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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF POLYAMIDE MACROCYCLIC METAL COMPLEXES

BY

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Getinet Ashagrie
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Dedication

TO MY *FATHER* AND *MOTHER*

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Getinet Ashagrie

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A^0	Angstrom
DMSO	Dimethyl sulfoxide
DMF	Dimethyl formamide
DMG	Dimethyl glyoxime
δ	Deformation
EDTA	Ethylenediaminetetraaceticacid
^{1} H NMR	Proton Nuclear Magnetic Resonance
IR	Infrared
λ_{max}	Maximum wavelength
Λ_m	Molar conductivity
MeCN	Methyl cyanide
M	Molar
m.pt	melting point
mmol	Millimole
nm	nanometer
Oh	Octahedral
Ω	Ohm
ϕ	Wagging
ppm	partspermillion
THF	Tetrahydrofuran
TLC	Thin layer chromatography
Td	Tetrahedral
ν_{asy}	Asymmetric stretch
ν_{sym}	Symmetric stretch

ABSTRACT

Syntnesis and physico-chemical studies of polyamide macrocyclic metal complexes.

By
Getinet Ashagrie
Advisor: Prof. Mohammad Shakir

The synthesis of bis(macrocyclic) complexes bearing tetraamide groups has been achieved by template condensation reaction between propylenediamine, formaldehyde, benzidine, and succinic acid in the molar ratio of 4:4:1:2, respectively. The appearance of four characteristic amide bands and two single sharp bands corresponding to υ(N-H) of secondary of secondary amine and coordinated amide groups at their appropriate positions and the absence of bands assignable to primary amine and hydroxyl group in the IR spectra strongly suggest the formation of the proposed macrocylic framework. The assigned band positions in the electronic spectra of Co(II), Ni(II) and Cu(II) confirm their octahedral geometry. However, the low molar conductivity values indicate their non-electrolytic nature. The results of elemental analyses agree well with the proposed stoichiometry of the bis(macrocyclic) complexes.

A new series of polyamide macrocyclic complexes have also been prepared by condensation reaction of hydrazine hydrate and succinic acid with metal ion in 4:4:1 molar ratio, respectively. The diagnostic amide bands appearing at their appropriate positions and two single bands corresponding to υ(N-H) of coordinated amide and uncoordinated amide group and non-existence of uncondensed bands corresponding to primary amino and hydroxyl groups provide enough evidence for the formation of the proposed macrocyclic structure. Two major peaks, a broad signal in the region 8.0-8.8 ppm and a broad signal in the region 2.3-3.2 ppm in the ^{1}H NMR spectrum of the zinc(II) complex corresponding to amide group protons (CO-NH, 8H) and methylene protons of dicarboxylic moiety (CO-$(CH_2)_2$-CO, 16H) further corroborates the proposed macrocyclic framework. The band positions in the electronic spectra of Co(II) and Cu(II) and conductivity data supported their final geometry. The stoichiometry has been confirmed on the basis of elemental analysis.

1. INTRODUCTION

The field of macrocyclic chemistry has been a vast area of research and study. The innumerable work done by countless researchers comprising of hundreds of papers and reviews, many patents about the coordination chemistry of macrocyclic ligands cannot be confined to few pages.

Macrocyclic ligands have traditionally been divided into two classes, those with oxygen donors, such as the crown ethers and cryptands [1] and the nitrogen donor macrocycles [2]. The sulfur-donor macrocycles [3] resemble the nitrogen donor macrocycles more closely in their coordinating properties and thus grouped with them. The division into oxygen donor macrocycles on the one hand and nitrogen donor macrocycles on the other has been derived based on selection of metal ions for complexation. The oxygen donor macrocycles tend to complex well with metal ions such as the larger alkali and alkaline earth metal ions and the larger-post transition metal ions such as Pb(II), Tl(I) or Hg(II). The nitrogen macrocycles complex well with transition metal ions, as well as the post-transition metal ions. The sulfur donor macrocycles are weakly complexing with all metal ion, but complex best with the same group as the nitrogen donor macrocycles.

Macrocyclic ligands and their complexes in general have the following characteristics [4].

(a) They can stabilize unusual oxidation states that are not normally readily attainable.

(b) A marked kinetic inertness both to the formation of the complexes from the ligand and metal ion and to the reverse, the extrusion of the metal ion from the ligand.

(c) They have high thermodynamic stability and formation constants. For example the formation constants of (N_4) macrocycles is of greater order than the formation constants for non-macrocyclic (N_4) ligands [5], termed as the macrocyclic effect .

(d) Functional groups can be systematically introduced into macrocycles without much difficulty.

(e) The donor atom members and ring sizes can be successively altered, so that the basic skeleton can be easily optimized.

The macrocyclic effect is both enthalpic and entropic in origin. The donor atoms are constrained near the required coordination sites in the macrocycles therefore, the ligand is pre-strained to suggest additional stability compared with the non-macrocycle. The macrocyclic effect is best understood by the thermodynamics of the metal complexation reactions [6].

There are two factors that govern the complexation of metal ions by macrocyclic ligands. These are the origin of the macrocyclic effect [7] that is the extra thermodynamic stability shown by complexes of macrcocycles compared to those of their open chain analogues, and the selectivity displayed by macrocycles for metal ions. Two aspects of metal ion selectivity of macrocycles are of importance. These are the preference of some metal ion types to bind with oxygen donor macrocycles or with nitrogen donor macrocycles and selectivity for metal ions on the basis of their sizes, i.e., size match selectivity, that means a macrocyclic ligand will complex best with metal ions that fit most closely into the cavity size of the macrocycle.

The thermodynamic macrocyclic effect is the extra stability observed in complexes of macrocycles as compared with their open-chain analogues, and correspond to the equilibrium:

$$[\mathrm{M(open\text{-}chain)}]^{n+} + \text{macrocycle} \rightleftharpoons [\mathrm{M(macrocycle)}]^{n+} + \text{open-chain}$$

where “open-chain” refers to the open chain analogue of the macrocyclic ligand .

The macrocyclic efffect was first noted by Cabbiness and Margerum [7] in complexes of tetrazamacrocycles as compared to their open chain analogues. It was concluded [8] that the macrocyclic effect arose entirely from a favorable enthalpy contribution. There have been several suggestions [7,8] on the origin of the macrocyclic effect. Factors that have been considered to play a role are:

1) preorganization (prestraining, preorientation, and multijuxtapositional fixedeness) of the ligand, in the sense of the free ligand having a limited number of conformers, some of which have structures that are similar to the conformation required to complex the metal ion.
2) desolvation of the donor atoms in the confined space of the macrocyclic cavity .
3) intrinsic basicity effects due to electron releasing (inductive) effects of ethylene bridges between donor atoms; and
4) enforced repulsion between the lone pairs of the donor atoms in the cavity of the macrocycle, which is relieved on complex formation.

The ideas suggested under effect one, all carry the intuitively appealing idea that the entropy of the free macrocyclic ligand is lower than that of its open chain analogue. In addition, there is less steric strain involved in taking the macrocycle from its minimum energy conformation in the free ligand to those conformations required in the complex, than is found to be the case for the open chain analogue.

The chemistry of macrocycles containing nitrogen, sulfur, and oxygen atoms have been studied widely mainly with multidentate macrocycles. Multidentate macrocyclic ligands are cyclic molecules consisting of an organic framework made up of heteroatoms which are capable of interacting with a variety of metal species. It is now well established that macrocyclic molecules containing the binding centers as $[N_4]$, $[N_6]$, $[N_8]$, $[N_4O_2]$, $[N_4S_2]$ and $[N_2S_2]$ display unique and exciting role in that they can stabilize unusual higher oxidation states of metal ions.

It is often difficult to predict with confidence the relative binding preference of many polydentate ligands, particularly multi-donor ligand systems, towards particular metal ions because of the number of the variables, such as nature of the donor atoms, number and size of the chelate rings formed, flexibility of the system, relative position of the donor atom and the nature of the ligand backbone. For macrocyclic systems, the macrocyclic ring size is another parameter. Thus, the cyclic ligands have additional stereochemical constrains which may influence metal ion binding and hence thermodynamic discrimination.

The recognition of the importance of the complexes containing macrocyclic ligands has led to considerable effort being invested in developing reliable and inexpensive synthetic routes for these compounds [9]. These macrocycles which contain varying combinations of aza (N), oxa (O), phospha (P) and sulfa (S) ligating atoms can be tailored to accommodate specific metal ions by fine tunning of the ligand design features, such as the macrocyclic hole size nature of the ligand donors, donor set, donor array, ligand conjugation, ligand substitution, number and sizes of the chelate rings, ligand flexibility and the nature of the ligand backbone. The different types of the macrocyclic ligands are particularly exciting because of the importance in generating new areas of fundamental chemistry and many opportunities of applied chemistry.

2. LITERATURE SURVEY

The field of macrocyclic chemistry have grown rapidly and now a series of macrocyclic ligands are available. The sphere of coordination chemistry of polyazamacrocycles had undergone a rapid change after the early 1960's chiefly due to the pioneering independent contribution of curtis [2] and Busch [10].

The first macrocyclic compound prepared from a diacid was, dimeric ethylene succinate reported [11] in 1894 (Fig. 1). Subsequently, very little work was done with macrocyclic diester until the 1930's when Cartothers and his associates commenced a study of polyesters including the macrocyclic monomeric and dimeric carbonates, oxalates, etc., [12].

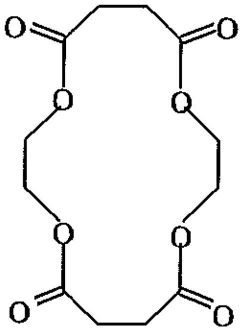


Fig.1

The main interest in macrocyclic diester compounds involved their use in the preparation of perfumes [13]. First documented macrocycle possessing a subhetrocyclic ring (pyrrole) was synthesized [14] in 1886 by Bayer via the condensation of pyrrole and acetone in the presence of mineral acid (Fig. 2).

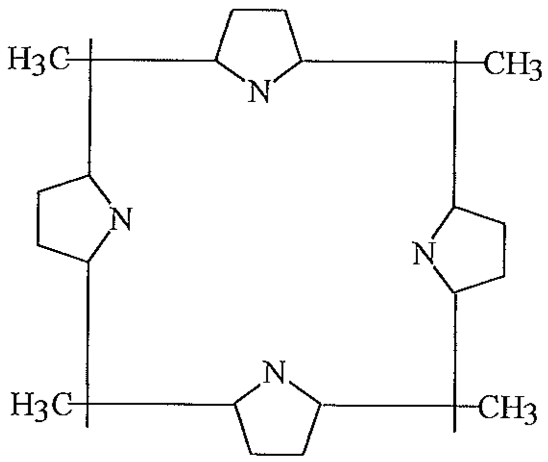


Fig. 2

2.1 Applications of macrocyclic complexes

The metal complexes of naturally occurring macro cyclic ligands have been known for over 70 years e.g. porphyrin, corrin ring derivatives and phthalocyanin. The ever present curiosity and quest in designing new macro cyclic ligands stem mainly from their use as models for protein-metal binding sites in biological systems [6], as models for metalloenzymes [15], as synthetic ionophores [16], as catalysts [17], in biomedical [18], in fuel cell applications [19], as medical imaging agents [20], as therapeutic reagents [21] for the treatment of metal intoxication, as chemical sensors [22] and batteries, as models to study the magnetic exchange phenomena [23] and as sequestering reagents for specific metal ions [24]. It would not be an exaggeration to state that macrocyclic complexes lie at the center of life for example roles of these systems as the iron porphyrin core in haemoglobin, the cobalt corrin of vitamin B_{12} and magnesium hydroporphyrin in chlorophyll.

It is only during the past two decades that a large number of synthetic macrocyclic compounds capable of binding cations or anions have been prepared and investigated. Many of these macrocyclic polyethers, polylamines, polythioethers and other related molecules have been shown to possess very interesting and unusual binding properties [25].

2.2 Synthesis of macroyclic ligands and their complexes

Macrocycles are generally synthesized either "*free*" or " *bound* " to a given metal ion . But there are some potential disadvantages in the later. The advantages of the preparation of the "*free*" macrocycle are :-

Firstly, purification of the organic product may be more readily accomplished than purification of its complexes and secondly, characterization by physical techniques will be more easy. But the free macrocycles are often of low yield for the desired product with side reactions. In order to circumvent this problem, the ring closing step in the synthesis may be carried out under conditions of *high dilution* [26] or a *rigid group* may be introduced to restrict rotation in the open-chain precursors [27], there by facilitating cyclization.

