ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND CHARACTERIZATION OF SOME NEW SERIES OF Zn(II), Co(II) AND Cu(II) COMPLEXES OF TETRADENTATE TETRAAZA MACROCYCLES AND PENTAAZA BIS(MACROCYCLES)

BY

GUTTA GONFA

JUNE 2002

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Dedication

To my wife and parents

ABSTRACT

In this study the template synthesis and characterization of two new series of Zn(II), Co(II), and Cu(II) metal complexes of polyaza macrocyclic ligands are presented.

In the first part of this work template condensation reaction of o-phenylenediamine with succinic acid in a 1:1 molar ratio in the presence of divalent transition metal ions [Zn(II), Co(II) and Cu(II)], led to the formation of new series of polycrystalline macrocyclic complexes. The synthesis is a remarkably facile one requiring only stirring under room temperature for short period of time. Elemental analysis shows that the complexes have a 1:1 ligand to metal stoichiometry. The absence of bands characteristic of primary amines and carboxylic acids functional groups and the presence of bands characteristic of coordinated secondary amine in the N-H and M-N region gave a strong evidence for the formation of the proposed metal complexes. The ^{1}H and the ^{13}C NMR spectra for Zn(II) complex from the first series also confirm the formation of the macrocyclic frame work. The coordination geometry is found to be octahedral for the Zn(II) and Co(II) complexes and square planar for the Co(II) complex.

In the second part of the work, template condensation reaction of p-phenylenediamine, ethyelenediamine, formaldehyde and succinic acid in the presence of metal ions [Zn(II), Co(II) and Cu(II)] produced metal complexes of octahedral geometry of bis(macrocycles) framework. The formation of such series of complexes was confirmed by physico-chemical

studies such as elemental analysis for the metal and chlorine, infrared spectroscopy, electronic spectral studies and conductivity data.

Lastly, preliminary investigation on the potential hydrolytic nature of the Zn(II) metal complexes revealed that the complexes possess no significant catalytic nature in the hydrolysis of p-nitrophenyl phosphate and carboxylate ester. This is probably due to the presence of elctrophilic carbonyl carbon site on the macocycles of the complex that compete for Zn-OH$^-$ nucleophile and thereby deactivating its catalytic activity and the formation of polymeric hydroxide precipitate of the complexes at higher pH.

1. INTRODUCTION

Macrocyclic chemistry is a field of coordination chemistry that has thrown light on a vast number of interesting and important naturally occurring and synthesized macrocycles and their complexes. It is a very active and rapidly growing field of research that overlaps with some interesting fields of chemistry such as catalytic chemistry, biomimetic chemistry and supramolecular chemistry to which a number of scientists have been attracted. The significance of the subject matter of macrocyclic chemistry extends from large number of life composing and naturally occurring complexes with enormous biological functions to vast number of synthetically made ones for diverse biological and non-biological functions. Some of the important and life giving naturally occurring macrocyclic metal complexes are the iron porphyrin of hemoglobin, the cobalt-corrin of vitamin B_{12}, the magnesium-hydroporphyrin of chlorophyll and the crown ethers and cryptands of alkali and alkaline earth metals.

Basically, macrocycles or macrocyclic ligands in inorganic chemistry usually refer to nine membered or greater ring containing organic molecules usually with twelve or more atoms in which three or more hetero-atom donors such as N, O, S, P, etc binding sites have been interspersed [1]. Consequently, classification of such multidentate macrocyclic ligands is: tridentate, tetradentate, pentadentate, etc depending on the number of binding sites. The other way of classifying them is as aza (N), oxa (O), thia (S), phospha (P), etc, and a combination of these, depending on the type of hetero-atom(s) involved. Apart from these there had been a traditional classification of such ligands as oxygen donor crown ethers and cryptands, and nitrogen donors. The oxygen donor macrocycles tend to complex well with larger alkali and alkaline earth metal ions as well as larger post-transition metal ions such as Pb(II), Tl(I), or

