – ACAC - 20 together with that of HBHTz / for comparison purpose/ are listed in table 6.

Table 6. **IR** spectral bands of HBHTz & Tz – ACAC - 20 (L)

Cpd	ν_{N-H}(sec.)	$\nu_{C=N}$ Azomethine	ν_{C-H}, methyl	ν_{C-N}, aromatic	$\nu_{\delta CH3}$, bending	$\nu_{\delta N-H}$, wagging	ν_{O-H},in plane deformation
HBHTz	3307.81(d)*	-	-	1572	-	935	1432
L	3433 (s)*	1594	2928	1547	1366	969	1400

d =doublet, s* = singlet,

The strong doublet band at 3307cm^{-1}, attributed to the symmetrical stretching mode υ (NH_2), in the spectrum of the HBHTz, shifted to a weak singlet band at 3432cm^{-1}, which is assigned to the symmetrical stretching mode ν (N-H). This is due to the condensation reaction between the carbonyl groups of acetylacetone and the amine groups of HBHTz.

Bands at 2928cm^{-1} which are absent in the spectra of HBHTz are due to symmetric stretching of νC-H(CH_3) that is derived from acetylacetone.

The strong sharp band in the region 1620 -1590cm^{-1} in the L spectrum is attributed to νC =N (azomethine group), which confirms the occurrence of condensation reaction between carbonyl groups of acetyl acetone and the amine groups of HBHTz .The strong sharp band at 1547cm^{-1}is assigned to ν_{C-N},,heteroaromatic ring stretching (s- triazine moiety) stretching.

The strong intensity band structure at 1400cm^{-1} & 1432cm^{-1} in the spectra of L& HBHTz respectively is due to ν_{O-H} in- plane deformation or CH_3 deformation vibration (these two bands may probably be merged in to one).

The sharp bands at 969cm^{-1} and 809cm^{-1} are attributed to $\nu_{\delta N-H}$, wagging. These observations from the IR spectra together with the difference in physical properties of the HBHTz and L (Mpt & solubility) confirm the formation of the Tz – ACAC - 20 ,L.

NMR spectra

The ^{1}H and ^{13}C NMR spectra of the Tz – ACAC - 20 were obtained in deutrated chloroform ($CDCl_3$) at room temperature using TMS as internal standard.

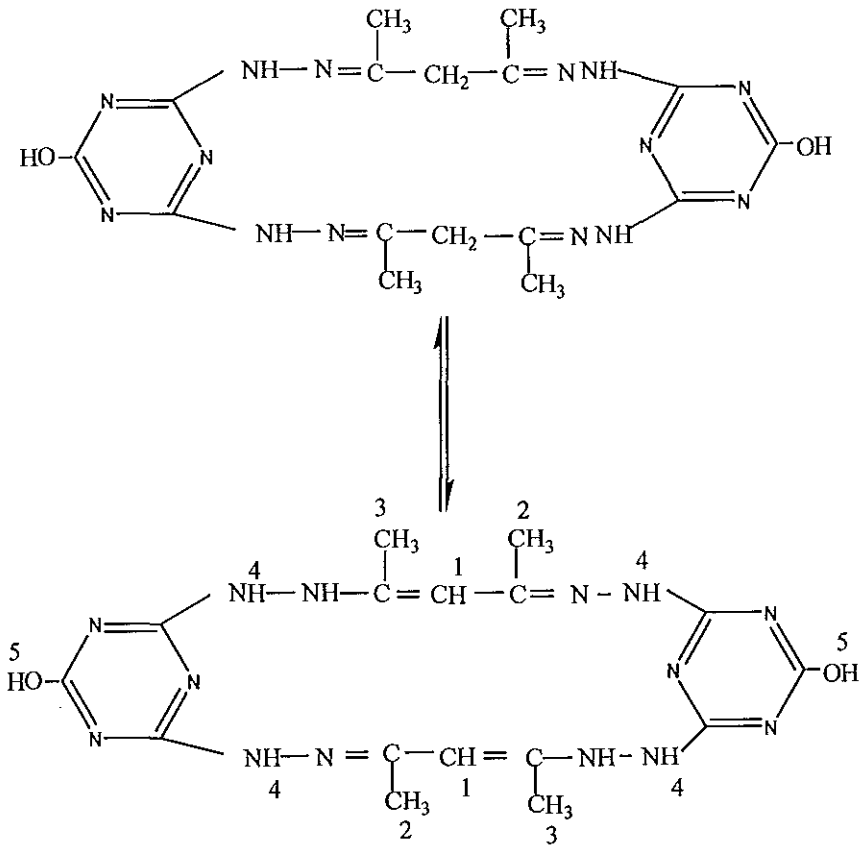
The ^{1}HNMR spectrum of the ligand shows signals at 6.1, 2.8, 2.4 and 2.2 down field from TMS assigned to CH (methine), CH_3 (1) , CH_3(2) & NH protons respectively. Two separate signals due to the two methyl protons indicate the presence of mobile proton that is responsible for the shift of the double

bond from the azomethine to the methine moieties.This breaks the equivalency of the two methyl groups.The Tz – ACAC - 20 thus exhibits tautomerization as a result of the movement of protons from methine to azomethine groups. Since the NH and OH protons are labile and the solvent contains some water impurity , some protons of OH can be deutrated. They can also be deprotonated during refluxing. Thus OH protons maynot have characteristics chemical shift range in the ^{1}HNMR spectra of the ligand. Those protons on a nitrogen (^{14}N) (I=1) atom are subjected to partial or complete decoupling by the quadrapolemoment of the ^{14}N nucleus. Hence they produce relatively broad peak in ^{1}HNMR spectra.Due to the above mentioned factors the NH protons or OH protons may provide no or in appropiate ^{1}HNMR spectra ,as a result the integeral value maynot also match with the total number of protons present in the compound.

The integeral values for the methine and methyl protons(CH_3 (1) & CH_3(2)) exactly match with their corresponding total number present in the proposed structure of the ligand. The ^{1}HNMR chemical shifts with the corresponding integeral values of the macrocyclic ligand are listed in table 7.

Table 7. ^{1}HNMR spectroscopic data (ppm) of the Tz – ACAC - 20 (L)

Ligand (L)	Types of proton & its chemical shift			
	1	2	3	4
^{1}HNMR	6.1	2.8	2.4	2.2
Integeral value	1.00	3.05	3.25	1.57



Scheme 8. Tautomeric forms and the types of protons of the Tz – ACAC - 20 .

Multiplying all the ratios by 2 yields, the total number of protons present in the macrocyclic ligand less two OH & two NH protons (labile protons), which is in agreement with the proposed structure.

2(	1	3.05	3.25	1.57	)
	2	6	6	4	= 18

^{13}CNMR and DEPT spectra provide clear picture about the strucure and composition of th Tz – ACAC - 20.

In ^{13}CNMR spectra, peaks at δ = 164, δ = 153, δ = 144 correspond to the quaternary carbons on heteroaromatic ring(s- triazine moiety) ,1 & 2 (Fig.10), and the azomethine groups (3) respectively. The other peaks at δ = 111, 16 & 15 are assigned to methine (CH) and methyl carbons ,CH_3(5) & CH_3(6) respectively.

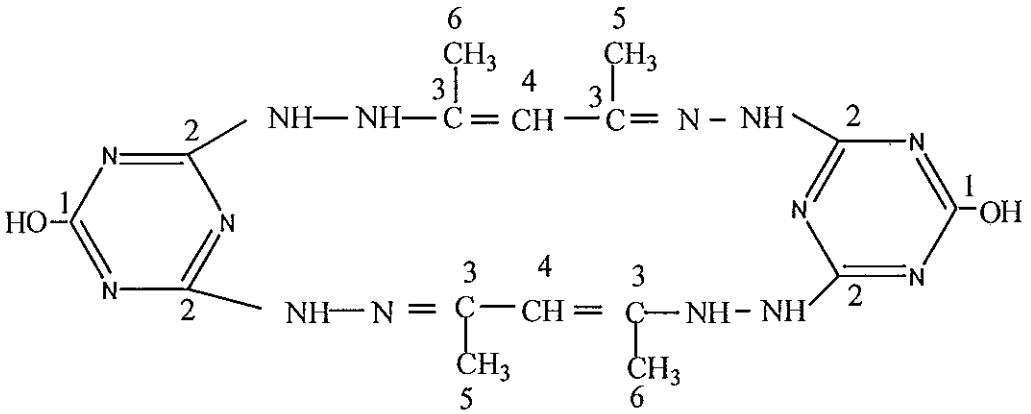


Fig.10. Types of carbon atoms on the Tz – ACAC – 20.

The DEPT spectrum shows three distinct signals that can be assigned to CH (δ =111), CH_3(1) (δ = 15) & CH_3 (2) (δ = 14) protons that are derived from acetylacetone. DEPT also indicates the presence of three quaternary carbons and thus six equivalent carbon atoms.This exactly matches to the total number of carbon atoms present in the proposed Tz – ACAC - 20 structure. Such observations provide information about the incorporation of the acetylacetone & the s-triazine moieties in the proposed structure which confirms the formation of the Tz – ACAC - 20 .The types of carbons with their corresponding chemical shifts are presented in table 8

Table 8. ^{13}CNMR spectroscopic data (ppm) of the Tz – ACAC – 20.

Ligand (L)	Typeof carbon atom & its chemical shift (δ ppm)					
	1	2	3	4	5	6
^{13}CNMR	164	153	144	111	15	14
DEPT	-	-	-	111	15	14

3.3. Physicochemical characteristics of the Metal complexes

3. 3. 1. Physical characteristics of metal complexes.