One effective method for the synthesis of macrocyclic complexes involves an in-situ approach where in the presence of metal ion in the cyclization reaction markedly increase the yield of the cyclic product. The metal ion plays an important role in directing the steric course of the reaction and this effect is termed as "*metal template effect*" [28]. The metal ion and the anion are important to the template process because the balance between the size of the cation and anion will determine the degree of dissociation of the metal salt in the reaction medium [29].

The formation of "1+1" macrocycle via intramolecular mechanism or "2+2" macrocycle via the bimolecular mechanism depends on one or more factors during the synthesis of Schiff base macrocycles as mentioned below:

a) The insufficient chain length to span two carbonyl groups in the diamine will block the formation of "1+1" macrocycle [30].

b) A "2+2" condensation may occur if the template ion is large with respect to cavity size of the "1+1" ring.

c) The electronic nature of the metal ion and the preferred geometry of the complex.

d) The conformation of the "1+1" acyclic chelate.

Curtis has demonstrated [31] the template potential of metal ions in the formation of the isomeric tetraazamacrocyclic complexes by the reaction of $[Ni(en)_3](ClO_4)$ with acetone as shown in Scheme 1.

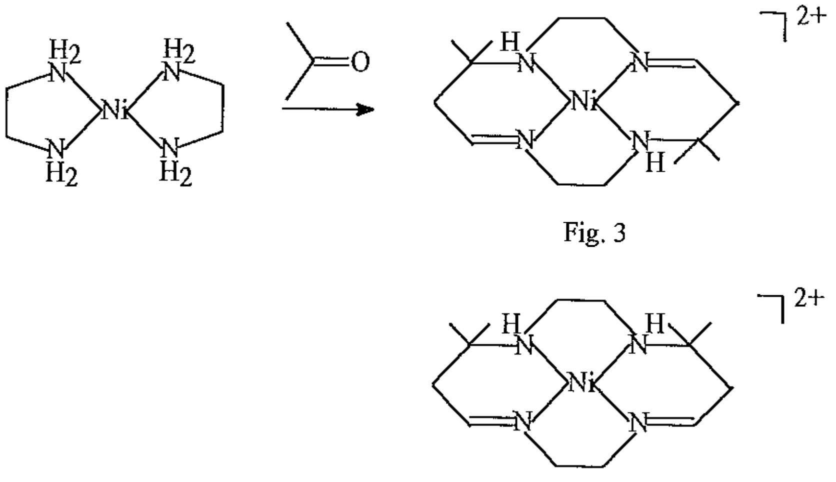


Fig. 3

Fig. 4

Scheme 1. Illustration of the formation of macrocyclic complexes by the metal template method .

The first example of a delibrate synthesis of a macrocycle using this process was described by Thompson and Busch [32] to synthesize the complex as shown in Scheme 2. The diamine Schiff base macrocycles obtained by the condensation of one molecule of each of the dicarboxyl compounds and diamine precursors have been termed "1+1 " macrocycles and the tetraamine macrocycles obtained by the condensation of two molecules of the dicarboxyl compounds with the two molecules of the diamine moiety have been termed "2+2" macrocycles as a consequence of the number of head and lateral units present [33]. The metal template method for multidentate macrocyclic ligands has been recognized as offering high yielding and selective routes to new ligands [9,28,34] and their complexes [35].

Much of the early work featured the use of transition metal ions in the template synthesis of quadridentate macrocycles. The directional influence of orthogonal d-orbitals was regarded as instrumental in guiding the synthetic pathway [34]. This technique has been extended in the last decade by using organotransition metal derivatives to generate tridentate cyclononane complexes [36].

The synthesis of macrocyclic complexes by the metal template method was extended by the use of s-p block cations as template devices to synthesize penta- and hexadentate Schiff base macrocycles [37] and a range of tetraamine Schiff base macrocycles by the Sheffield [38] and Belfast research groups [33,39].

The template potential of a metal ion in the formation of a macrocycle depends on the cations for sterochemistries in which the bonding d-orbitals are in the orthogonal arrangements. This is exemplified by the observation that neither copper (II) nor nickel(II) acts as template [40] for the pentadentate "1+1" macrocycles (Fig. 6-8) derived by Schiff base condensation of 2,6-diacetylpyridin with triethylenetetraamine, N,N'-bis(3-aminopropyl) ethylenediamine or N,N'-bis(2-aminoethyl)-1,3-propanediamine, respectively.

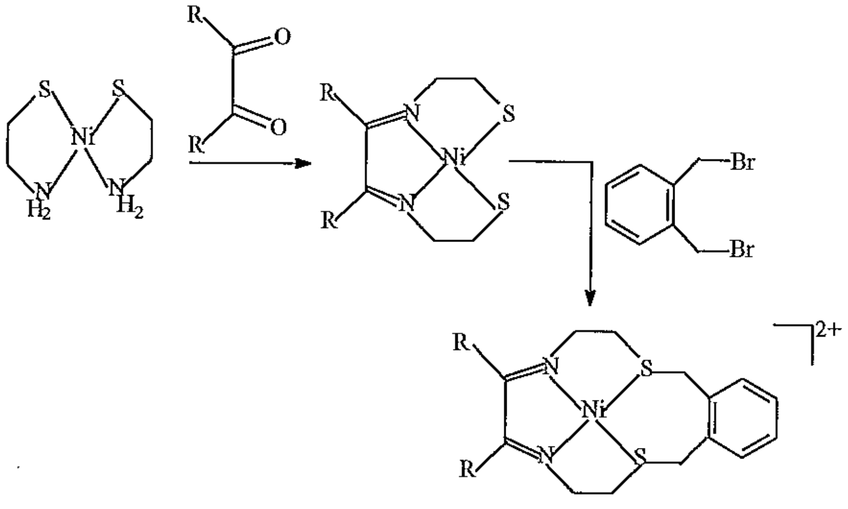


Fig.5

Scheme 2. The first example of a delibrate synthesis of a macrocycle.

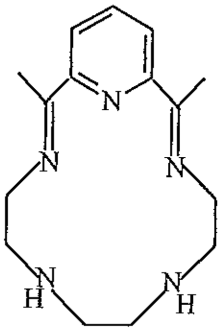


Fig. 6

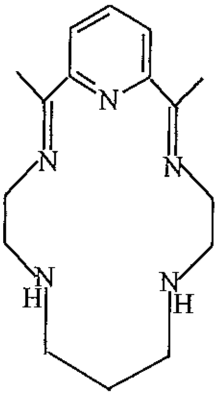


Fig. 7

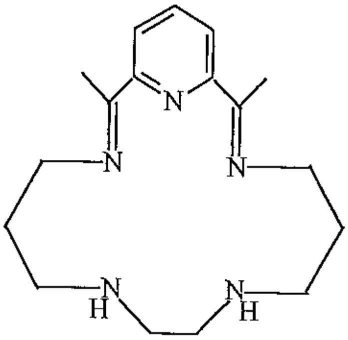


Fig. 8

However, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} serve as effective templates leading to the formation of 7-coordinate complexes (Fig. 6 and Fig. 7) and pentagonal bipyramidal geometries for Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, and Cd^{2+} and 6-coordinate pentagonal pyramidal geometries for Co^{2+}, Cd^{2+}, and Hg^{2+} [41].

In the synthetic path way of macro cycles the size of cation used as template has proved to be of much importance . The compatibility between the radius of the templating cation and the "hole " size of the macrocycle contributes to the effectiveness of the synthetic pathway and to the geometry of the resulting complex. For example, cation of radius less than $0.80A^0$ do not seem to generate complexes as shown in Fig. 8.

Fenton and his co-workers [37,42] demonstrated cation-cavity "best-fit" in the formation of Schiff base macrocycles by synthesizing oxaazamacrocycles using alkaline earth cations as templating device.The smaller metal ion favors the formation of "1+1" macrocycle (Fig. 9) while the larger metal ion favors the formation of "2+2 " macrocycle (Fig. 10) as shown in Scheme 3. Of the alkaline earth cations, for example, only magnesium generates the pentadentate "1+1" macrocycle (Fig. 9) but is ineffective in generating the hexadentate "1+1" macrocycle (Fig. 11) which is readily synthesized in the presence of larger cations such as Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}. The preference for the formation of "1+1" or "2+2" Schiff base macrocycle in the template condensation depends on the cation radius .

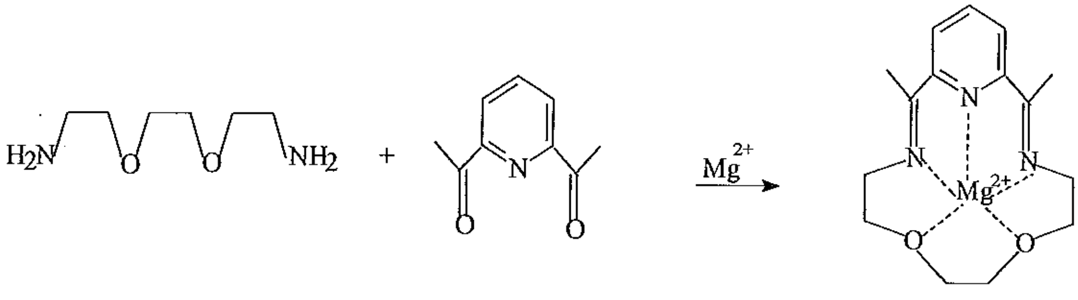
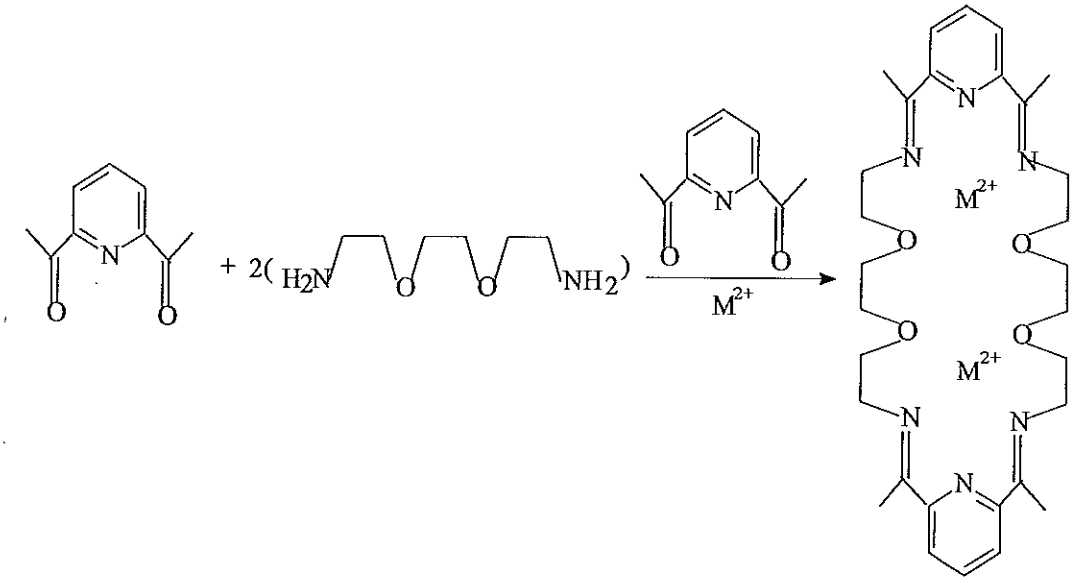
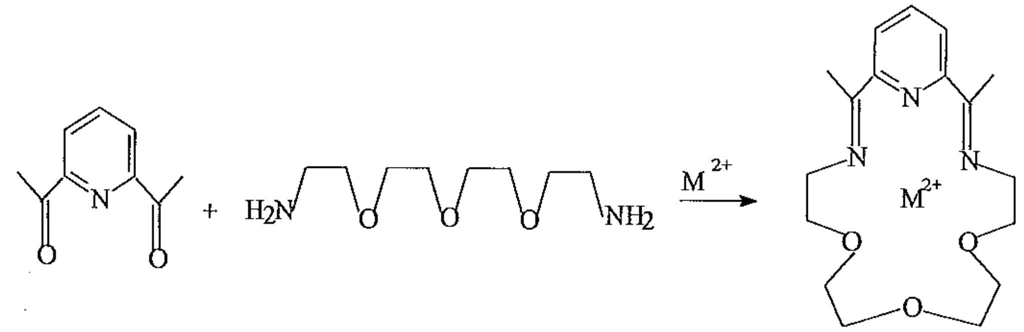


Fig. 9



$M^{2+} = Sr^{2+}$, Ba^{2+}, Pb^{2+}

Fig. 10



$M^{2+} = Ca^{2+}$, Ba^{2+}, Sr^{2+}

Fig. 11

Scheme 3. The formation of Schiff base macrocycles using alkaline earth cations.