Hg(II) due to their tendency to have trigonal planar optimum strain geometry that provides larger cavity [2]. The nitrogen donor and other types (sulfur, phosphorous, and arsenic donor macrocycles) [3], on the other hand, tend to complex well with smaller transition metal ions as well as post-transition metal ions because of their tendency to possess tetrahedral optimum geometry that provide smaller cavity. For the sake of simplicity polyaza macrocyclic complexes are designated as [n] ane N_m, where as the crown ethers as n- crown-m, where n corresponds to the number of rings and m corresponds to the number of O and N binding sites. The formation of metal complexes is closely related to many naturally occurring ones. Complexation with such macrocycles has stimulated a number of scientists to synthesize and investigate many macrocycles for their possible binding sites.

In general, there are two major factors that determine the selection of macrocycles for metal ion complexation to form stable complexes. Selection of macrocycles for metal ion complexation is based on the size of their cavity, i.e., size match selectivity [4] and on the type of donor atom used. Such selection of macrocycles for metal ions or other substrate complexation is critically dependent on the structure of the macrocycles and electronic effects, i.e., charge, polarity, polarizability of the binding site or the type of donor atoms. Some of the major aspect of these are: the number of binding sites, the arrangement of the binding sites, the preferred configuration of the macrocycles that dictate the propensity of the lone pairs to bind a metal ion internally or externally to the cavity, the identity of the macrocyclic frame work and the size of the macrocyclic cavity that determine the flexibility of the ligand and its propensity for metal ion binding.

Macrocyclization of linear polyamines and other ligands to form macrocycles and their metal complexes generally impart the following major characteristics to the macrocycles and their complexes when compared to the equivalent complexes of linear ligands.

1. They possess considerably greater kinetic inertness [5] both to the formation of the complexes from the ligand and the metal ion and to the reverse, i.e., their dissociation.
2. They are capable of stabilizing an unusual oxidation state [6] of central metal which attribute to the redox property of some higher oxidation state transition metal complexes in living cells acting as oxidizing enzymes such as cytochromes, peroxidases, and catalases in iron (IV) porphyrin complexes. The other unusual metals oxidation state stabilized by such macrocycles includes Ni(III), Ni(I), Cu(III), Co(I), Ag(II), Pd(III) and Pt(III) [6-9].

3. They have also high thermodynamic stabilities and formation constant compared to the non-cyclic complexes. Cabbiness and Margerum [6,7] have compared complexes of tetraaza macrocycles with their open-chain analogues. They suggest the term “macrocyclic effect” which appears to be a logical extension of the well-known chelate effect.

“Macrocyclic effect” refers to the amazing stability of macrocycles and their complexes, which is attributed to both entropic and enthalpic origin. The detailed discussion of macrocyclic effect is found in a literature [1]. In general the major factors that attribute to the “macrocyclic effect” include: greater preorganization of the macrocyclic ligands as compared to their open chain analogues, steric hindrance to solvation of the donor atoms in cavity of the macrocycles [10, 11], intrinsic basicity effect [12] due to the electron releasing inductive effects, and enforced electrostatic repulsion between ion pairs [13] of the donor atom in the cavity of the macrocyclic which is relieved on complex formation.

4. Functional groups can be systematically introduced into macrocycles without much difficulty.

Metal ions that compose the vast number of complexes in general and the macrocycle complexes in particular, play a vital role in a vast number of widely differing biological processes. Some of these processes require a specific metal ion with specific oxidation states that can fulfill the necessary catalytic and structural requirements, while other processes may be much less specific with most probable reduced activity [14].

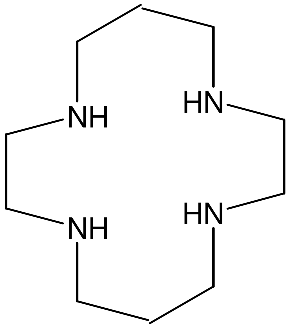
It is well-known that the biological significance of organic or inorganic phosphate esters, anhydrides and carboxylate esters extend beyond the wide variety of naturally occurring examples to man made derivatives that are employed for pest control, chemical warfare and numerous industrial tasks [15]. So it is not difficult to judge the environmental side effects of pollution by such widely used chemicals. As a result, there is a need to carry out research activity aimed at minimizing such side effects to supplement the work done so far by a number of scientists. To this end, the synthesis and study of the chemistry of exchange of substituent, such as hydrolysis, at phosphorous (V) of phosphate ester centers as well as at carbonyl carbon of carboxylate ester centers [16] by some complexes of metal ions has received considerable attention, because such process occur in many crucial enzymatic reactions and are relevant to the detoxification of some pesticides and chemical weapons [15].