The most important physical characteristics of the metal complexes are listed in table 9.

Table 9. Physical characteristics of the metal complexes.

Complex	color	Mpt (in ^{0}C)	Solubility	Yield,%
Ni(II) complex-t	Bluish yellow	345	Chloroform,methanol DMF, ethanol	51
Cu(II)complex- t	Green	275	Chloroform,methanol DMF, DMSO	48.5
Cu(II)complex-d	Dark green	263	Chloroform,methanol DMF	34.5

3 3. 2. Analytical data

3.3. 2A. Atomic absorption spectroscopic (AAS) results

0 .01g (5 x 10^{-4} mmol.) of each complex was digested in 2ml of HNO_3 and diluted to25ml using deionized water . Three trials were performed for each complex to get the average absorbance. The metal concentration was deterimined from the absorbance by the equation

$$\text{concentration (}\mu\text{g /ml)} = \frac{\text{(Absorbance of the sample) (concentration of the standard)}}{\text{Absobance of the standard}}$$

and percentage of the metal in the complex was determined using the relation

$$\text{M(II)\%} = \frac{\text{Concentration (}\mu\text{g/ml) x volume diluted to (ml)x 100}}{\text{mass of the dry sample}}$$

The atomic absorption spectroscopy results show 9.55% and 17.14% copper in the Cu complex- d and Cu(II)complex- t, which corresponds to one and two copper atoms in the complexes respectively. Atomic absorption spectroscopy also provides the metal to ligand ratio to be 1: 1 in Cu(II) complex-d and 2: 1 in Cu(II) complex –t. Thus , based on the atomic absorption spectroscopy results , Cu(II)complex- d is suggested to be mononuclear and that of the Cu(II) complex- t a binuclear complex. The atomic absorption data is presented in table12.

Table 10. The atomic absorption spectroscopic(AAS) data of metal complexes.

Complex	Absorbance	Concentration (ppm)	M(II) % in the sample
Cu (II) complex - d	0.5918	12.74	10.55
Cu(II)complex-t	1.5974	34.28	17.14
Ni (II) complex-t	-	-	-

Ni (II) estimation was not carried out by the AAS method due to the instrumental problem. It was attempted to estimate nickel(II) by the back titration method using EDTA as a complexing agent and EBT as an indicator. How ever due to very smallness of the yield , quantitative determination of N(II) was not feasible.Due to the scarcity of the sample Ni (II)estimation gravimetrically using dimethyl glyoxime was not also carried out. Thus, the quantity of Ni (II) was suggested using information obtained from magnetic, analytical, conductance & spectroscopic data.

3. 3. 2B. Chloride Estimation results

The chloride estimation results are listed in table

Table11. Chloride analysis data of the complexes

Complex	chloride		% Cl
	Absent	Present	
Cu (II) complex -t		✓	8.8
Cu (II) complex - d	✓		-
Ni (II) complex - t		✓	8.35

3 .3. 2C. Elemental analysis

The elemental analysis results for metals estimated using atomic absorption spectroscopy, chlorine by titration and C, H, and N using C, H, N analyzer respectively have been obtained. C, H ,N elemental

analysis was carried out only for nickel complex -template due to the malfunctioning of the analyser. The obtained results were recorded in table 12.

Table 12. Elemental analysis result of Tz-ACAC – 20 and the complexes.

Cpd	Found (cal..), %				
	M	Cl	C	N	H
L	-	-	43.40(43.44)	44.34	4.99 (4.97)
Ni(II)complex- t	12.64	8.35	46.17(45.70)	30.08	5.18 (5.43)
Cu(II)complex-t	15.4	8.04(8.8)	38.52	27.65	5.19
Cu(II)complex-d	10.55(11.64)	-	38.5	39.58	3.98

The above results for the ligand & Ni (II) complex show the closer agreement of the experimental & the calculated values. In the other cases only calculated values are listed as they deviate more than 0.5%. The deviation might have occurred due to some impurities which couldn't be avoided during filtration & recrystallization processes. However, the elemental analysis together with other sources of information (spectroscopic,physical,magnetic) provides conclusive evidence about the formation of the ligand as well as the Ni (II) complex.

3. 3 .2D. Conductivity results

Conductance's of each complex has been deterimined using DMF as a solvent. The results show that each of the copper (II) complex-t & Cu (II) complex - direct incorporating chloride anions yielded a conductance value in DMF which approximated that expected for a non electrolyte which implies that the anionic groups on average coordinated to (or associated with) the cation under the conditions employed. In contrast, the nickel (II) complexes with chloride anions yielded value which fall those expected for a 1:1 and a 1: 2 electrolyte.The conductance data are given in table10.

Table 13. Conductance data of Cu(II) and Ni(II) complexes.

Complex	Molar conductance (λ) (ohm^{-1} cm^2mol^{-1})	Type of electrolyte
Ni (II) cplx-template	109	1: 2
Cu (II) cplx-template	54	Non electrolyte
Cu (II) cplx - direct	17	Non electrolyte

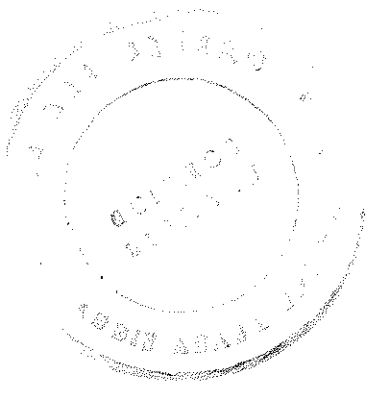
The conductivity data indicates that ClO_4^- are coordinated in the copper complex-d or absent, however from chloride test the absence of ClO_4^- was confirmed, and chloride anions are coordinated in the copper complex-t. In the case of nickel complex two of the chloride ions are either coordinated to nickel or absent,however spectroscopic and elemental analysis data confirm their absence and the other two are non coordinated, which make the complex to be ionic / 1: 2 electrolyte.

3. 3. 2. Infra red (IR) spectroscopy results

The important IR spectral bands of the Ni (II) & Cu (II) complexes along with that of the macrocyclic ligand are given in table 8.

Table 14. Important IR bands of the complexes & the Tz – ACAC - 20 (in cm^{-1})

Compound	νN-H	ν-OH	νC-H	νC=N	νC-O	ν_{O-H},in plane def.	νC-N	νM-N
Cu(II) -template	3422	3422	weak	1591	1108	1482	1325	625
Cu(II -direct	3436	3436	weak	1600	1088	1487	1113	626
Ni(II) - template	3351	3351	weak	1627	1110	1405	1325	625
Tz – ACAC - 20	3432	-	2928	1594	1096	1400	1339	-



The IR data shows that all the three prepared complexes & the Tz – ACAC - 20 contain secondary NH groups. It has been reported in literatures that Ni(II) and Cu (II) complexes with macrocyclic ligands containing a secondary amino group show a single absorption band at around 3350cm^{-1}.
In the present work, absorption band was observed in 3422 – 3351cm^{-1} region corresponding to υ(N-H) of the secondary amino group, which is consistent with the literature report. Bands at 1627, 1110, 1482 cm^{-1} are due to – C=N- (azomethine) , -C-O stretchings and $\nu_{O\text{-}H,}$in plane deformation, respectively [**26, 30**].

The corresponding stretching frequencies in the free ligand (1594, 1096, 1400 cm^{-1}) are shifted to higher or lower wave numbers by 5- 33cm^{-1} after coordination confirming the complexation.
Bands at 2928 cm^{-1} in the free ligand shifted to very weak absorption band after coordination, which may be ascribed as polarization effect. When the N- atom donates electrons to the vacant orbitals of the metal, the charge density around carbon moves (migrates) to wards nitrogen, which is accompanied by the weakening of the C –H bond.
New bands in the metal complexes (796 & 625 cm^{-1}) probably are due to M –N stretching. Such observation from the IR spectra ascertains formation of the complexes.
In the other hand, the broad bands with distinict structures in the region 3200 – 3400cm^{-1} in the spectra of Cu(II) and Ni (II) complexes can be attributed to VN-H as well as OH groups. The weak and broad bands centered at 3422cm^{-1} is due to OH stretch .Thus the band expected in the range of 3200 – 3400cm^{-1} for VN-H stretching is probably merged with ν-OH stretching in the spectra of the complexes.

4. 3. 3. Electronic spectroscopy

Electronic spectral determinations were performed for the complexes, the ligand and the salts (for comparison) in methanol / chloroform mixture. The results for the complexes are presented in table 11.

Table 15. Electronic spectra data for the Cu (II) and Ni (II) complexes

Complex	Band maxima (nm)	Assignment
Cu(II)complex-t	757 352 257	Overlapping of transition from B_1 ground states to B_2, A_1 & E states LMCT
Cu(II) complexplx-d	650 340 315 265 257	Overlapping of transition from B_1 ground to B_2, A_1& E states LMCT Intra ligand C .T
Ni (II) complexplx - t	972 604 487	$^3A_2(F) \leftarrow {}^3T_1(F)$ $^3T_1(P) \leftarrow {}^3T_1(F)$ $^3T_2(F) \leftarrow {}^3T_1(F)$

In the case of the Cu(II) compex – t a broad low intensity band appears at 757nm which is attributed to the d-d transition of the Cu (II) ion. This band is low absorptivity, being Laborte forbidden [**26**].

Litrature surveys reveal that octahedral Cu (II) complexes have transitions in the region 909nm -625nm, besides a charge transfer band.