2.3 Macrocycles containing amines and amides

The chemistry of synthetic macrocyclic polyamines and macrocyclic dioxopolyamines has been drawing much interest [9,43] due to the fact that these macrocycles form much more stable and selective complexes with various transition metal ions than do open chain analogues having the same donor arrangement. The metal complexes of the 14-membered cyclic tetraamines 1,4,8,11-tetraaza cyclotetradecane (Fig. 12) represent reference systems [44] in the coordination chemistry of aza macrocycles. The synthesis of ligands [45] led the study of their complexes (Fig.13, 14 and 15). Studies of their complexes with transition metal ions [46] reveals that the Cu $^{2+}$ complex of the 14-membered cyclic tetraamine (Fig. 14) is the most stable among the three complexes [43].

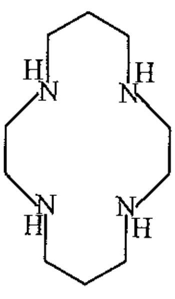


Fig. 12

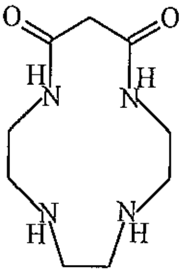


Fig. 13

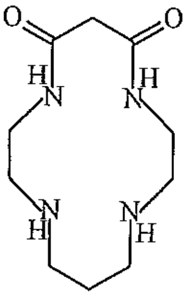


Fig. 14

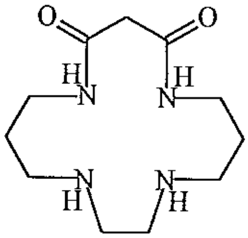


Fig. 15

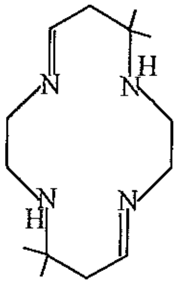


Fig. 16

Majority of nitrogen donor macrocycles that have been studied are quadridentate e.g. ligands as shown in Fig. 12 and 16. In order to fully encircle a first row transition metal ion, macrocyclic ring sizes resulted by 13 and 16 memberes are required provided that the nitrogen donors are spaced such that five, six or seven membered chelate rings are produced on coordination [28].

In view of the presence of two possible potential donor atoms nitrogen and oxygen, the coordination chemistry of amide macrocycles deserve special interest. Very recently, a unique strategy has been adopted for the [47,48] synthesis of amide macrocyclic complexes and a wide variety of tetraza, hexaaza and octaaza macrocyclic complexes bearing amide groups have been prepared (Fig.17-19). Most of them were prepared via the template condensation reaction of "2+2" dicarboxylic acid with di- or tri amines and self condensation of o-amino benzoic acid.

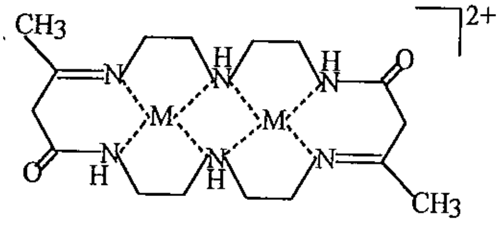


Fig.17

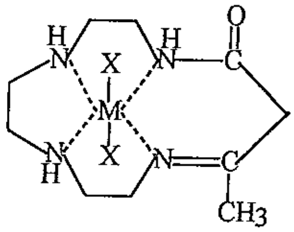


Fig.18

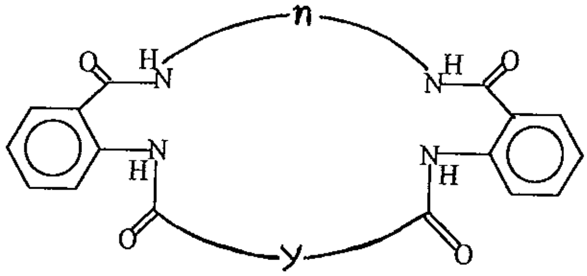


Fig.19

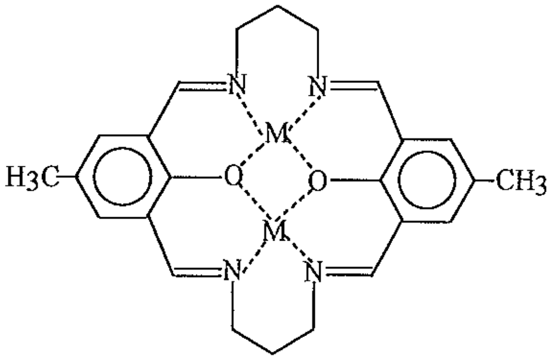


Fig.21

2.5 Macrocyles with pendant arm donor groups

Great efforts have been made in the incorporation of functionalized pendant groups into a saturated macrocyclic tetraamine structure to modify its conformation and redox properties of the metal complexes. Pendant arm macrocycles have been employed in the synthesis of metal-chelating agents for medical applications which makes them resistant to decomplexation [45]. The uses of pendant armed macrocycles, for example in the tagging of tumours using technetium containing macrocycles and covalently bound to an antibody which is specific for the tumour cells or in the production of novel synthetic membrane materials where the reactive function is used to covalently bind the complex to the backbone of a synthetic polymer.

Pendant donor groups have been added to triaza macrocycles, principally 9-aneN_3 which with full substitution on the nitrogen donors gives hexadentate ligands best suited for coordinating to smaller octahedral metal ions. Addition of pendant acetate groups to the nitrogens of tetraazamacrocycles, principally 12-aneN_4 gives octadentate ligands best suited for coordinating larger metal ions [44]. In addition, ligands with pendant donor have been generated by substitution on the nitrogens of mixed donor macrocycles to give differing requirements of geometry and coordination number.

Kimura and his coworkers have reported [52] a few examples of the macrocyclic dioxotetraamines bearing functionalized pendant groups (Fig. 22). Macrocyclic oxotetraamines bear dual structural features of macrocyclic tetraamines and oligopeptides and can stabilize higher oxidation states of some of the transition metal ions [53].

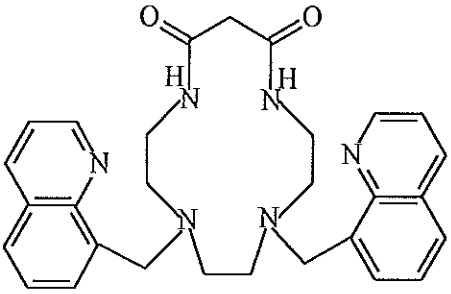
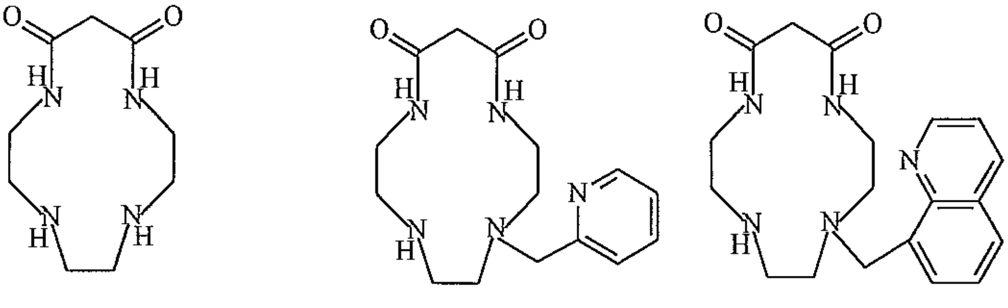


Fig. 22

The above properties have been applied to superoxide - dismutase like catalysts and some of these compounds have been used as metal ion carriers. Hay and his associates [54] studied tetraza system which has a pendant primary amine function, able to coordinate to the metal center. Novel macrocyclic ligands bearing 2-methylpyridine and 8-methylquinoline as additional pendant donors have been reported very recently [55]. It was mentioned that these complexes can remarkably stabilize the trivalent oxidation states of nickel H_2L^1 (Fig. 23) while destabilizing the trivalent oxidation states of copper compared with the unsubstitued H_2L^0.



H_2L^{o}

H_2L^{1}

Fig. 23

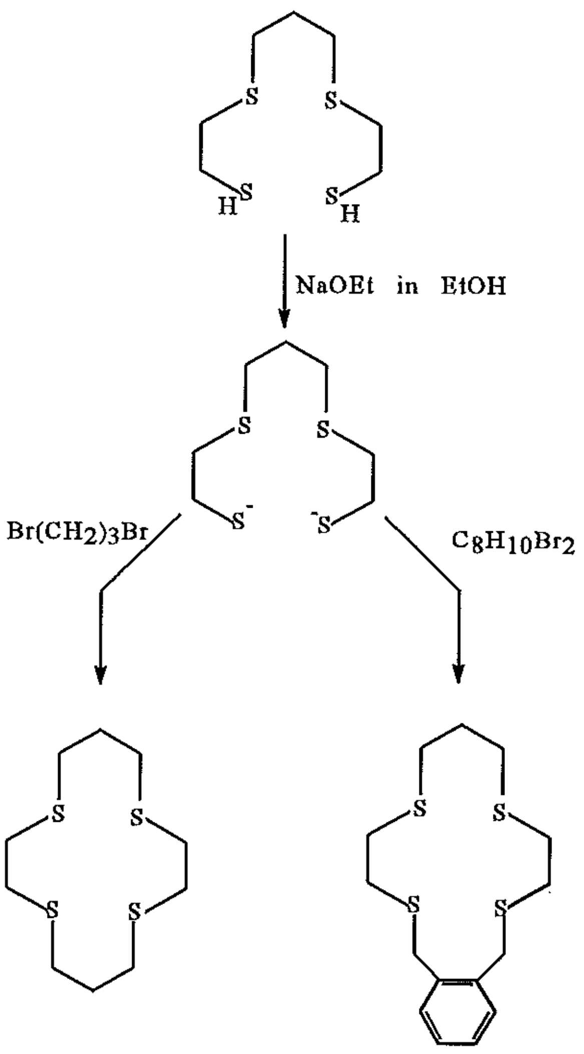
Kanda and his coworkers discussed the preparation and reaction of a tetradentate Schiff base ligand having a pendant thioether function [56]. Stephenson and his co-workers produced [57] a fifteen membered macrocycle bearing a hydroxy group and investigated its reactivity. Recently Busch and his co-workers [58] studied a macrocycle with a pendant pyridyl function which is sterically restricted in its binding to the metal centers.

2.6 Sulfur and phosphorous containing macrocycles

Rosin and Buch [59] have used the reaction sequence in scheme 5 (Fig.24) to prepare the quadridentate macrocycles. The ring closing step gave a 38% yield. Initially the corresponding yield of the sulfur analogue of cyclam was 7.5%, although the reaction was performed at moderate dilution.

Busch and his coworkers have synthesized several sulfur-nitrogen containing macrocycles by in situ methods where a metal ion is present yielding the complex directly. Metal complexes of nickel (II) and cobalt (II) with macrocyclic ligands containing two sulfur and two nitrogen donors, four sulfur and nitrogen donors, two sulfur and four nitrogen donors and one sulfur and four nitrogen donors have been synthesized and in some cases the metal free ligand has also been obtained [60].

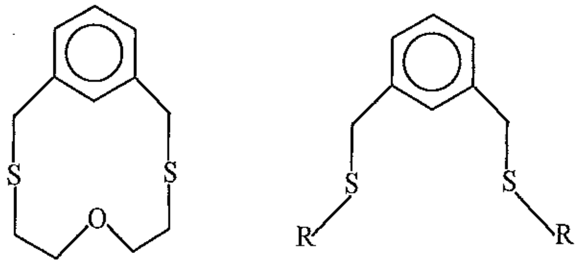
Phosphorous macrocycles are synthesized via the template condensation of coordinated polyphosphine ligands and dibromoalkanes. Experimental difficulties, multistep procedures, low yields, unstability of the formed product etc., probably explained the reason why such a research field did not earlier evoke more interest.



Scheme 5. Preparation of quadridentate macrocycles. Fig. 24

2.7 Macrocyclic complexes containing mixed donor atoms

Novel attention has been devoted in recent years for the development of macrocyclic complexes containing nitrogen-sulfur or nitrogen, sulfur and oxygen donor atoms. Because these macrocyclic complexes which contain the stated donor atoms can stabilize unusual higher oxidation states of metal ions and also can function as a receptors for substrates of widely differing physical and chemical properties. The compounds like $[\{HgL^1(NO_3)\}_2]$, $Cl[\{AgL^2(NO_3)\}_x]$, and $[\ \{CuL^3\}_2\ ]$ also appeared in the literature [61] (Fig. 25) .