A wide range of biologically important hydrolytic enzymes usually contain Zn(II) ion as constituent of active sites so as to effectively catalyze the hydrolysis of organic and inorganic esters [17]. Even though Co(II), Cu(II) and some other metal ions can substitute Zn(II) from the active site, they cannot match with this Zn(II) analogues in activity, because Zn(II) has larger ionic potential and low polarizability with larger charge. It is designed by nature in metalloproteins to generate nucleophiles (e.g. OH^-, OR^-, and H^-) and to attack at electrophilic centers such as carbonyl $C^{\delta+}$, and phosphate $P^{\delta+}$ [15]. As a result, attempt is made in this work to synthesize quadridentate tetraaza and pentaaza macrocyclic ligands of Zn(II) complexes in order to evaluate their potential hydrolytic nature.

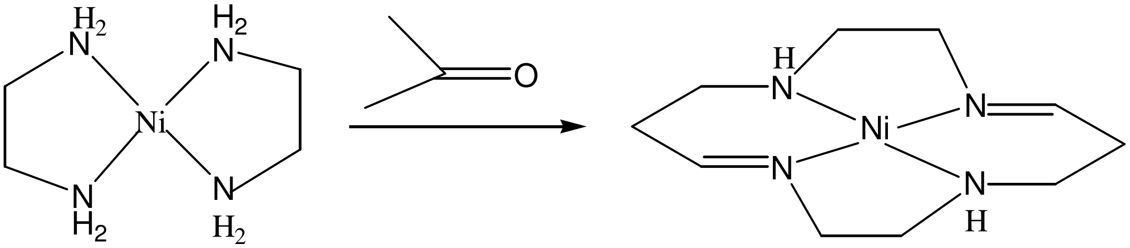
In general, the present interest in designing some new tetradentate tetraaza and pentaaza bis(macrocycles) complexes stems from the above general concepts and the use of such macrocycles and their complexes for diverse applications. They may: (i) serve as models for metalloenzymes [18]; (ii) act as protein metal binding sites in biological systems [19]; (iii) serve as models to study magnetic exchange phenomena [20]; (iv) behave as catalysts [21]; (v) be useful as imaging agents [21]; (vi) act as therapeutic reagents for the treatment of metal toxification [22], (vii) be useful in fuel cells [23], (viii) function as synthetic ionophores [17], chemical sensors [24] and batteries and (ix) help for extractions of ions by transport through artificial and natural membrane, etc.

2. LITERATURE SURVEY

Some reports on synthetic macrocycles appeared as early as in 1936 when the first synthesis of 1,4,8,11-tetraaza cyclotetradecane cyclam, compound (**1**) was reported [25]. Nevertheless, the field only began to blossom in the early 1960s, with the pioneering work of Busch [26] and Curtis that led to the discovery of nickel mediated condensation of $[Ni (en)_3]^{2+}$ and acetone.



Cyclam **(1)**



(**2**)

Scheme I, Ni mediated condensation with acetone

The early macrocycles were synthesized to mimic biologically occurring ones such as porphyrins, corrins, chlorins and more recently the corphins.

Another area of macrocyclic development began in the late 1960s with initial applications focused towards modeling biological processes such as ion transport. These macrocycles initially include the oxygen based crown ethers of Pedersen [27] and cryptands of Lehn [28] both of which exhibit high selectivity toward alkali and alkaline earth metal ions. Several years later the concept of "pre-organized" cavity resulted in the synthesis of cavitands by Cram [29] for selective encapsulation of metals so as to be used in metal ion extraction.