In this work, the absorption band observed at 757nm assigned to $^2T_{2g} \leftarrow {}^2E_{2g}$ transition indicates that the complex has an octahedral geometry.How ever, regular octahedral geometry is rare due to Jahn teller effect, thus these bands are better assigned to overlapping of transition from B1 ground states to B2, A1 & E states. The absorption at 352 and 257nm assigned to ligand to metal charge transfer (LMCT) which is a characteristics of copper (II) complexes with amines.

Three absorption bands for tetrahedral Ni (II) complexes with Tz – ACAC - 20 are generally observed for a tetrahedral Ni (II) ion. Here, the electronic spectrum of the Ni (II) complex is compatible with tetrahedral geometry. Three absorption bands are observed for the Ni (II) complex at 972, 604, and 487nm corresponding to the $^3A_2(F) \leftarrow {}^3T_1(F)$

, $^3T_1$ (P) ← ^{3} T_1(F) , and $^3T_2$ (F) ← ^{3} T_1(F) respectively. The last transition is obscured by intense charge transfer transitions. On the basis of spectral bands, a tetrahedral geometry is therefore suggested for the Ni (II) ion [**26, 31**].

The electronic spectra of the Ni cpx in methanol / chloroform media show an intense absorption band at 375nm due to charge transfer from the azomethine nitrogen to the d (E_{2g}) orbital of the Ni (II) ion .The intense absorption band at 257nm has also been observed in the spectra of Cu (II)complex-d which probably arises due to the ligand to ligand (intra ligand) charge transfer transition[**31**].The other bands can be assigned to Overlapping of transition from B_1 ground to B_2, A_1& E

3 .3. 4. Magnetic moments

Magnetic susceptibilities of the complexes calculated from room temperature instrumental data and metal ligand stoichiometries are presented in table 8.

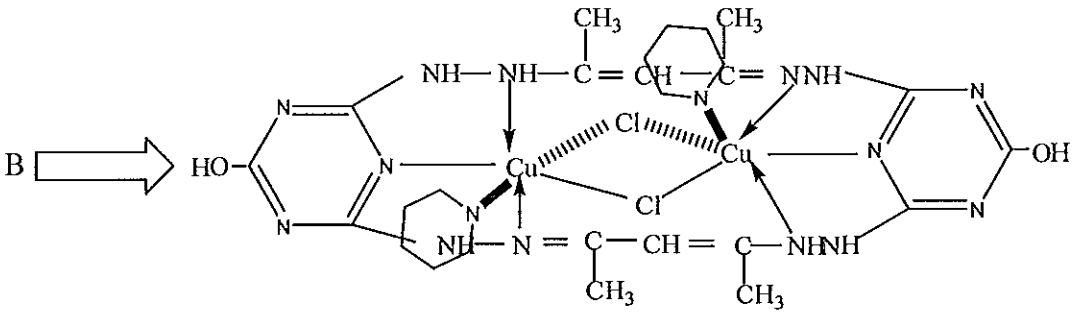
The effective magnetic moment (μeff) of the complexes were calculated by the equation

μeff = 2.828 (T (Xm) $)^{1/2}$, where Xm molar magnetic susceptibility and T absolute temperature.

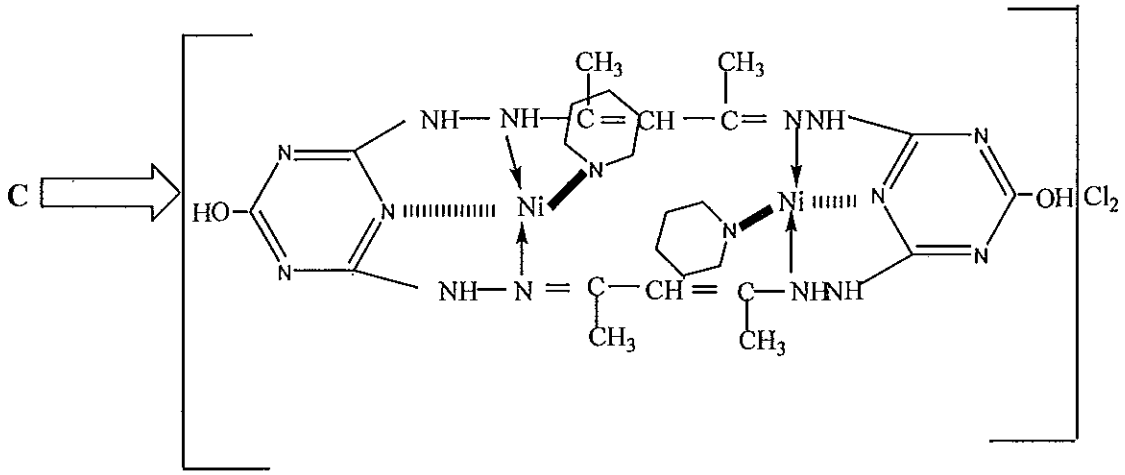
In general, the magnetic moments are in a good agreement with the expected configurations. The magnetic moments in Bohr Magneton's are 3.1 and 2.2 for Ni (II) & Cu (II) respectively. They correspond with d^8 and d^9 configurations respectively in tetrahedral & octahedral stoichiometry . The value is a little higher than the spin-only value observed for Cucplx-template. This may be ascribed to the weak ferromagnetic interaction leading to a triplet ground state.In the other hand magnetic moments of Nicplx-template is a little lower than spin-only value expected for tetrahedral complexes, this may be due to weak ferromagnetic interaction b/n the two Ni(II) ions. The values also show that both copper cplx-d & copper cplx -t have the same geometry.The results are presented in table 11.

Table 16. Magnetic suscebtibility data of Cu(II) and Ni(II) complexes measured at 22.5^0c

complex	X_g	X_M	μeff (BM)
Cu(II) cplx-direct	3.01×10^{-6}	1.51×10^{-3}	1.89
Cu(II) cplx-template	3.04×10^{-6}	2.42×10^{-3}	2. 02
Ni(II)cplx-template	5.52×10^{-6}	4.42×10^{-3}	3.24



.Scheme 10. Proposed structure for Cu (II)complex-synthesized by the template – t method



Scheme 9. Proposed structure for Ni (II)complex-synthesized by template – t method

4. Conclusion

- Synthesis of macrocyclic chelates via template condensation provides better results compared to that of the high dilution technique.
- Macrocyclic cavity size determines the degree of complexation ,number of metal ions coordinated and coordination number.It is governed by the principle of host – guest complexation (lock& key model principle). This conclusion is reached from the observation of Ni(II) complexation through the high dilution method. Probably due to its smaller ionic radius than the macrocyclic cavity size, Ni (II) provided no isolable solid product in the direct route. In the otherhand, Cu (II) can be complexed with the macrocyclic ligand using both the high dilution & direct methods.This selectivity of metal cation binding to macrocycles illustrates the principle of molecular recognition and the basis for many applications.
- The chelating system is more stable than the nonchelating one as it is realized in the copper (II) complexes. Cu (II) complex synthesized by the direct method is coordinated with only the macrocycilc donor atoms, the chloride or water molecules or other non chelating ligandes are not coordinated. In the template case, the non chelating ligandes may be coordinated before cyclization (formation of the macrocycle) takes place.Thus
  the two are non comparable.