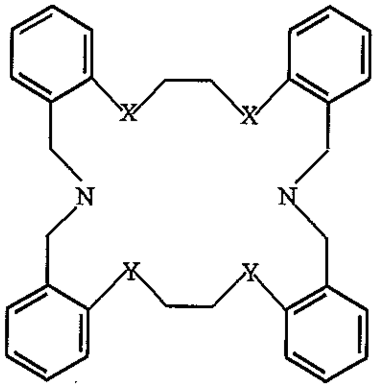
L^1

R = Et; L^2

R = C_6H_5 ; L^3

Fig. 25

Lindoy and his coworkers [62] synthesized a 22-membered macrocyclic ring incorporating mixed (O_4N_2, O_2S_2, and N_2S_4) donor atom sets towards copper(II), silver(I) and lead II) . But the behavior towards silver(I) was a great interest since inherent in the design of these systems are structural features, which appeared likely to enhance their relative affinity for this ion over other ions of interest (Fig. 26).



L^1 ; X = Y = O
L^2 ; X = O , Y = S
L^3 ; X = Y = S

Fig. 26

Funkemier and his coworkers recently, reported [63] 14-membered *trans*-N_2S_2 dibenzo macrocycle (Fig. 27). The well-known ability for *cis*-dithiolate complexes of nickel(II) diamine derivatives to template the synthesis of thioethers and thioether macrocycles have been extensively exploited.

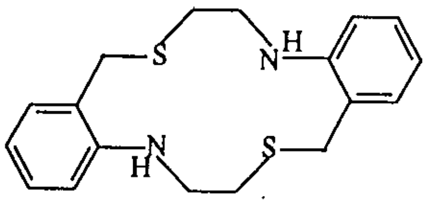


Fig.27

Sellman and his coworkers have been investigating metal complexes with thioether thiolate ligands [64]. The ultimate goal of these investigation are to find complexes that show enzyme like catalytic activity but are capable of existing in the absence of proteins.

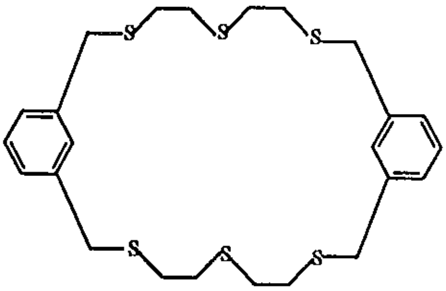


Fig.28

The synthesis of new macrocyclic polythioether ligands and their study of coordinating abilities towards transition metal ions have come into great prominence in the years . It is mainly because of their possible use as models of some metalloprotiens [65]. Extensive work has been reported on the chemistry of aliphatic macrocyclic polythioethers, especially 1,4,7-thiacyclononane and 1,4,7,13,16-hexathiacyclooctadecane ligands which exhibit remarkable complexing properties [66]. Escirche and his co-workers reported [67] the synthesis of a large macro cycle incorporating 6- sulfur atoms into the macro cyclic frame work (Fig.28). The structure of this large macrocycle was determined on the basis of x-ray crystallography.

Thus the field of macrocyclic chemistry have grown rapidly and now a series of macrocyclic ligand and their complexes are available. The chemistry of macrocyclic compounds is an expanding field which needs intensive research and thus thought worth while to carry out some synthesis of novel macrocyclic moieties which may add up to this vast area of knowledge.

The characteristic vibrations for various functional groups associated with the present project are discussed below:

3.1.1 N-H stretching frequency

The N-H stretching vibration occur in the region 3300-3500 cm^{-1} in dilute solution [68]. The N-H stretching band shifts to lower value in the solid state due to extensive hydrogen bonding. Primary amines in dilute solutions, in non-polar solvents give two absorption bands, the first of which due to symmetric stretch is usually found near 3400 cm^{-1}, and the second which corresponds to asymmetrical mode is found near 3500 cm^{-1}. Secondary amines show only a single N-H stretching band in dilute solution in the range 3310-3490 cm^{-1}.

3.1.2 Methyl group vibration

Absorption arising from C-H stretching in the saturated hydrocarbons containing methyl groups showed two distinct bands occurring at 2960 cm^{-1} ($\nu_{asy.}$) and 2870 cm^{-1} ($\nu_{sym.}$).

3.1.3 Amide bands

All amides show a carbonyl absorption band known as the amide I band [69]. Primary amides have a strong amide I band in the region of 1650 cm^{-1} in the solid phase but in dilute solution, near 1690 cm^{-1}. All primary amides show a sharp absorption band in dilute solution (amide II) resulting from NH_2 bending at a lower frequency than the C=O band. A weaker band near 1250 cm^{-1} results from interaction between the N-H bending and C-N stretching (amide III). A band which appears around 650 cm^{-1} is due to C=O deformation (amide IV).

3.1.4 C-N , M-N and M-X stretching frequencies

The C-N stretching absorption gives rise to strong bands in the region 1150-1350 cm^{-1} in all diamines. Different amine complexes exhibited the metal-nitrogen frequencies in the region 300-450 cm^{-1}. Metal-halogen stretching vibrations are generally observed in the low frequency infrared region (200-400 cm^{-1}) [70]. The IR spectra (4000-200 cm^{-1}) were recorded as KBr discs on a Pye -Unicam SP 2000 infrared spectrophotometr.

3.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The NMR spectroscopy is concerned with nuclei having spin quantum I = 1/2, examples of which include ^{1}H , ^{31}P, ^{19}F,etc. For a nucleus with I = 1/2 there are two values for the nuclear spin angular momentum quantum number m = ± ½ which are degenerate in the absence of a magnetic field, in the presence of magnetic field, however, this degeneracy is destroyed such that the positive value of m corresponds to the lower energy state and negative value to higher energy state separated by an energy gap ΔE.

In an NMR experiment, one applies strong homogeneous magnetic field causing the nuclei to precess. Radiation of energy comparable to ΔE is then imposed with radio frequency transmitter is equal to precision or Larmor frequency and the two are said to be in resonance. The energy can be transferred to and from the source and the sample and NMR signal is obtained when a nucleus is excited from low energy to high energy state.

Positions of proton resonances for amines, amides and other groups are [69]:

Aliphatic amines	3.0-0.5 ppm
Aromatic amines	5.0-3.0 ppm
Amides	8.5-5.0 ppm
Methyl group (attached to the carbonyl)	2.0-2.5 ppm

The molar conductance (Λ_m) is related to the conductance value [71] as follows:

$$\Lambda_m = \text{cell constant} \times \text{conductance} / \text{concentration of solute (mol cm}^{-3}\text{)}$$

The electrical conductivities of 1 mM solutions in DMSO were obtained on a Philip Harris conductivity meter equilibrated at 25 ± 1^0 C.

3.5 ELEMENTAL ANALYSIS

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligand as well as its metal complexes. Carbon, hydrogen, and nitrogen analyses were carried out and obtained from Institute of Inorganic Chemistry, Goettingen, Germany.

The metal complexes have been analyzed for metals and chloride. Ni(II) and Cu(II) were estimated gravimetrically [71] as $Ni(DMG)_2$ and Cu(benzoin-α-oxime), respectively. Co(II) and Zn(II) were determined volumetrically with standard EDTA solution [72]. Chloride contents were analyzed as AgCl precipitate.

Thin layer chromatography technique was used to check the purity and formation of ligands. Moisture content determination was also carried out. The melting point of the complexes was determined using a BOCK MONOSCOP apparatus.

4. EXPERIMENTAL SECTION

4.1 *OBJECTIVES*

(i) The prime objective was the synthesis and isolation of interesting polyazamacrocyclic ligands containing amide groups and their complexes.

(ii) Characterization of the isolated products using different spectroscopic techniques.

4.2 *Materials and Methods*

The metal salts, $CoCl_2.6H_2O$ (Aldrich); $NiCl_2.6H_2O$ (BDH); $CuCl_2.2H_2O$ (BDH) and $ZnCl_2$ (Riedel-deHaen) and the chemicals benzidine (Aldrich), formaldehyde (39% solution, BDH) 1,3-diaminopropane (BDH), succinic acid (Aldrich), hydrazine hydrate (80% solution, d = 1.03 kg/l, Riedel-deHaen) were analar grade and used as received. All the reactions were done in methanol medium.

4.3 *Synthesis of the complexes*

A. Synthesis of tetrachloro[1,1'-diphenyl bis(8,11-dioxo-1,3,7,12,16-pentaaza cycloheptadecane)dimetal(II)] [M_2LCl_4], [M=Co(II), Ni(II), Cu(II) and Zn(II)].

To a stirred methanolic (20 mL) solution of benzidine (2.5 mmol, 0.4605 g) taken in a two-necked round bottomed flask were added simultaneously, formaldehyde 39% (10 mmol, 0.75 mL) and 1,3-diaminopropane (10 mmol, 0.862 mL). The mixture was stirred for 2 hrs. This was followed by the addition of a methanolic solution of metal salt (5 mmol), $CoCl_2.6H_2O$ (1.1896 g), $NiCl_2.6H_2O$ (1.1855 g), $CuCl_2.2H_2O$ (0.8524 g) and $ZnCl_2$ (0.6815 g) and succinic acid (5 mmol, 0.5904 g) where a change in color of the solution was noticed.

Furthermore, the reaction mixture was refluxed for 7 hrs.The solid product thus obtained was filtered, washed with methanol, dried in vacuo and kept in a desiccator.

B. Synthesis of dichloro-3,6,9,12,15,18-hexaoxo-1,2,7,8,13,14,19,20, octaazacyclotetraeicosa metal(II), [$MLCl_2$][M=Co(II) and Zn(II)] and Synthesis of 3,6,9,12,15,18-hexaoxo-1,2,7,8,13,14,19,20-octaazacyclotetraeicosa copper(II) chloride, [CuL]Cl_2.

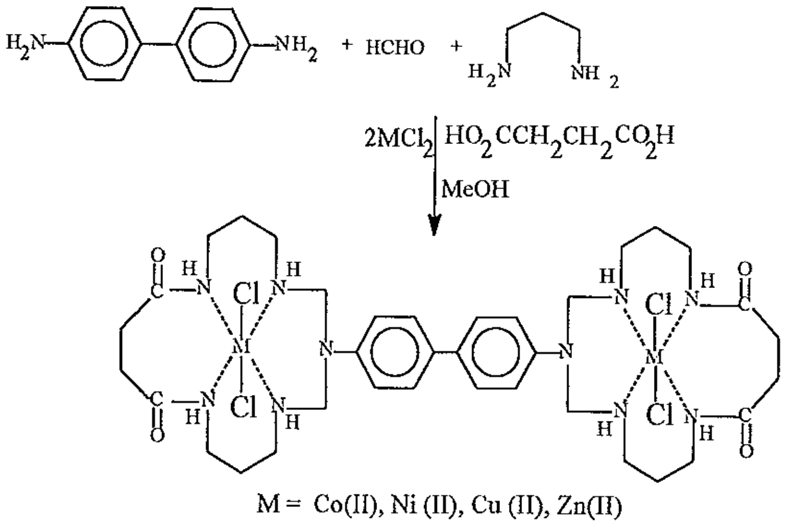
To 5 mmol solution of a metal chloride, $CoCl_2.6H_2O$ (1.1896 g), $CuCl_2.2H_2O$ (0.8524 g) and $ZnCl_2$ (0.6815 g) dissolved in 20 mL of methanol, 20 mmol (1.215mL) of hydrazine hydrate and 20 mmol (2.3646 g) of succinic acid was added simultaneously while stirring. The reaction mixture was kept stirring for about 7 hrs giving a solid material which was filtered, washed with methanol, vacuum dried and kept in a desiccator.

5. RESULTS AND DISCUSSION

Part A

5.1A General

A new series of polyamide bis(macrocyclic) complexes formulated as $[M_2LCl_4]$, [M = Co(II), Ni(II), Cu(II), and Zn(II); L = ligands] have been sythesized from the template condensation of propylenediamine, formaldehyde and benzidine followed by the addition of succinic acid in 4:4:1:2 molar ratio (Scheme 6), respectively. All the complexes exhibit octahedral geometry around the metal ion.



Scheme 6. Synthesis of 17-Membered polyamide bis(macrocyclic) complex.

5.2A Purity of the complexes

The purity of all the complexes were checked by TLC by dissolving the appropriate complex in dimethylformamide and using ethyl acetate (80%) methanol (15%) acetic acid (5%) as eluent. Only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure.

5.3A Physical properties of the complexes

The solubilities of the complexes were examined in common organic solvents. The complexes were found to be slightly soluble in DMSO, MeCN, THF, DMF and $CHCl_3$. However, the complexes were found to be insoluble in EtOH, $C_2H_5OC_2H_5$, CH_3OCH_3, CCl_4 C_6H_6 and C_7H_8. All the complexes are stable to the atmosphere and are polycrystalline in nature. All the complexes have high melting points/decomposition temperatures (Table-1).

Table-1. Colors, melting points/decomposition temperatures and yields of the compounds.