The recognition of the importance of the complexes of macrocyclic ligands has led to considerable efforts being invested in developing reliable and inexpensive synthetic routes for these compounds [30].

The macrocycles with various ligating atoms (N, O, P, S, etc) can be tailored to accommodate specific metal ions by fine-tuning of the ligand design features such as macrocyclic holes size, nature of the donor atoms, donor set, donor array, ligand conjugation, ligand substitution, number and size of the shelter rings, ligand flexibility and nature of the ligand backbone**.**

Macrocyclic ligands or their complexes can be generally synthesized by three general methods developed so far. These are: -

a. The high dilution techniques [31] under a condition of high dilution apparatus with solvents under high temperature and inert atmosphere,
b. The use of rigid groups such as dicyclohexyl carbodiamide, DCC and [(Dimethylamino) pyridine], DMAP to restrict the rotation in the open chain precursors [32], and
c. The "metal template effect" method [33] in which the presence of especially transition metal ions promote the macrocyclic formation by its orthogonal d-orbital directing effect.

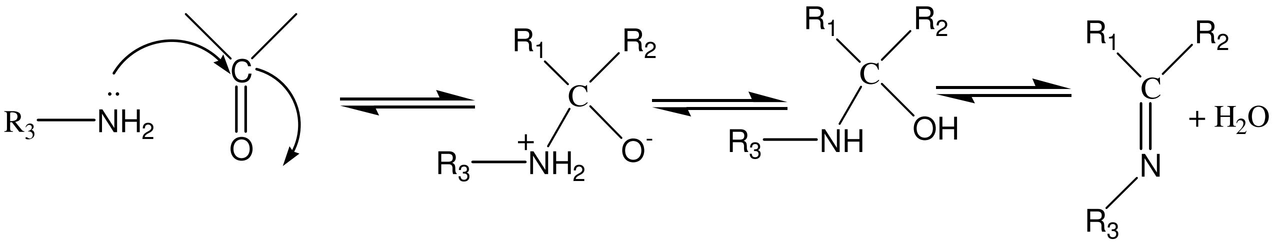
The first two methods can be used for the synthesis of free macrocyclic ligands. In the second method the DCC and DAMP could act as good condensing reagents for the condensation of primary diamines and carboxylic acids.

The "metal template effect" method is an effective and more selective method than the other two for the synthesis of macrocylic complexes and involves an in situ approach where in the presence of metal ions in the cyclization reaction markedly increase the yield of the products. The metal ion plays an important role in directing the steric course of the reaction preferentially toward cyclic rather than oligomeric/polymeric product and/or stabilize the macrocycles once formed.

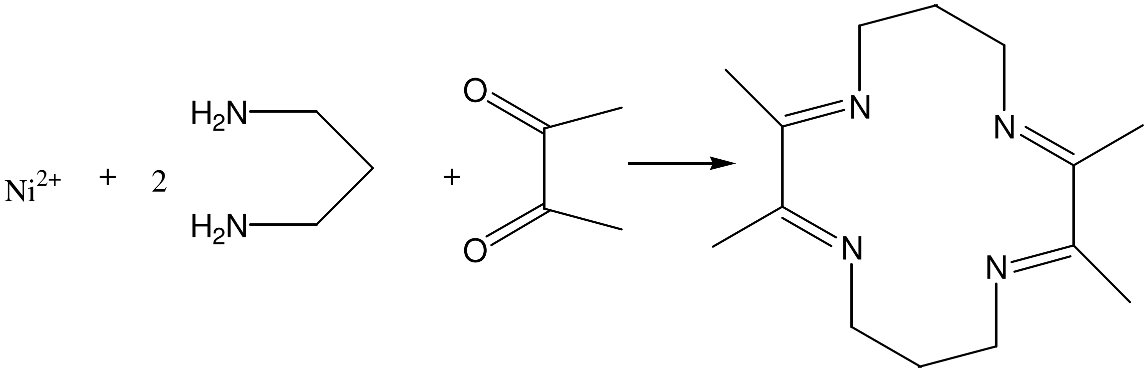
Curtis has demonstrated [34] the template potential of metal ions in the formation of isomeric tetraaza macrocyclic complexes by the reaction of $[Ni\,(en)_3]\,(ClO_4)_2$ with acetone as shown in scheme I, compound (**2**).