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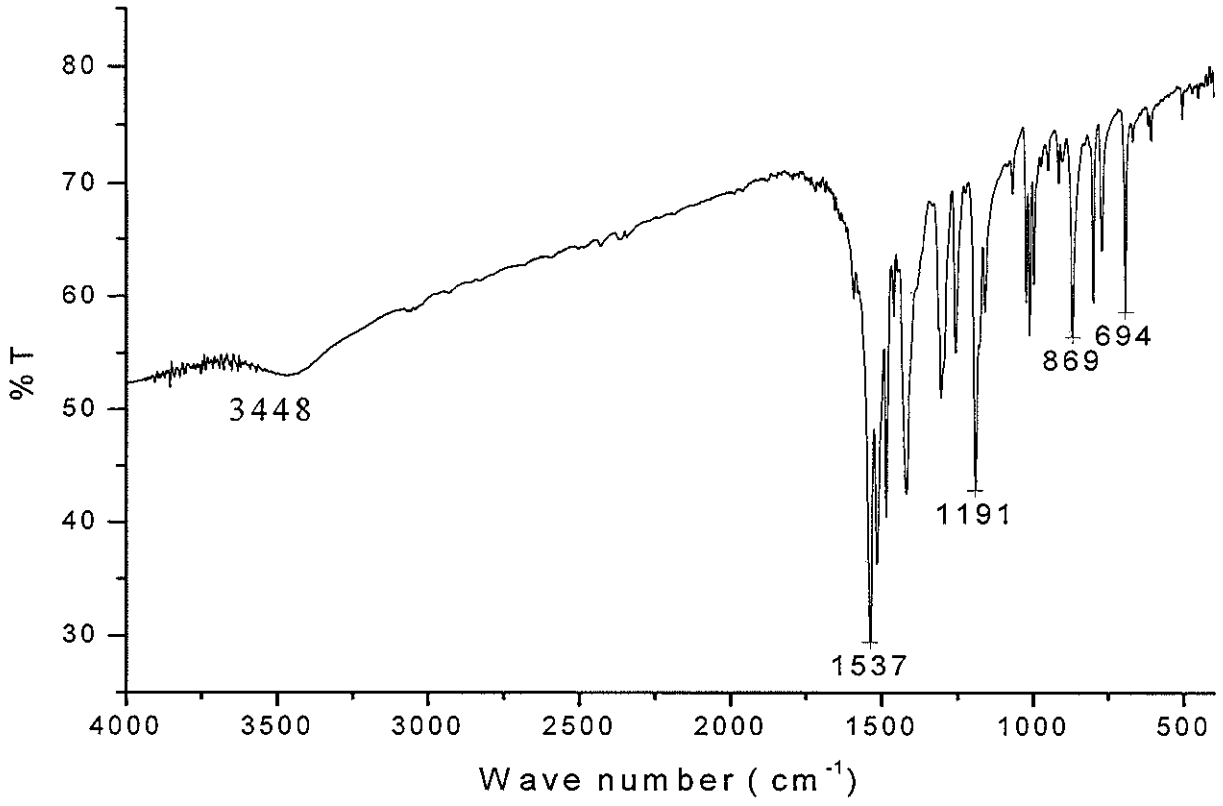
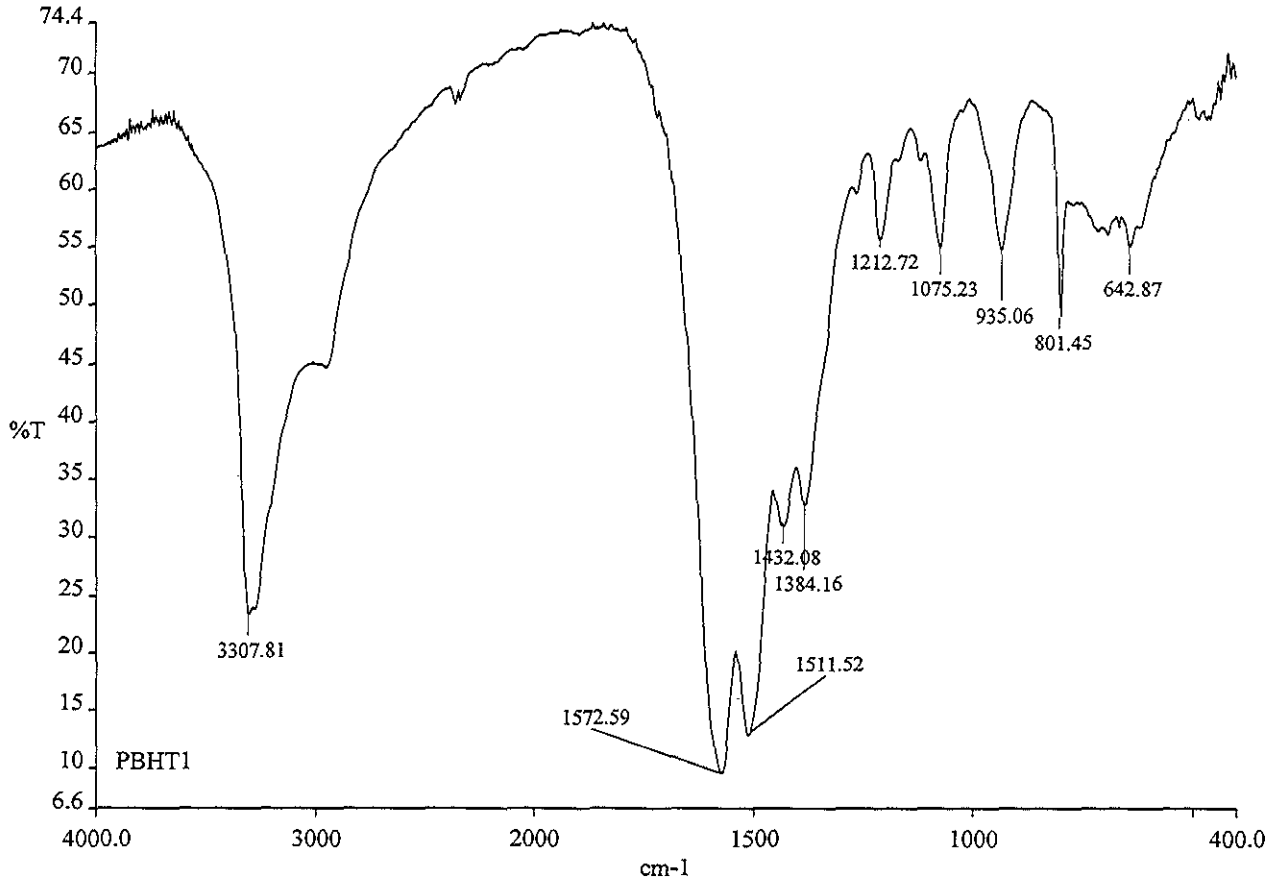
APPENDICES