Compounds	Colour	M.pts / Dec.T (⁰C)	Yields (%)
$[Co_2LCl_4]$	Dark brown	268-272	68
$[Ni_2LCl_4]$	Light green	330-334	62
$[Cu_2LCl_4]$	Green	298-303	70
$[Zn_2LCl_4]$	Cream	310-314	64

5.4A Elemental analysis

The results of elemental analyses (Table-2) agree well with the proposed stoichiometry of bis (macrocyclic) complexes. The moisture content of the complexes were also checked as follows. 0.1 g of each sample was taken in different crucible and heated to a temperature of 125°C for 1 hr. Then the change in weight (Δw) was calculated. This was done for a prolonged time and no change in weight was noticed indicating that the complexes are free of moisture.

Table-2 Elemental analysis of the complexes.

Complexes	Found (calc.);% M	Cl	C	N	H
[Co_2LCl_4]	12.0 (12.40)	14.5 (14.90)	46.88 (45.99)	15.47 (15.02)	5.06 (5.46)
[Ni_2LCl_4]	11.8 (12.30)	14.7 (14.90)	46.80 (45.89)	15.45 (15.01)	5.10 (5.50)
[Cu_2LCl_4]	13.1 (13.20)	14.6 (14.80)	46.44 (45.90)	15.39 (15.03)	5.00 (5.40)
[Zn_2LCl_4]	13.0 (13.50)	14.4 (14.70)	46.30 (45.86)	15.39 (15.10)	5.03 (5.34)

5.5A Conductivity results

The low molar conductance values (Table-3) are indicative of non - electrolytic [73] nature of the complexes.

Table-3 Molar conductance value of the compexes.

Complexes	[Co_2LCl_4]	[Ni_2LCl_4]	[Cu_2LCl_4]	[Zn_2LCl_4]
Λ_m (cm^2 Ω^{-1} Mo^{-1})	20	14	22	15

5.6A Infrared spectral studies

The important IR spectral results are presented in Table-4. In all the complexes, two single sharp bands observed in the regions 3220-3300 and 3200-3240 cm^{-1} which may be assigned sharp bands observed in the regions 3220-3300 and 3200-3240 cm^{-1} which may be assigned to ν(N-H) of the secondary amine and coordinated amide group respectively [74]. In addition to the above information, the most important feature of the IR spectra of the complexes is the absence of bands assignable to primary amino or hydroxy group stretching modes.The amide bands which were identified in the 1680-1730,1460-1550,1230-1280 and 650-690 cm^{-1} regions may reasonably, be assigned [75] to amide I [ν(C=O)], amide II [ν(C-N)+δ(N-H), amide III [δ(N-H)] and amide IV [ϕ(C=O)] bands respectively.

All the complexes gave bands around 1170 cm^{-1} which may be assigned to the ν(C-N) vibration [76]. All the complexes show bands around 2920 and 1440cm^{-1} corresponding to ν(C-H) and δ(C-H) vibrations. All the complexes show bands around 260-350 cm^{-1} assignable to ν(M-Cl) vibration [77]. The appearance of bands in the 420-460 cm^{-1} region in all the complexes corresponding to ν(M-N) vibration confirm the involvement of the nitrogen in coordination [76]. Bands appearing in the regions 1410-1460,1070-1100 and 720-760 cm^{-1} are the usual modes of the phenyl ring vibrations [78].

Table -4. Infrared Spectroscopic data (cm^{-1}) of the complexes and their band assignments.

			Amide Bands							Ring
Complexes	ν(N-H)	ν(C-H)	I	II	III	IV	ν(C-N)	ν(M-N)	ν(M-Cl)	vibrations
[Co_2LCl_4]	3280,3200	2900	1685	1470	1250	670	1170	450	270	1430,1050,760
[Ni_2LCl_4]	3290,3230	2880	1690	1450	1270	680	1160	420	300	1420,1040,730
[Cu_2LCl_4]	3270,3220	2870	1680	1470	1225	650	1180	410	280	1410,1030,750
[Zn_2LCl_4]	3300,3240	2990	1690	1450	1230	670	1175	450	325	1450,1060,740

5.7A Electronic spectral studies

The cobalt complex shows two bands appearing in the regions 13,700-14250 centerd at 14,000 cm^{-1} and 21,850-22,450 cm^{-1} centered at 22,340 cm^{-1} corresponding [79-81] to $^4T_1$ (F)→$^4A_2$ (F) and $^4T_1$(F)→ $^4T_1$ (P) transitions, respectively consistent with the presence of octahedral geometry around the cobalt (II) ion (Table-5). Two bands appearing for the nickel complex in the regions 20,100-20,600 centered at 20,400 cm^{-1} and 25,600-27,000 cm^{-1} centered at 26,000 cm^{-1} may be assigned [79-81] for $^3A_2$ (F)→ $^3T_1$ (F) and $^3A_2$ (F)→ $^3T_1$ (P) transitions respectively,suggesting an octahedral geometry of nickel (II) ion. The electronic spectra of the copper complex shows a broad band maxima around 19,900-20,400 cm^{-1} centered at 20,300 cm^{-1} with a shoulder on the low energy side about 16,300-16,500 cm^{-1} centered at 16,300 cm^{-1} which may unambiguously be assigned to the $^2B_1$→ ^2E and $^2B_1$ → $^2B_2$ transitions respectively, corresponding to a distorted octahedral geometry around the copper ion [81]. All complexes exhibit a high intensity band around 35,200 cm^{-1} which may be due to the charge transfer transition [82].

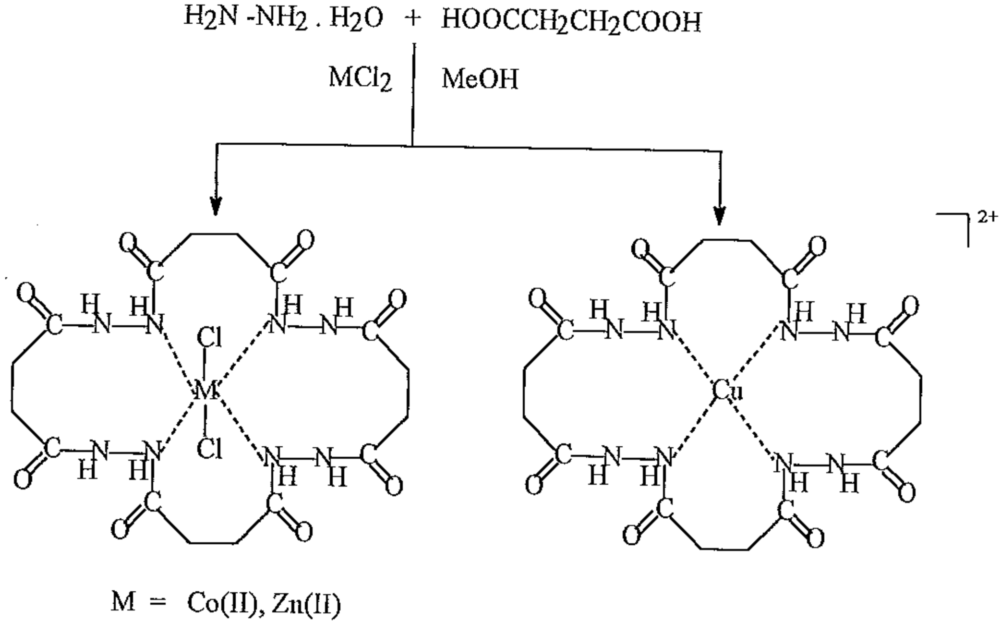
Table-5 Electronic spectral data, λ_{max} (cm^{-1}) of the complexes and their possible band assignments.

Complexes	Band positions	Assignments
[Co_2LCl_4]	14,000	$^4T_1$ (F) →$^4A_2$ (F)
	22,340	$^4T_1$ (F) → $^4T_1$ (P)
[Ni_2LCl_4]	20,400	$^3A_2$ (F) → $^3T_1$ (F)
	26,000	$^3A_2$ (F) → $^3T_1$ (P)
[Cu_2LCl_4]	16,300	$^2B_1$ → $^2B_2$
	20,300	$^2B_1$ → ^2E

Part B

5.1B General

A new series of polyamide macrocyclic complexes $[MLCl_2]$ and $[CuL]Cl_2$ where [M = Co(II) and Zn(II) and L = Ligands] have been prepared by the template condensation reaction of hydrazine hydrate and succinic acid with metal ion in methanol medium in a 4:4:1 molar ratio, respectively. An octahedral geometry were suggested for the cobalt(II) and zinc(II) complexes, while a square planar geometry was proposed for the copper complex.



Scheme 7. Synthesis 24-Membered polyamide macrocyclic complex.

5.2B Purity of the complexes

The purity of all these complexes were also checked by TLC by dissolving the appropriate complex in dimethylformamide and using ethyl acetate (80%) methanol (15%) acetic acid (5%) as eluent. Only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure.

5.3B Physical properties of the complexes

The solubilities of these complexes were also examined in common organic solvents. The complexes were found to be slightly soluble in DMSO, MeCN, THF, DMF and $CHCl_3$. However, the complexes were found to be insoluble in EtOH, $C_2H_5OC_2H_5$, CH_3OCH_3, CCl_4 C_6H_6 and C_7H_8. All the complexes are stable to the atmosphere and are polycrystalline in nature. All the complexes have high melting points/decomposition temprature (Table-6).

Table-6. Colours, melting points/decomposition tempratures and yields of the compounds.

Compounds	Colour	M.pt / Dec.t (^0C)	Yield (%)
$[CoLCl_2]$	Rose	330-334	54
$[CuL]Cl_2$	Dark green	320-325	65
$[ZnLCl_2]$	White	280-286	58

5.4B Elemental analysis

The results of elemental analysis (Table-7) corresponds to 1:1 metal to ligand stoichiometry which agree with the mononuclear structure as shown in scheme 2. The moisture content of the complexes were also checked as follows. 0.1g of each sample was taken in different crucible and heated to a temperature of 125°C for 1 hr. Then the change in weight (Δw) was calculated. This was done for a prolonged time and no change in weight was noticed indicating that the complexes are free of moisture.

Table-7. Elemental analysis of the complexes.

	Found (calc.);%				
Complexes	M	Cl	C	H	N
[$CoLCl_2$]	10.24 (10.10)	12.05 (12.10)	32.57 (32.44)	3.99 (4.10)	18.98 (18.78)
[CuL]Cl_2	10.77 (10.75)	12.0 (12.00)	32.46 (32.40)	4.71 (4.30)	18.99 (18.87)
[$ZnLCl_2$]	10.89 (11.00)	11.7 (11.90)	32.40 (32.35)	4.10 (4.20)	18.95 (18.91)

5.5B Conductivity results

The molar conductance values for Co(II) and Zn(II) complexes in DMSO were indicative [73] of their non-electrolytic nature but a higher molar conductance value for copper complex suggest its 1:2 electrolytic nature (Table-8).

Tabler-8. Molar conductance value of the complexes.

Complexes	[$CoLCl_2$]	[CuL]Cl_2	[$ZnLCl_2$]
Λ_m ($cm^2\ \Omega^{-1} mol^{-1}$)	24	105	14

5.6B Infrared spectral results

The Infrared spectral results (Table-9) of the complexes gave strong evidence for the formation of the proposed ligand framework. The absence of bands characteristic of primary amino or hydroxy groups and the appearance of bands corresponding to an amide group provide, strong evidence for the presence of a closed cyclic product bonded through amide nitrogens.

Two single sharp band observed for all the complexes in the regions 3230-3300 and 3200-3240 cm^{-1} may be assigned to ν(N-H) of the coordinated amide and the uncoordinated amide group, respectively. The lowering of N-H frequency of the uncoordinated amide group (~50 cm^{-1}) in comparison to that of the coordinated amide group indicates [74] that the lone pairs of electrons on the nitrogen atoms can delocalize making the hydrogen atoms loosely attached to it and hence results in decreasing of its vibrational frequency, whereas the lone pairs of electrons on the coordinated nitrogen atom can no longer delocalize.

The amide bands which were identified in the 1675-1725, 1460-1550, 1230-1270 and 650-690 cm^{-1} regions may reasonably be assigned [75] to an amide I [ν(C=O)], amide II [ν(C-N)+δ(N-H), amide III [δ(N-H)] and amide IV [ϕ(C=O)] bands, respectively. Bands observed in the region 1160-1200 cm^{-1} may reasonably be assigned to (C-N) stretching vibrations [76]. However, it could not be possible to distinguish between the coordinated and uncoordinated amide groups though it is expected to get two types of amide bands in the IR spectra. This may be due to the fact that the bands were not well resolved.

The appearance of bands in the 410-450 cm^{-1} region in all the complexes correspond to ν(M-N) vibration [76]. All the complexes, except for copper, show band at 280-350 cm^{-1} assigned to ν(M-Cl) vibration [77].

Table-9. Infrared spectroscopic data (cm^{-1}) of the compounds and their band assignments.

			Amide Bands						
Compounds	ν(N-H)	ν(C-H)	I	II	III	IV	ν(C-N)	ν(M-N)	ν(M-Cl)
[$CoLCl_2$]	3300,3220	2920	1680	1490	1225	680	1175	420	325
[CuL]Cl_2	3290,3240	2870	1685	1510	1255	670	1160	450	-
[$ZnLCl_2$]	3300,3240	2900	1700	1530	1260	665	1180	440	300

5.7B Electronic spectra

The electronic spectra (Table -10) of cobalt (II) complex shows two bands appearing in the 13,700-14,255 cm^{-1} centered at 13,980 cm^{-1} and 21,900-22,800 cm^{-1} centered at 22,500 cm^{-1} regions corresponding to $^4T_1(F) \rightarrow {}^4A_2(F)$ and $^4T_1(F) \rightarrow {}^4T_1(P)$ transitions, respectively. This is consistent with the presence of octahedral geometry around the cobalt(II) ion [79-81].The electronic spectra of copper complex shows a broad band around15,800-16,200 cm^{-1} centered at 16,000 cm^{-1} attributable [79] to $^2B_1 \rightarrow {}^2A_1$ transition. However, two weak shoulders appearing in the regions 19,900-20,400 cm^{-1} centered at 20,000 cm^{-1} and 12,150-13,500 cm^{-1}centered at 12,500 cm^{-1} may be ascribed to $^2B_1 \rightarrow {}^2E$ and $^2B_1 \rightarrow {}^2B_2$ transitions, respectively, which suggest a square planar geometry around the copper(II) ion.

Table-10. Electronic spectral data, λ_{max} (cm^{-1}) of the complexes and their band assignments.

Complexes	Band positions	Assignments
$[CoLCl_2]$	13,980	$^4T_1(F) \rightarrow {}^4A_2(F)$
	22,500	$^4T_1(F) \rightarrow {}^4T_1(P)$
$[CuL]Cl_2$	12,500	$^2B_1 \rightarrow {}^2B_2$
	16,000	$^2B_1 \rightarrow {}^2A_1$
	20,000	$^2B_1 \rightarrow {}^2E$

5.8B ^1H NMR spectral data

The ^1H NMR spectrum of the Zn(II) complex shows a broad signal in the region 8.0- 8.8 ppm which may be assigned to [83] amide (CO-NH, 8H) protons. A broad signal in the region 2.20 -3.22 ppm is due to the methylene protons of [84] a dicarboxylic acid moiety ($CO-(CH_2)_2-CO$, 16H). However, D_2O exchange studies would be required for further details.

6. CONCLUSSION

The synthesis of polyazamacrocyclic complexes bearing polyamide groups has been achieved by involving template condensation reactions. The above method was adopted in view of restrictions imposed by metal ion for possible modes of coordination and is an efficient route to synthesize macrocyclic complexes in good yield (*ca* 70%). However, attempts to prepare metal free macrocyclic ligands were unsuccessful. Although, the proposed macrocyclic complexes have been characterized on the basis of number of physico-chemical data but application part could not be achieved due to the lack of time and facilities.

REFERENCES

1. Pederson, C.J., *J. Am. Chem. Soc.*, **1967**, 89, 2459.
2. Curtis, N.F., *J. Chem. Soc.*, **1960**, 4409.
3. Reid, G.; Schroder, M., *Chem. Soc. Rev.*, **1990**,19, 239.
4. Clay, R.M.; Corre, S.; Micheloni, M.; Paoletti, P., *Inorg .Chem.*, **1985**, 24, 3330.
5. Cotton, F.A.; Wilkinson, G., *Adv. Inorg. Chem.,* **1988**, 5th ed p.344.
6. Champbell, V.D.; Parson, E.J.; Pennington, W.T., *Inorg. Chem.*, **1993**, 32, 1773.
7. Cabbines, D.K.;Margerum, D.W., *J. Am. Chem.*, **1969**, 91, 6540.
8. Hinz, F.P.; Margerum, D.W., *Inorg. Chem.*, **1974**, 13, 2941.
9. Lindoy, L.F., " *The Chemistry of Macrocyclic Ligand Complexes*" Cambridge University Press, Cambridge, **1989**.
10. Thompson, M.C.; Busch, D.H., *J. Am. Chem. Soc.*, **1964**, 86 ,3561.
11. Vorlonder, D. ; Juslus, D., *J. Am. Chem. Soc,* **1894** , 280,167.
12. Carothers, W.H.; Arin, J.A.; Dorough, G.L., *J. Am. Chem. Soc.,* **1930**, 52, 3292.
13. Spanaged, E.W., *French Patent*, **1936**,796,410, *Chem. Abstr.*, **1936**, 30, 6138
14. Bacyer, A., *Ber.*, **1886**,19,2184.
15. Kodama, M.; Kimura, E., *J. Chem. Soc., Dalton Trans,* **1980**, 327.
16. Zinic, M.; Skaric, V., *J. Org. Chem.*, **1988**, 53, 2582.
17. Drago, R.S.; Corden, B.B.; Barnes, C.W., *J. Am. Chem. Soc.,* **1986**, 108, 2453.
18. Kimura, E.; Yatsunami, T., *Chem. Pharm. Bull.,* **1980**, 28, 994.
19. Collman, J.P.; Hendricks, N.H.; Leidnr, C.R.; Ngameni, E.; Her, N.L., *Inorg.Chem.*, **1988**,27,387.
20. Lauffer, R.B., *Chem. Rev.,* **1987**, 87, 901.
21. Cox, J.P.L.; Jankowski, K.J.; Kataky, R.; Parker, D.; Eaton, M.A.; Beelay, N.R.; Millican, A.T.; Walker, C., *J. Chem. Soc.,Chem. Commun.*, **1989**, 797.
22. Lever, A.B.P.; Hemsted, M.R.; Lenzoff, C.C.; Melnik, W.L.M.; Nevin,W.A.; Seymour, P., *Pure and Appl. Chem.*, **1986**, 58, 1467.
23. Tinken, M.D.; Marriff, W.A.; Gagne, R.R.; Sim, E., *Inorg. Chem.*, **1985**, 24, 4204.

24. Kodama, M.; Kimura, E., *J. Chem. Soc., Dalton Trans.*, **1979**, 325.

25. Christenson, J.J.; Eatough, D.J.; Izatt, R.M., *Chem. Rev.*, **1974**, 74.

26. Black, D.S.C.; Mclean, I.A., *Tettrahedron Lett.*, **1969**, 3961.

27. Shaw, B.L, *J. Am. Chem. Soc.*, **1975**, 97, 3856.

28. Lindoy, L.F.; Busch, D.H. In "*Prepartive Inorganic Reactions*", Jolly,W.L., Ed.; Wiley-Interscience: NewYork , **1971**,6,1.

29. Rest, A.J.; Smith, S.A. Tyler, I.D., *Inorg. Chem. Acta.*, **1976**, 16, 1.

30. Cabrol, J.; Cabnal, M.F.; Drew, M.J.B.; Rodgers, A.; McCann, M.; Nelson, S.M., *J. Chem. Soc., Dalton Trans.*, **1979**,414.

31. House, D.H. ; Curtis, N.F., *Chem. India.*, **1961**, 1708.

32. Thompson, M.C.;Busch, D.H., *J. Am. Chem. Soc.*, **1964**, 86, 3651.

33. Nelson, S.M., *Pure and Appl. Chem.*, **1986**, 52, 2461.

34. Fenton, D.E.; Vigato, P.A., *Chem. Soc. Rev.* , **1988**,17,69.

35. Comba, P.C. ; Curtis, N.F.; Lawerenc, G.A.; Sargenson, A.M.; Shelton, B.W. White, A.H., *Inorg. Chem.*, **1986**,88,760.

36. Diel, B.N. ; Haltiwanger, R.C.; Orman, A.D., *J. Am. Chem. Soc.*, **1982**, 104, 4700.

37. Cook, D.H.; Fenton, D.E., *J. Chem. Soc., Dalton Trans.*, **1979**, 810.

38. Fenton, D.E.; Cook, D.H.; Nowell, I.W.; Walker, P.E., *J. Chem. Soc.Chem. Commun.*, **1978**,279.

39. Drew, M.G.B.; Rodgers, A.; McCann, M.; Nelson, S.M., *J. Chem. Soc.Chem. Commun.*, **1978**, 415.

40. Carins, C.; McFall, S.G. ; Nelson, S.M.; Drew, M.G.B., *J. Chem. Soc. Chem. Commun.*, **1979**,446.

41. Drew, M.G.B.; Othman, A.H.; McFall, S.G.; Mcllory, P.D.A.; Nelson, S.M., *J. Chem. Soc. , Dalton Trans.*, **1977**,1173.

42. Fenton, D.E.; Cook, D.H.; Drew, M.G.B.; Rodgers, A.; McCann, M.; Nelson, S.M., *J. Chem. Soc., Dalton Trans.*, **1979**, 414.

43. Kodama, M.; Kimura,E., *J. Chem. Soc., Dalton Trans.*, **1979**,325.

44. DeBlass, A.; DeSantis, G.; Fabbrizzi, L.; Lichelli, M.; Lanfredi, A.M.M.; Marosivi,

P.; Pallovicin, P; Ugozozoli, F., *J. Chem. Soc., Dalton Trans.*, **1993**,1411.

45. Yatsunami, T.; Sakonaka, A.; Kimura, E., *Anal. Chem.*, **1981**, 53, 477.

46. Sigel, H.; Martin, R.B., *Chem. Rev.*, **1982**, 82, 305.

47. Shakir, M.; Mohamed, A.K.; Nasman, O.S.M., *Polyhedron*, **1996**, 15, 3487.

48. Shakir, M.; Nasman, O.S.M.; Mohamed, A.K.; Varkey, S.P., *Indian J. Chem*, **1996**, 35A, 710.

49. Goedeken, V.L.; Peng, S.M., *J. Chem. Soc., Chem. Commun.*, **1973**,62.

50. Pilkington, M.H.; Robson, R., *Aust. J.chem.*, **1970**, 23, 2225.

51. Fraser, C.; Johnston, L.; Rheingold, A.L.; Haggertg, B.S.; Williams, G.K.; Whelan.J.; Bosinch, B., *Inorg. Chem.*, **1992**, 31, 1835.

52. Bu, X.H.; An, D.L.; Chen, Y.T.; Shinoya, M.; Kimura, E., *J. Chem. Soc., Dalton Trans.*, **1995**,2289 and references cited there in.

53. Fabbrizzi, L.; Perotti, A.; Poggi, A., *Inorg. Chem.*, **1983**, 22, 1411.

54. Hay, R.W.; Pugan, M.P.; Daskiewicz, B.K.; Ferguson, G.; Ruli, B.L., *J. Chem.Soc., Dalton Trans.*, **1989**,85.

55. Bu, X.H.; An, D.L.; Cao, X.C.; Chen, Y.T.; Shinoya, M.; Kimura, E., *Polyhedron*, **1996**,15,161.

56. Kanda, W.; Okawa, H.; Kida, S.; Goral, J.; Nakamato, K., *Inorg. Chem. Acta.*, **1988**, 146, 193.

57. Stephenson, N.A.; Tweedy, H.E.; Busch, D.H., *Inorg. Chem.*, **1989**, 28,4376.

58. Tweedy, H.E.; Alcock, N.W.; Matsumoto, N.; Padloik, P.A.; Stephenson, N.A.; Busch, D.H., *Inorg. Chem.*, **1990**, 29, 616.

59. Busch, D.H.; Lindoy, L.F.; Rosin, R, *J. Chem. Soc., Chem. Commun.*, **1968**, 1589.

60. Blinn, E.L.; Busch, D.H., *Inorg. Chem.*, **1968**, 7, 820.

61. Romero, I.; Scastello, G.; Teixidor, F.; Whitaker, C.R.; Rius, J.; Miravitlles, C.; Flor, T.; Escriche, L.; Casabo, J., *Polyhedron*, **1996**,15,2057.

62. Ahearn, M.; Kim, J.; Leong, A.J.; Lindoy, L.F.; Mathews, O.A.; Meehan, G.V., *J. Chem. Soc., Dalton Trans*, **1996**,3591.

63. Funkemeier, D.; Matles, R., *J.Chem. Soc. , Dalton Trans.*, **1993**, 1313.

64. Sellmann, D.; Hoffmann, T.; Konch, F.Z., *Nature,* **1994**, 496, 821.

65. Solomon, E.I.; Penfield, K.W.; Wilcox, D.E., *Struct.Bonding* (Berlin), **1983**, 53,1.

66. Blake, A.; Schroder, M., *Adv. Inorg. Chem.*, **1990**, 72, 1.

67. Escriche, L.; Amajiano, M.; Casabo, J.; Teixidor, F.; Lockhart, J.C.; Forsyth, G.A.; Kivekas, R.; Sundberg, M., *Polyhedron,* **1996**, 15, 4203.