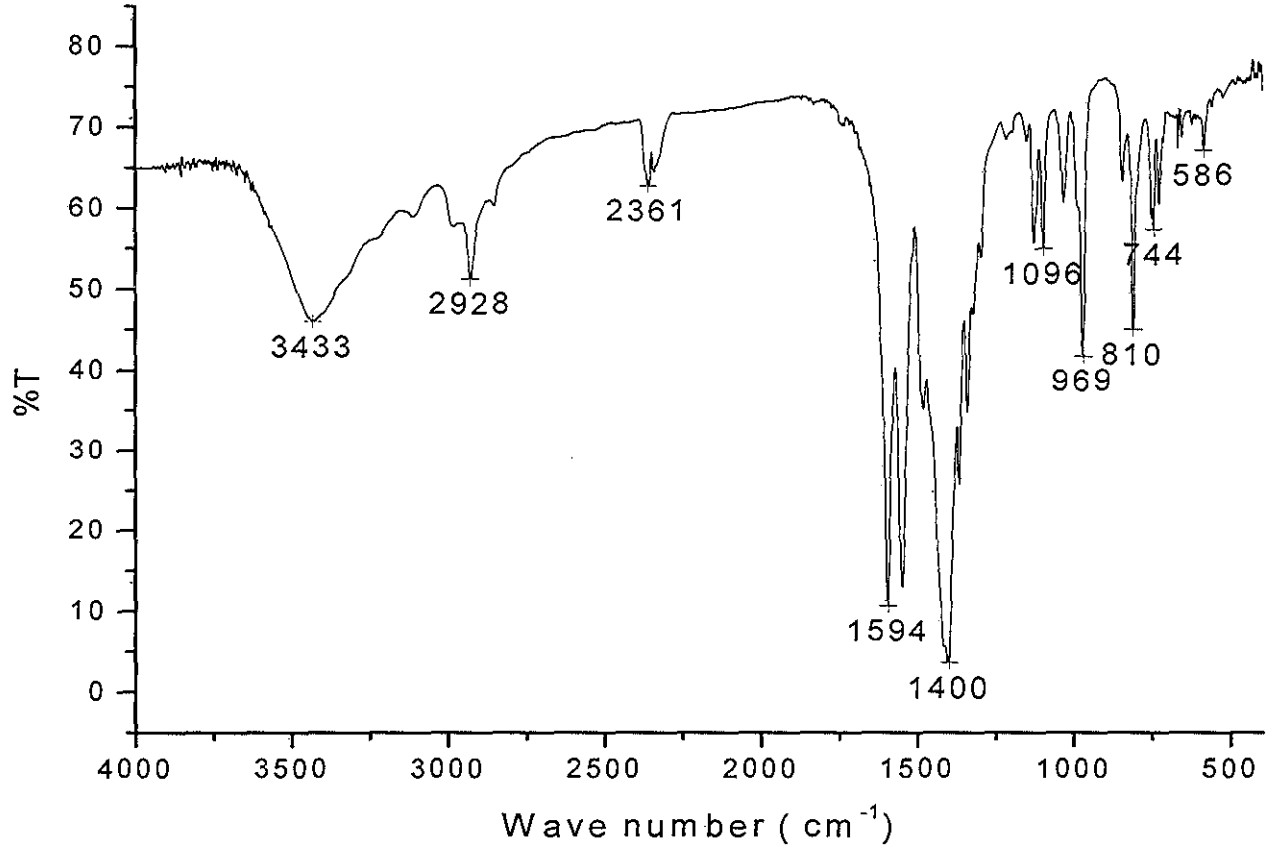


IR SPECTRUM OF DCHTz

IR SPECTRUM OF HBHTz

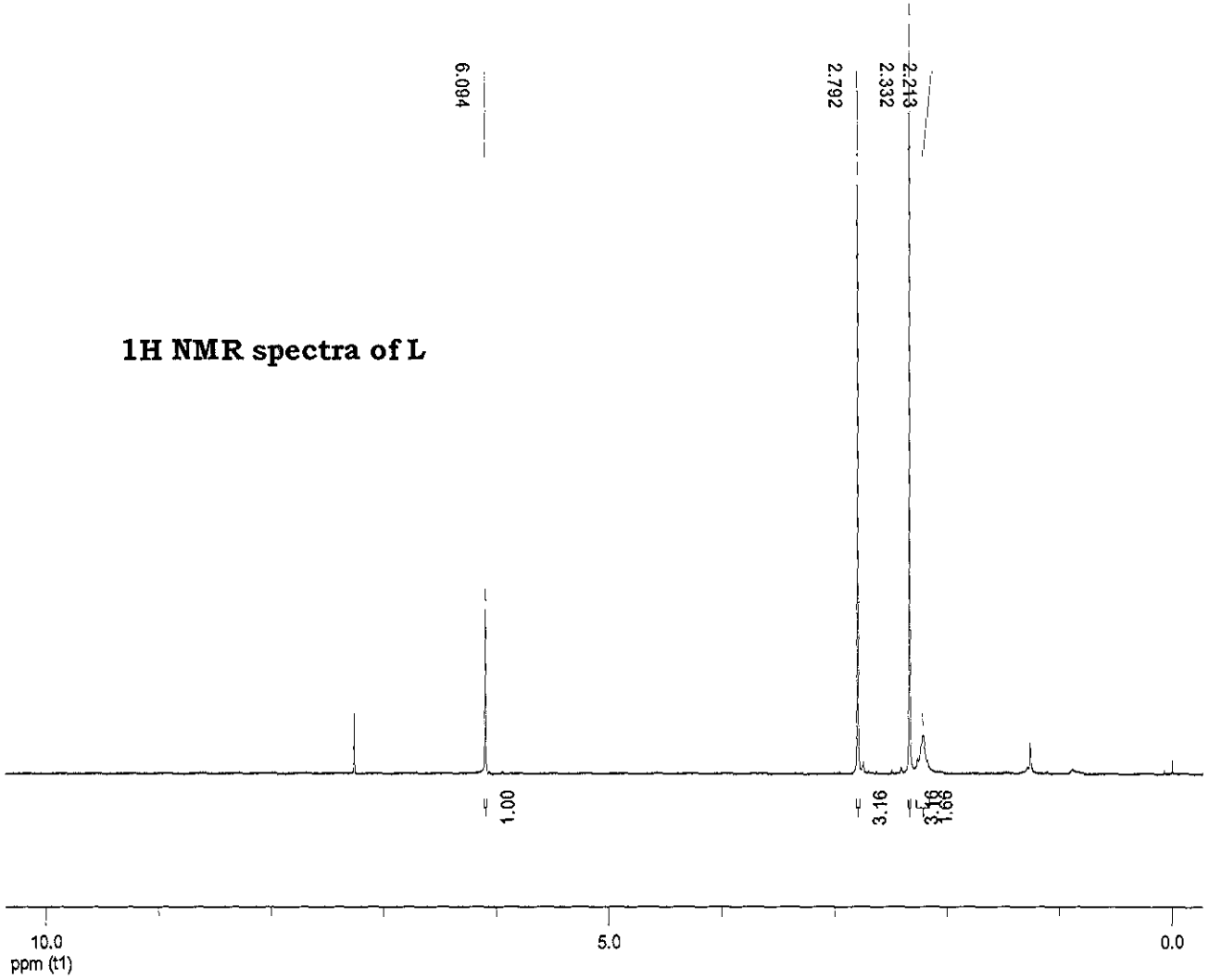


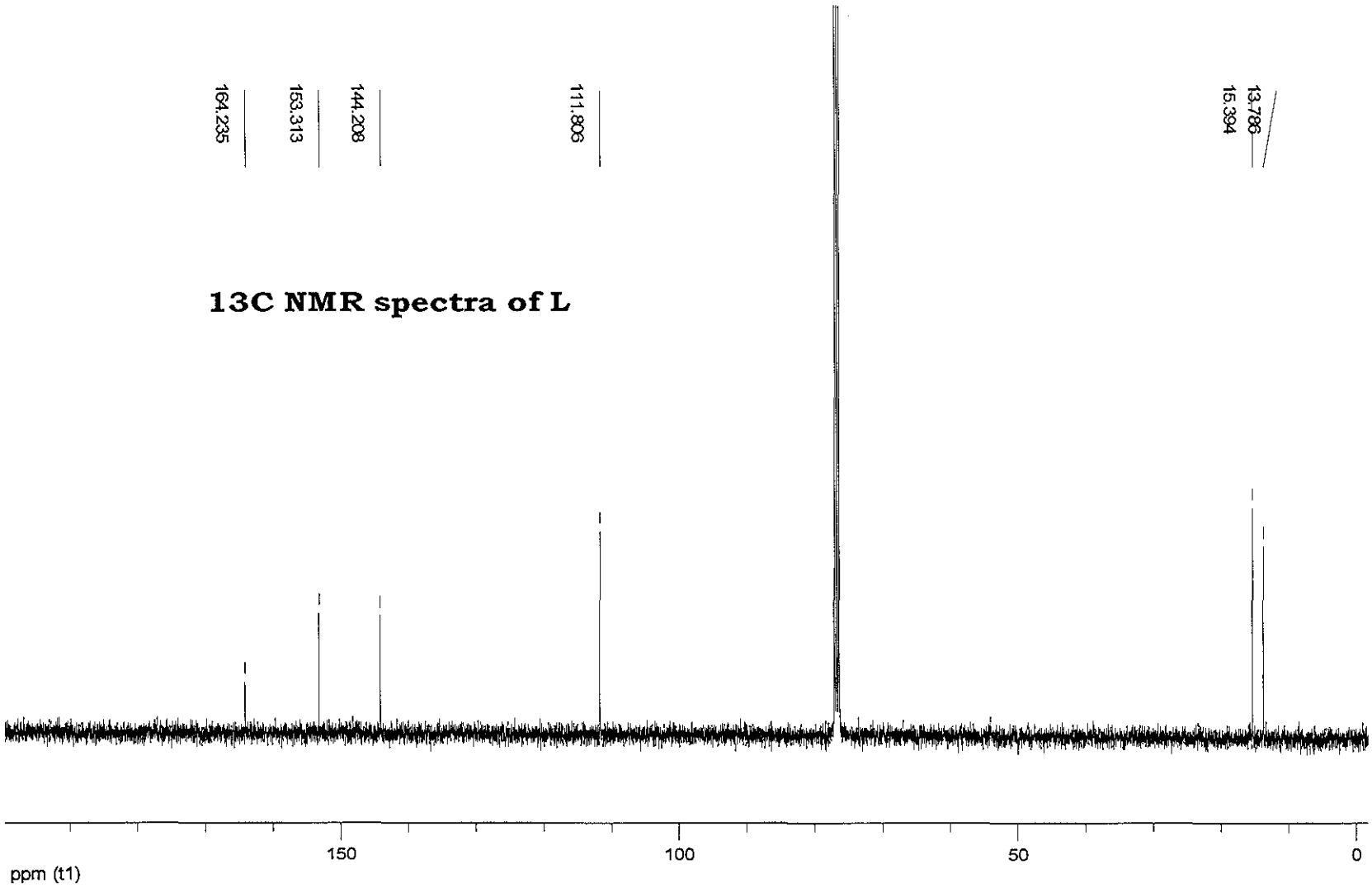
IR SPECTRUM OF THE Tz – ACAC – 20 (L)