68. Bellamy, L.J., " *The Infrared Spectra of Complex Molecules,*" John Wiley and Sons, NewYork, **1958**.

69. Silverstein, R.M., " *Spectrometric Identification of Organic Compounds,*" 4th Ed. John Wiley and Sons, NewYork, **1981**.

70. Nakamato, K., "*Infrared and Raman Spectra of Inorganic and Coordination Compounds,*" John Wiley and Sons, NewYork, **1978**.

71. Vogel, A.I., "*Text Book of Inorganic Analysis,*" Longmans, London, **1961**, 433.

72. Reilly, C.N.; Schmid, R.W.; Sadek, F.A., *J. Chem. Educ.***1959**, 36, 555.

73. Geary, W., *J. Coord. Chem. Rev.*, **1971**, 7, 81.

74. Roska, S, V.; Lampeka, Y.D.; Maloshtan, I.M., *J. Chem. Soc., Dalton Trans.*, **1993**,631.

75. Pandy, U.K.; Pandy, O.P.; Sengupta, S.K.; Tripathi, S.C., *Polyhedron,* 1987, 6,1611.

76. Nakamoto, K., *"Infrared Spectra of Inorganic and Coordination Compounds"*, Wiley Interscience, New York, **1970**.

77. Rana, V.B.; Singh, D.P.; Teotia, M.P., *Polyhedron,* **1982**, 1, 377.

78. Shakir, M.; Kumar, D.Varkey, S.P., *Polyhedron,* **1992**, 11, 2831

79. Lever, A.B.P., *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, **1984**.

80. Figgis, B.N., *Ligand* Fields, **1966**.

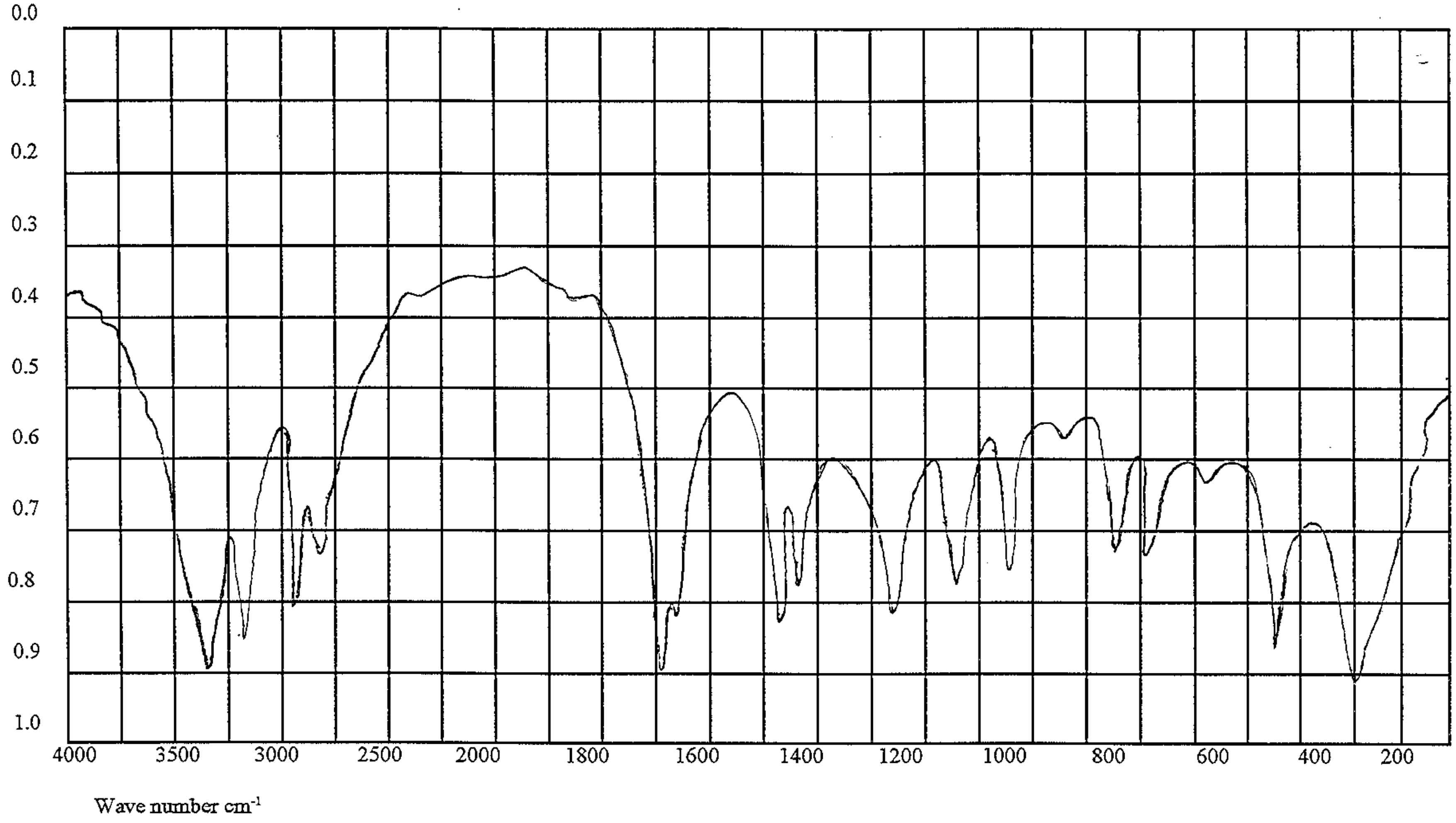
81. Baldwin, D.A.; Lever, A.B.P.; Parish, R.V., *Inorg. Chem.*, **1969**, 8, 107

82. Tait, A.M.; Busch, *D.H., Inorg. Chem.*, **1976**, 15, 197

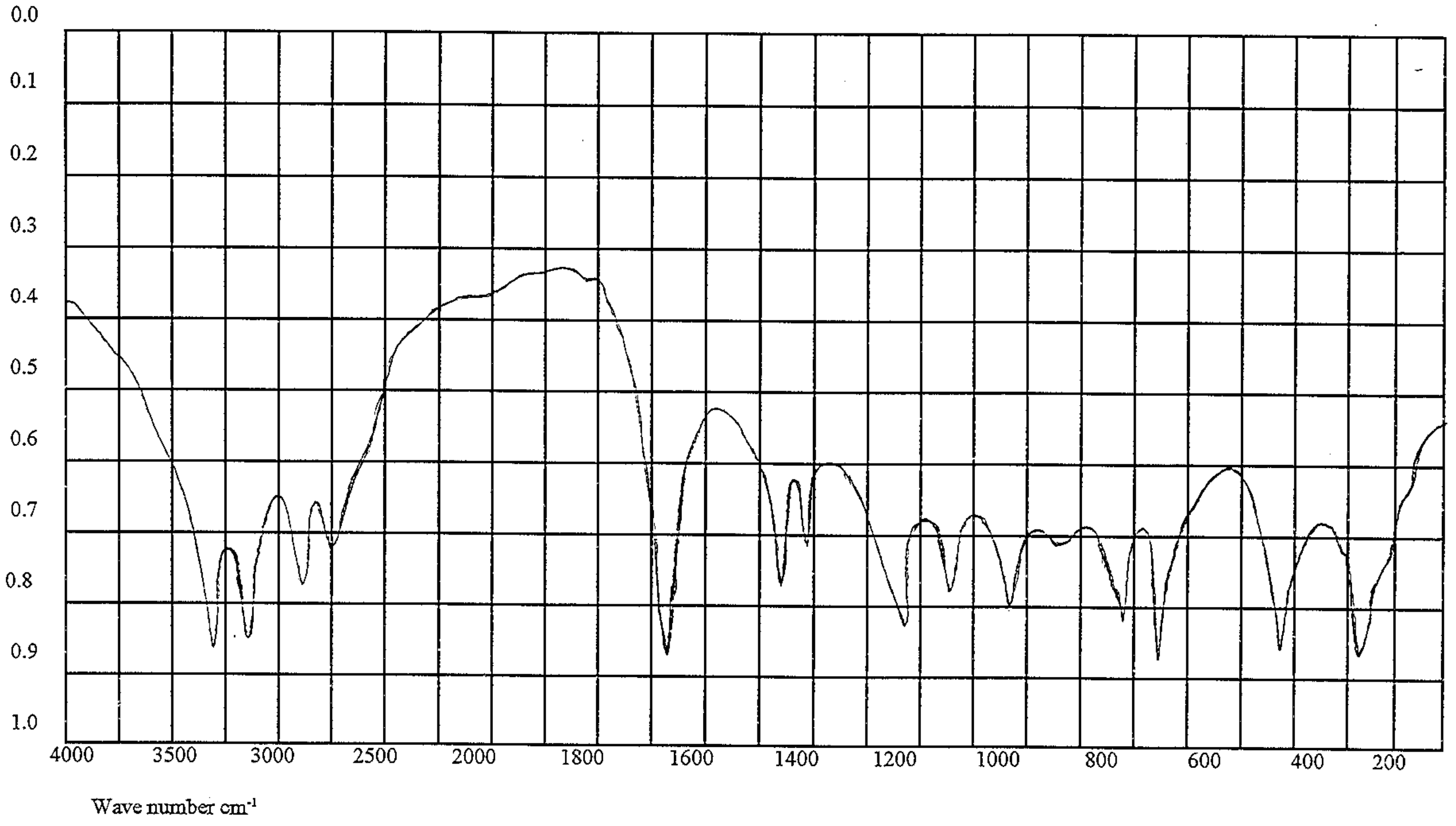
83. Parker, D.; Pulukkody, K.; Smith, F.C.; Batsanor, A.; Howard, J.A., *J. Chem. Soc., Dalton Trans.*, **1994**, 698.

84. Tabushi, I.; Taniguchi, Y.; Kato, H., *Tetrahedron Lett.*, **1977**, 12, 1049.

APPENDICES



Infrared Spectrum of [$Ni_2L Cl_4$]