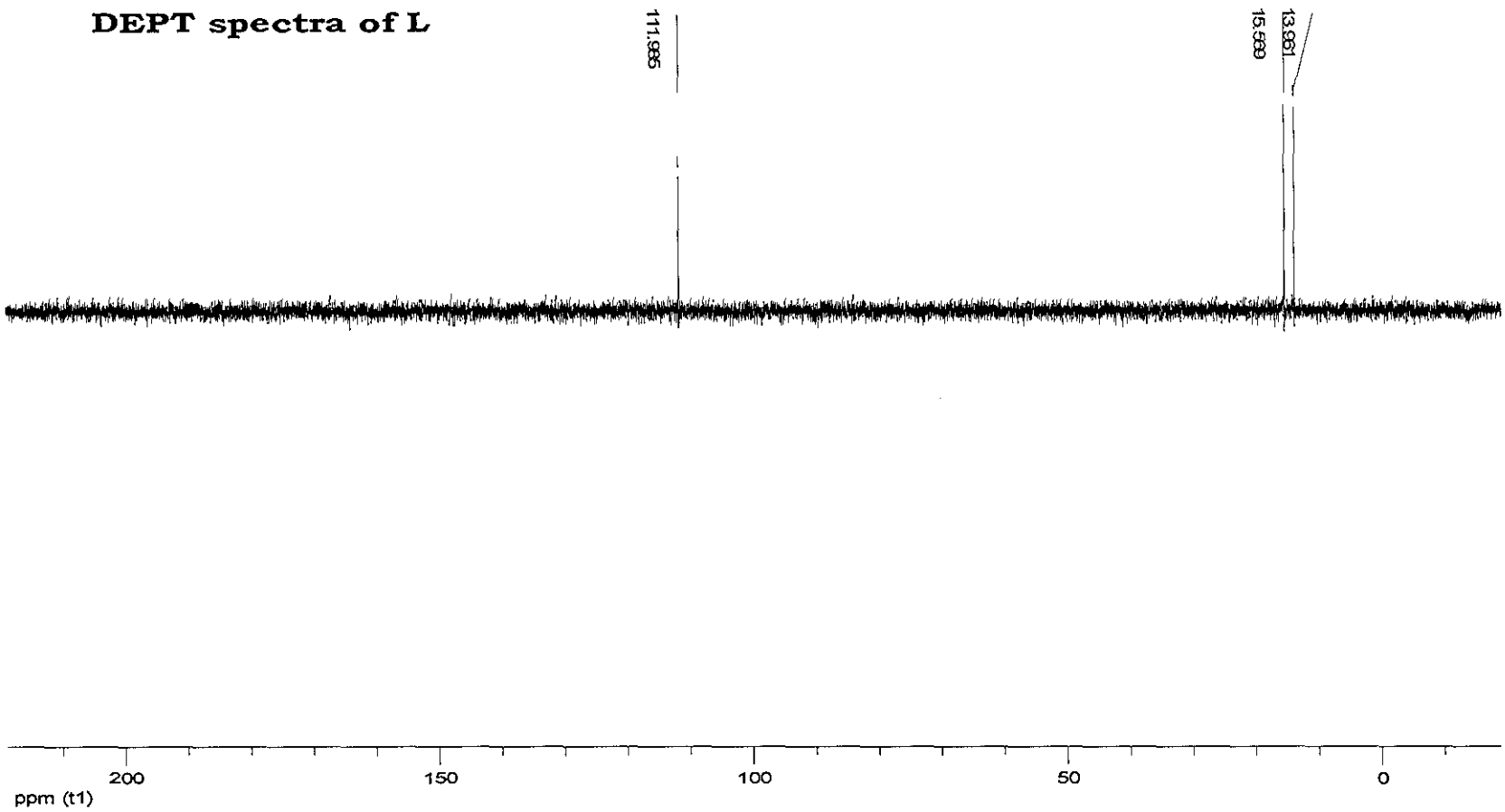
^{1}HNMR spectrum of TZ – ACAC - 20

1H NMR spectra of L



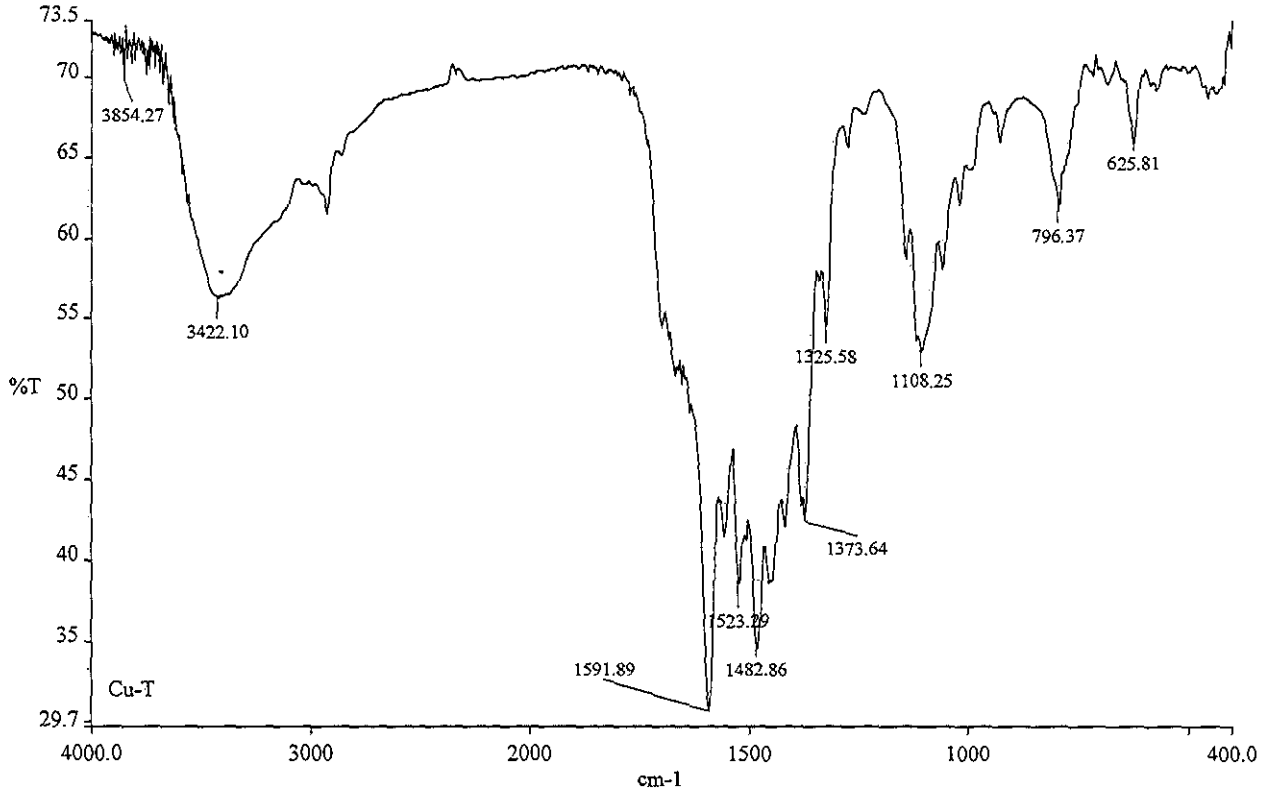


^{13}NMR spectrum of Tz-ACAC- 20

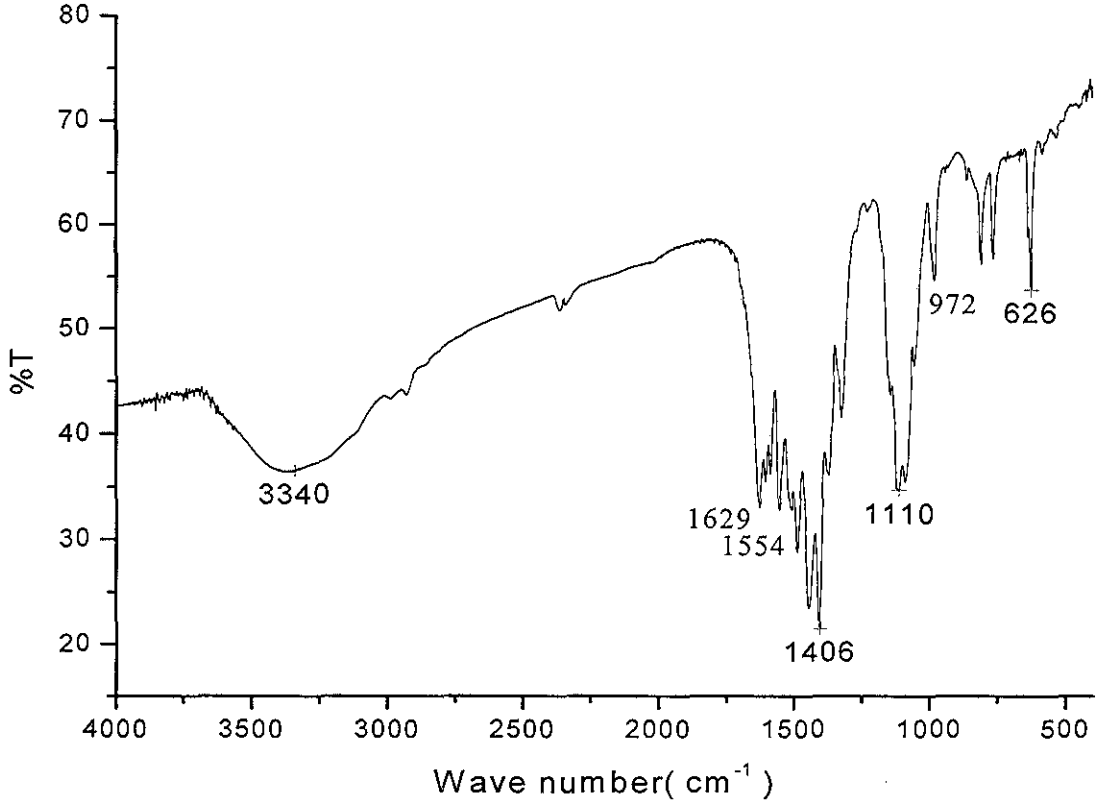


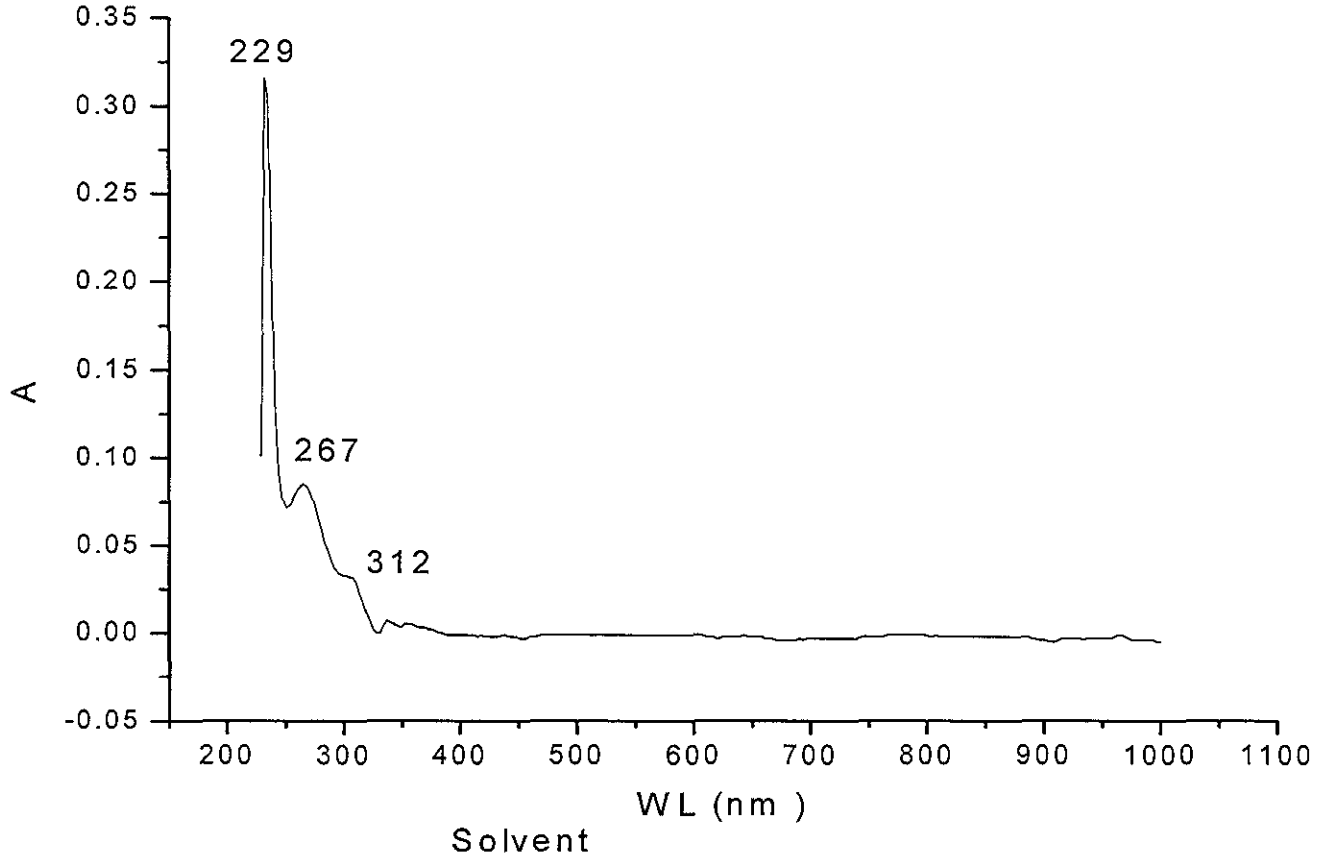
DEPT spectrum of Tz- ACAC-20

IR SPECTRUM OF Cu(II) COMPLEX-t



IR SPECTRUM OF Ni (II) - t

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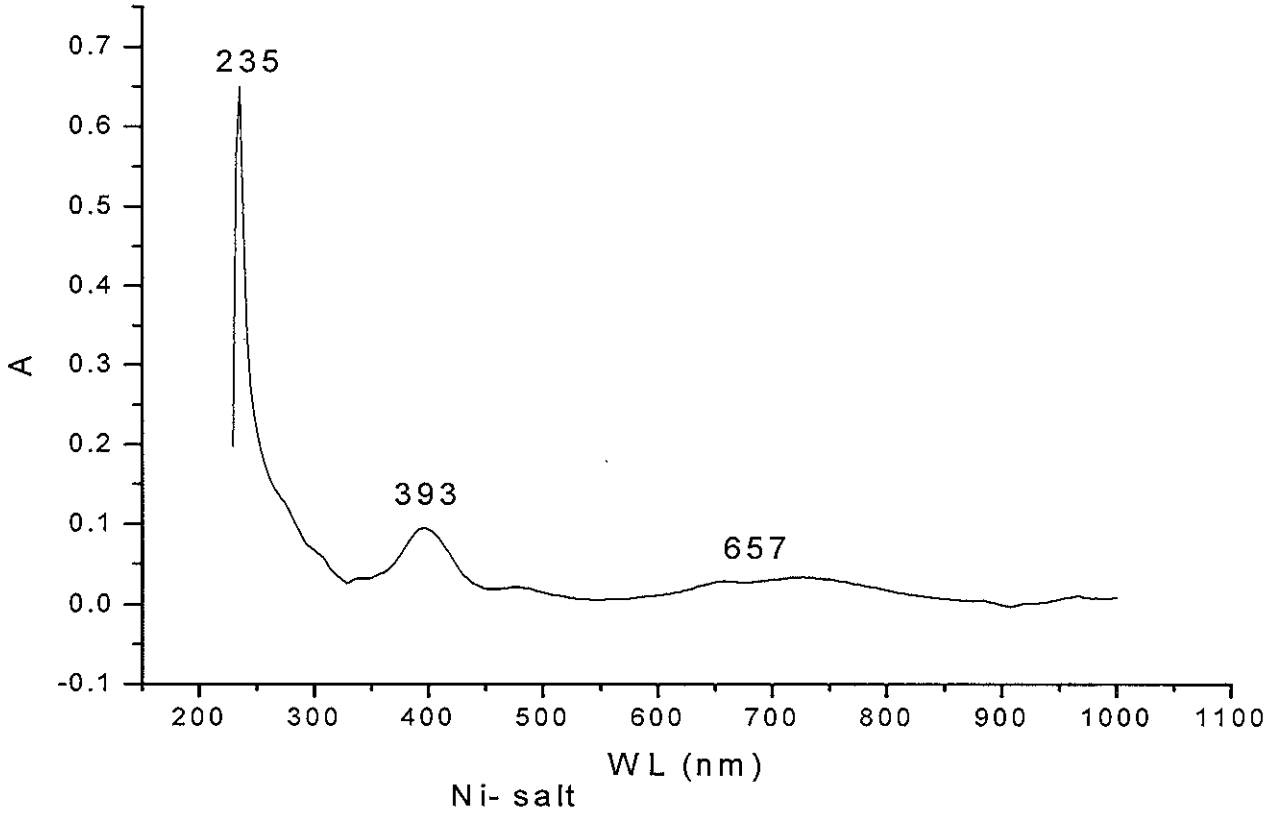
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WL (nm)
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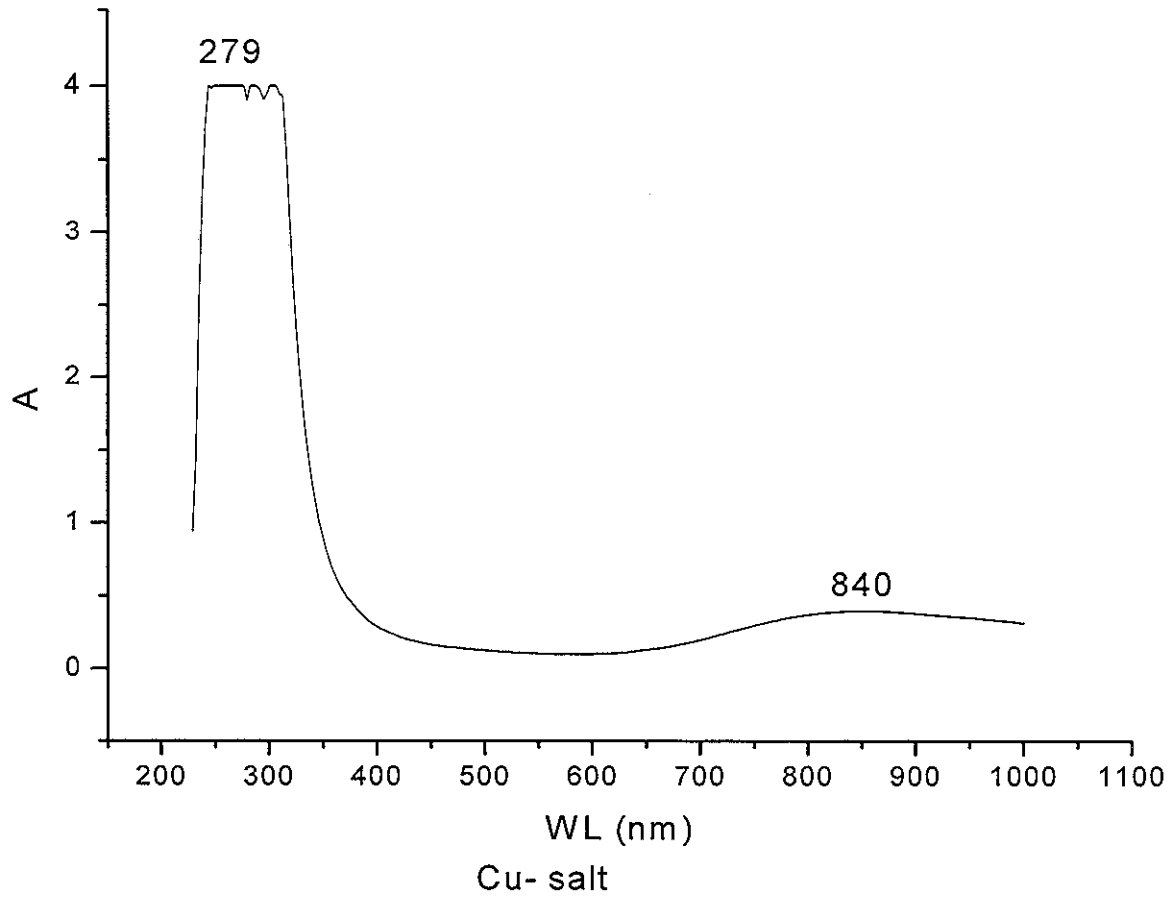
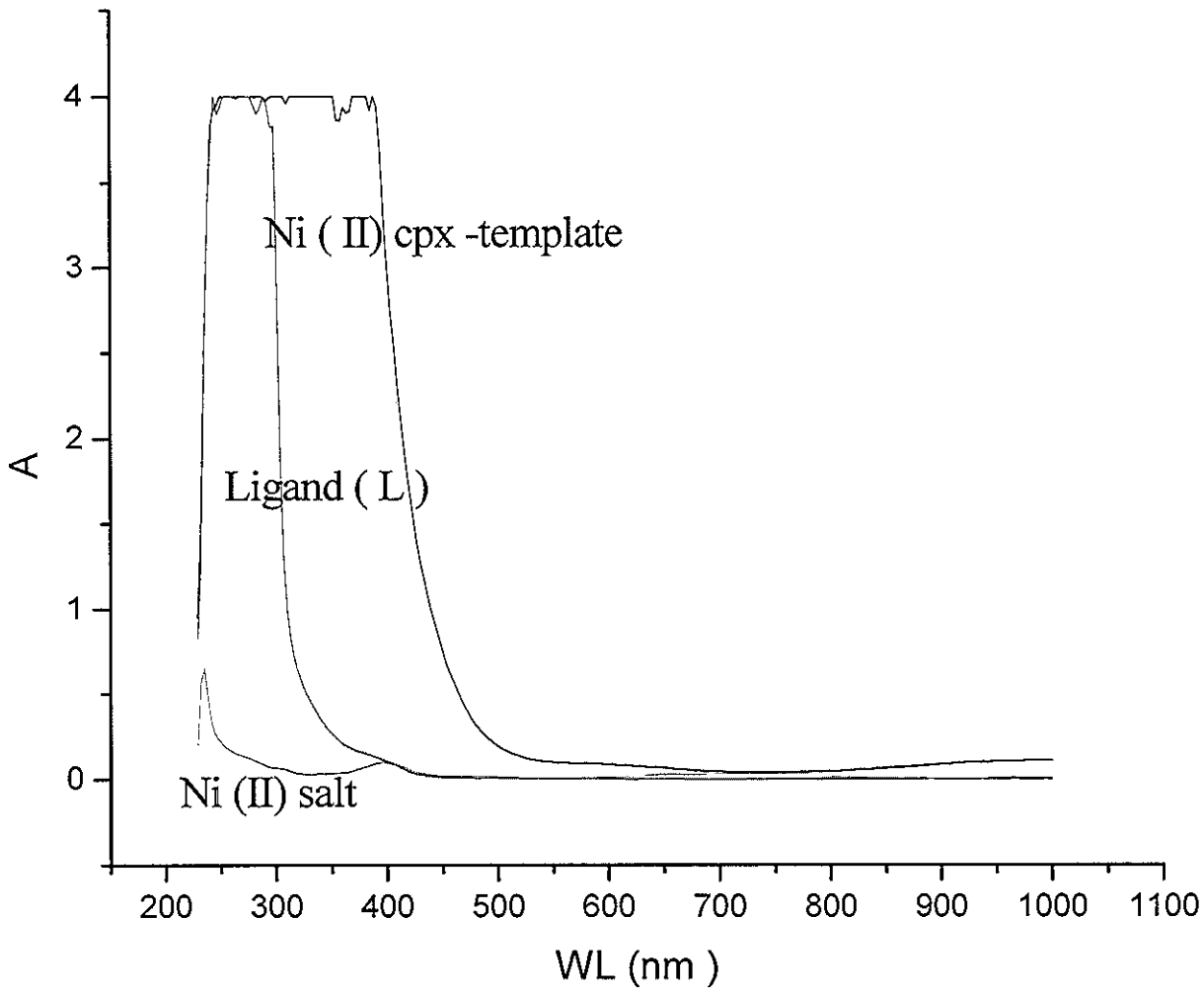