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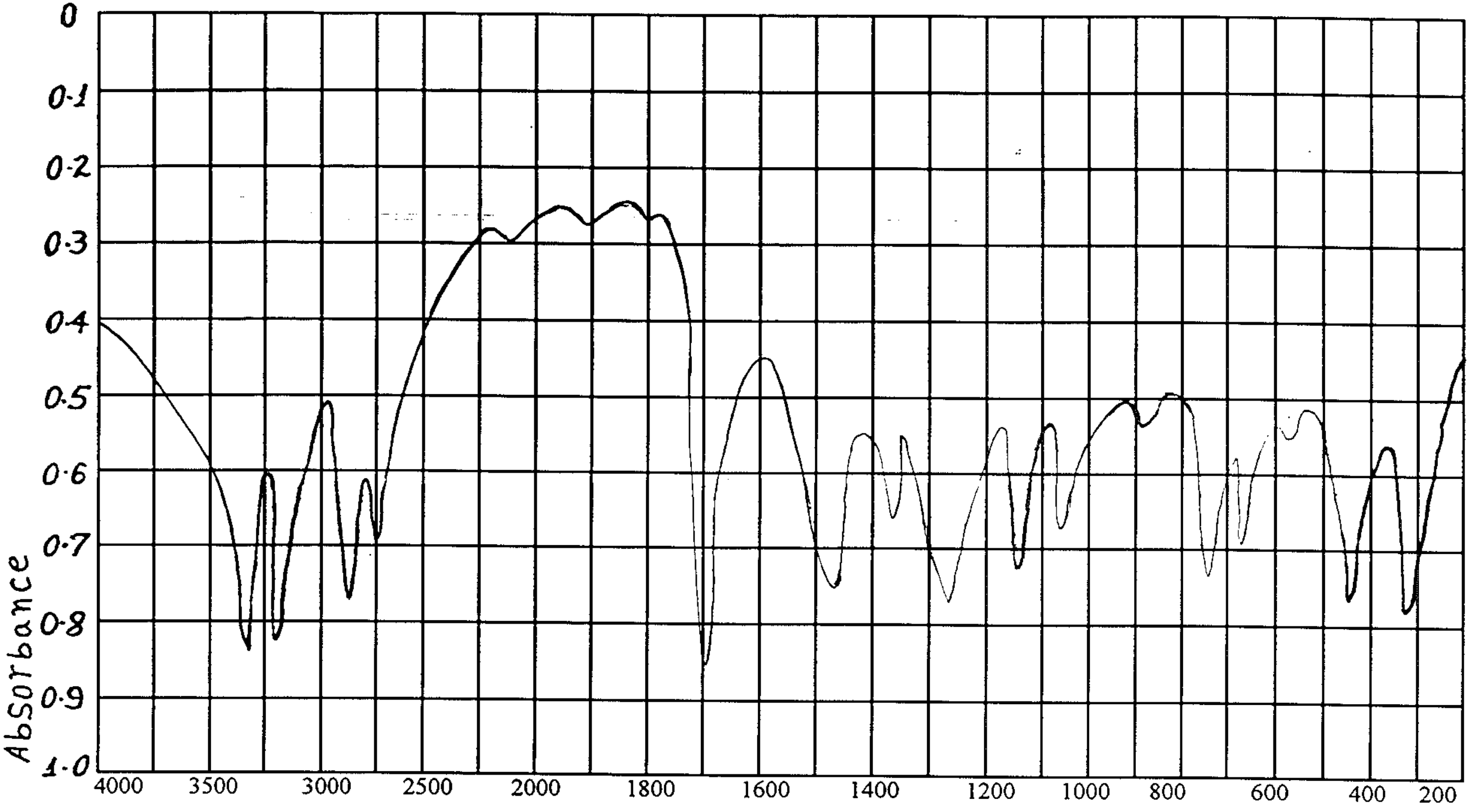
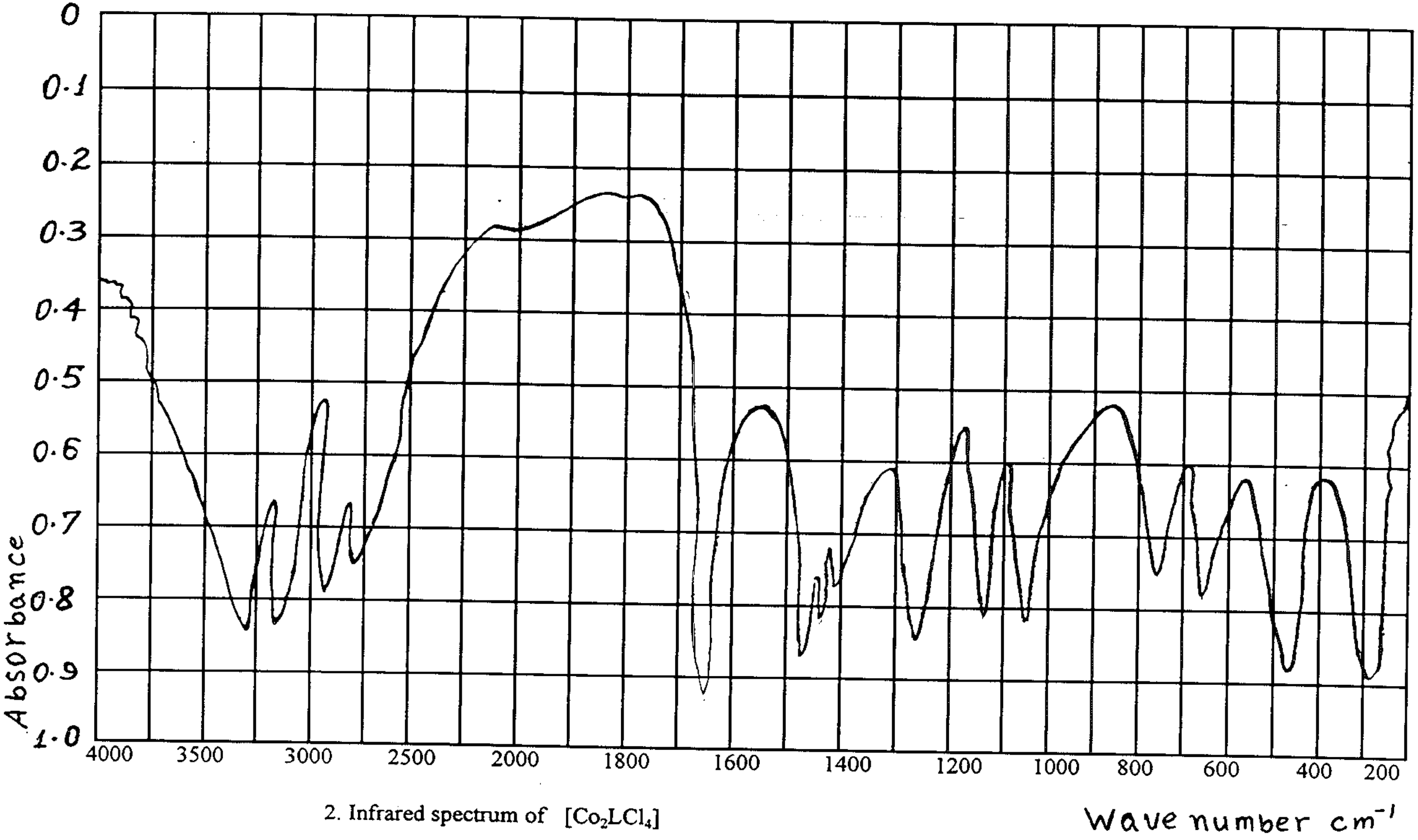
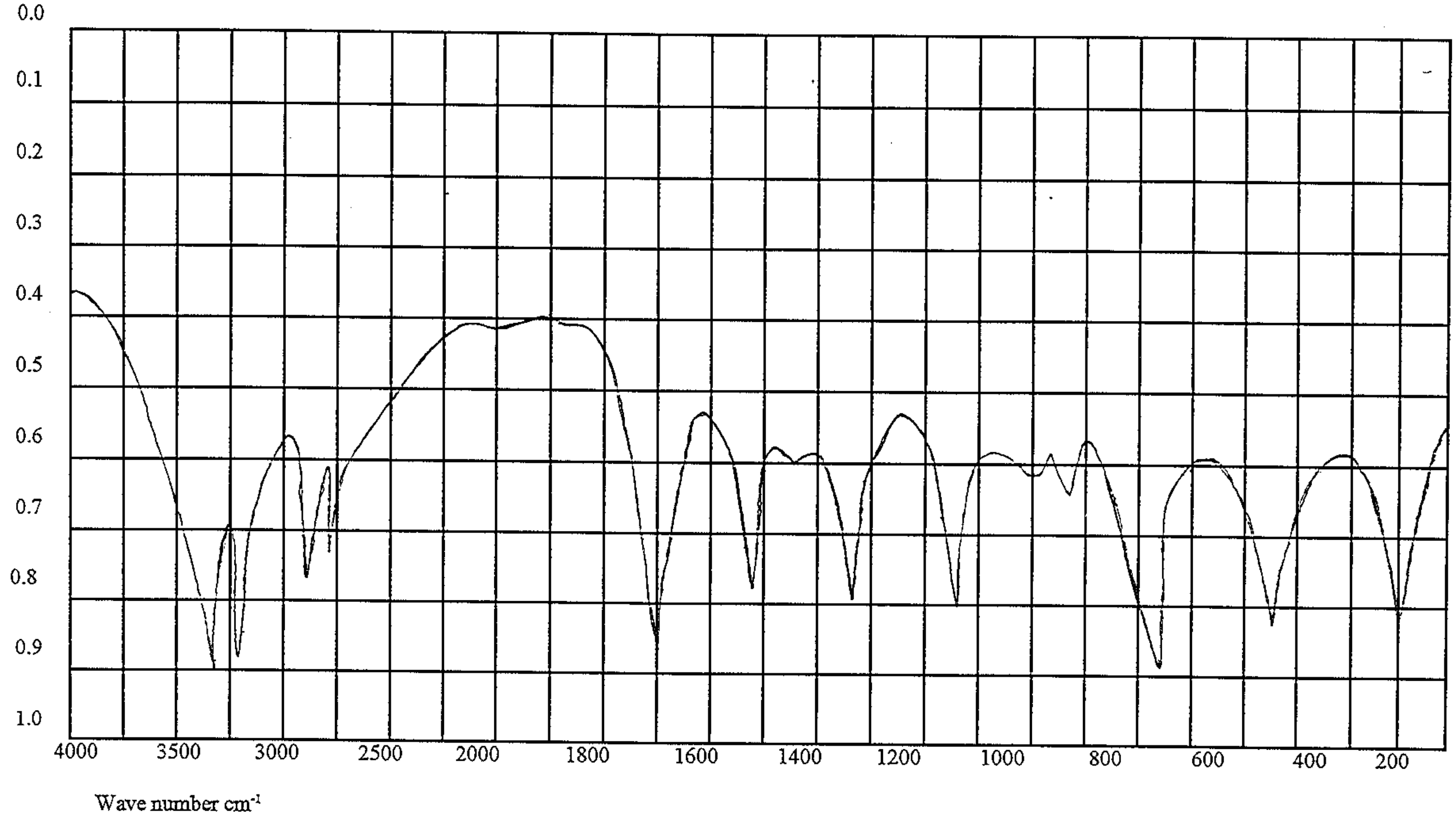


1. Infrared spectrum of [Zn_2LCl_4]



2. Infrared spectrum of [Co_2LCl_4]



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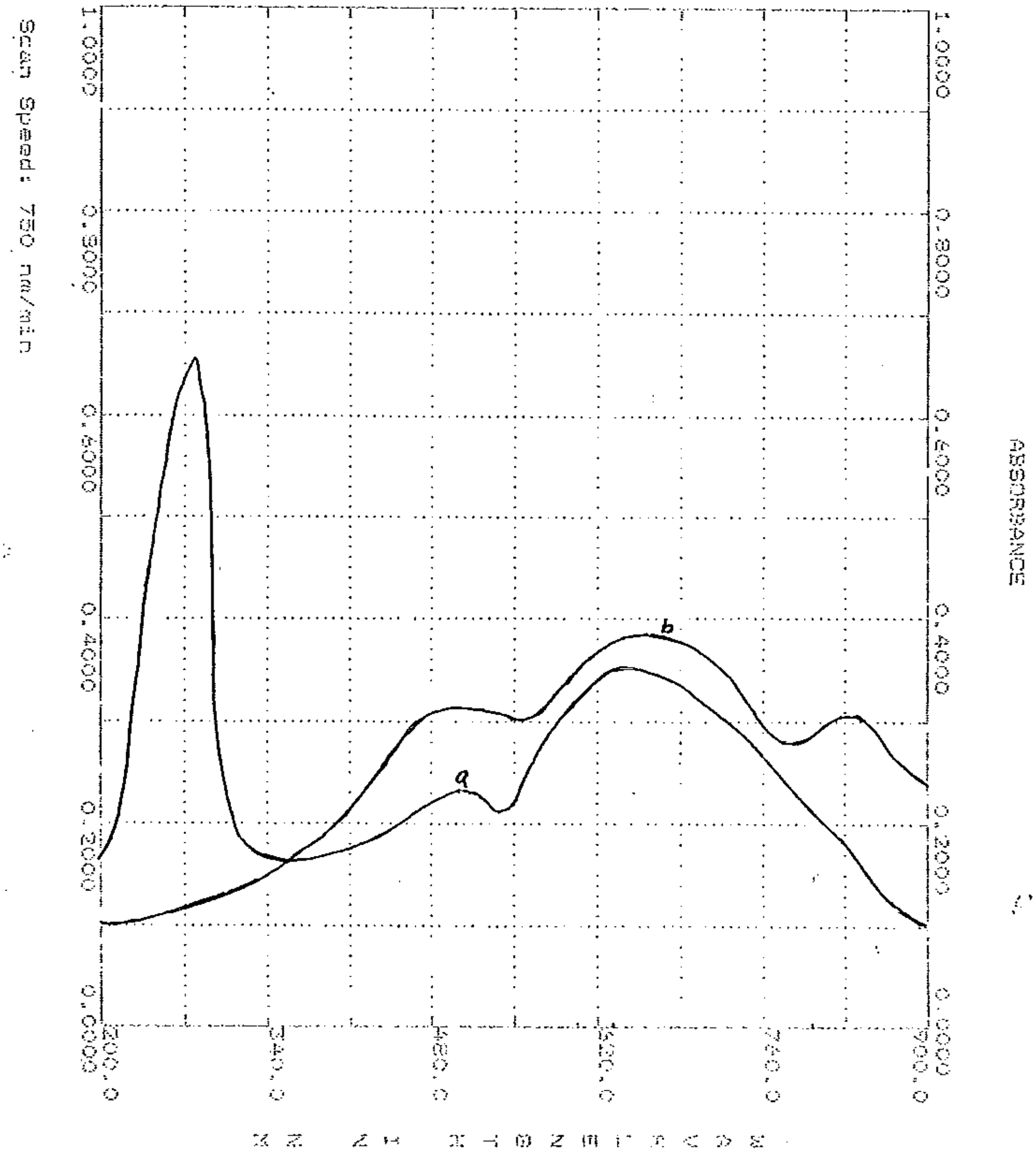

Electronic spectra of a) $[Cu_2LCl_4]$

b) $[CuL]Cl_4$