Cu- salt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Ni (II) salt
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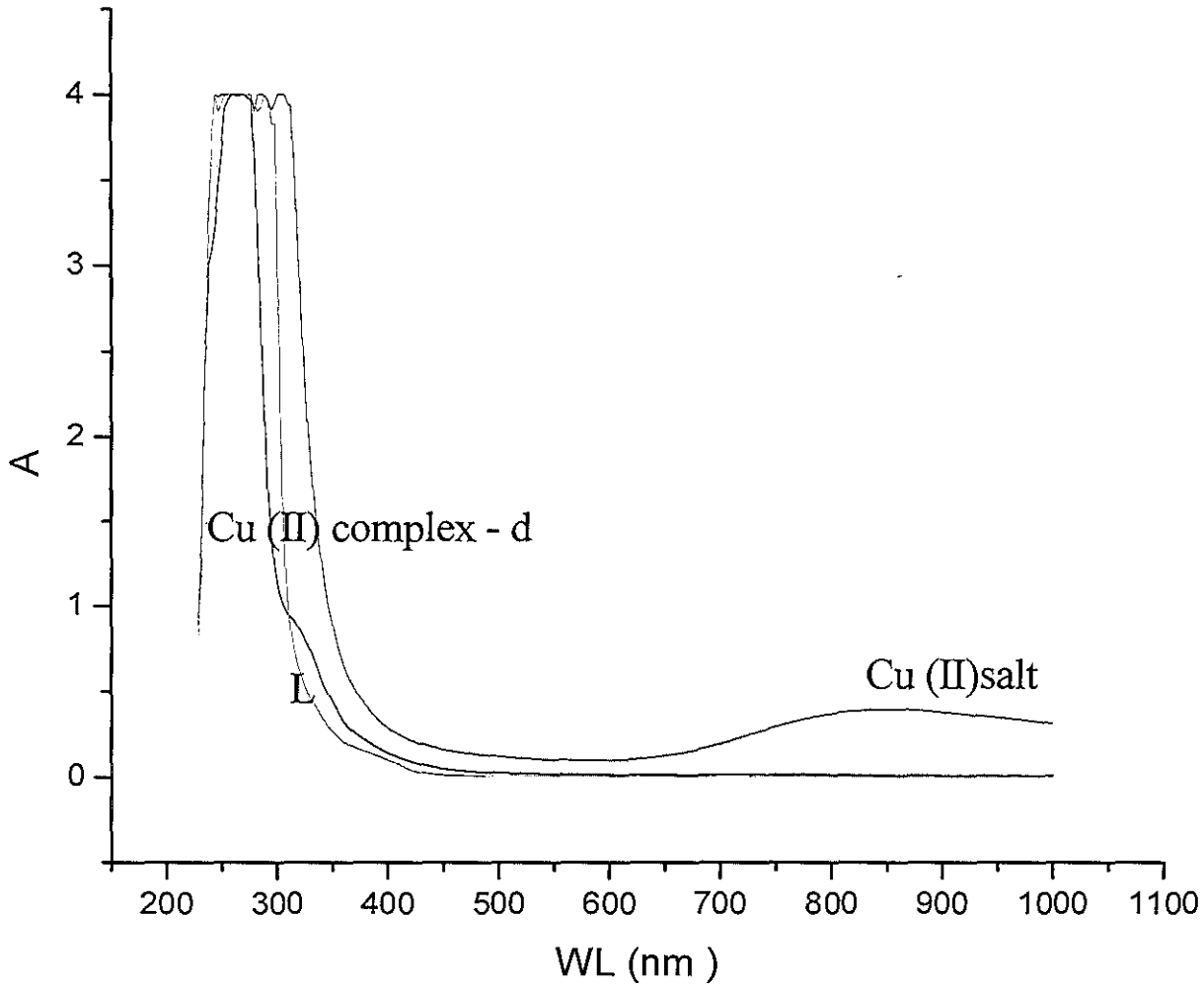
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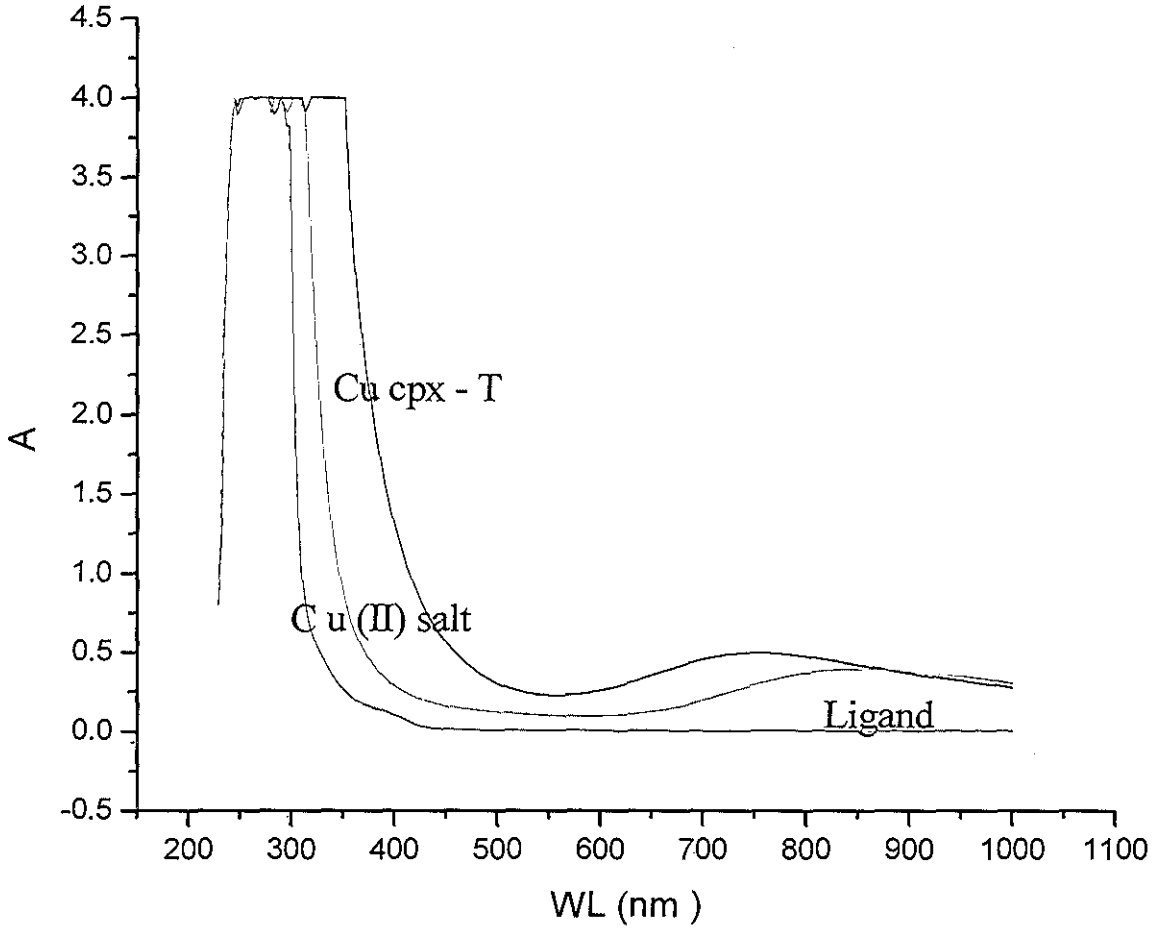
WL (nm)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Cu cpx - T
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WL (nm)