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-orbital was regarded as instrumental in guiding the synthetic pathway [35]. The compatibility between the whole sizes of a macrocycle contributes to the effectiveness of the synthetic pathway and to the geometry of the resulting complexes.

Reagents that contain carbonyl groups and amine donors have been particularly useful in the synthesis of certain cyclic structures by template method as shown in the general condensation reaction mechanism of diketones with pairs of amines to produce new chelate ring containing imine groups (Schemes **II** and **III** below).



Scheme II, Mechanism of the condensation of a primary Amine with Carbonyl Group

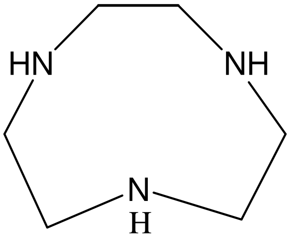


Scheme III, The first example of template synthesis

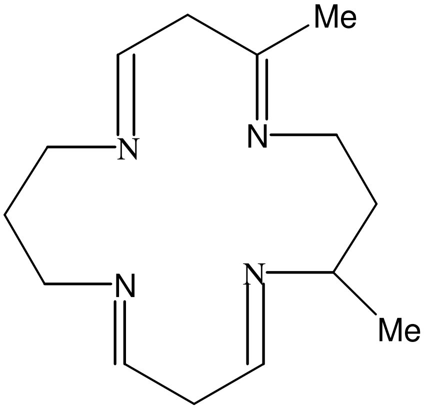
Baldwin and Rose [36] reported the first example of a ring closure utilizing such reagents.

2.1 Polyaza Macrocycles

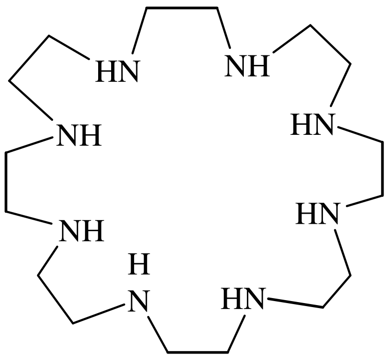
Until recently polyaza macrocyles, which are quadridentate such as cyclam and related ligands with extensive varieties of modifications including differing degree of saturation and ring size [37] had been the most widely studied ones due to their relationship to the porphyrin as well as their stability and selectivity in complexing with various transition metal ions. There are the so-called cyclidens as subset of polyaza macrocycles, which are the lacunar ligands, first synthesized and extensively studied by Busch [38]. Template assisted condensation of amines with formaldeyde yielded a wide variety of macrocyclic products [39-46]. A detailed discussion on classification, synthesis and the thermodynamic as well as structural aspects of the polyaza macrocycles is found in literature [1]. The following structures are some examples of polyaza macrocycles. (**3**-**5**)



(3)

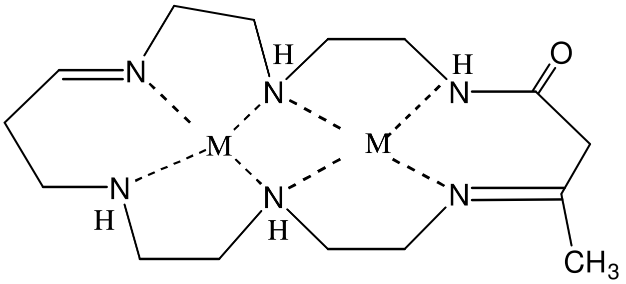


(4)

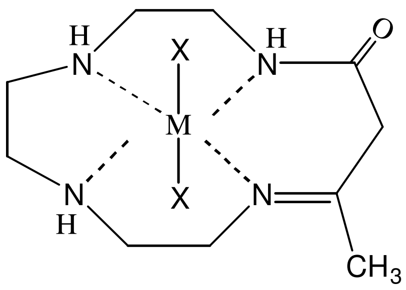


(5)

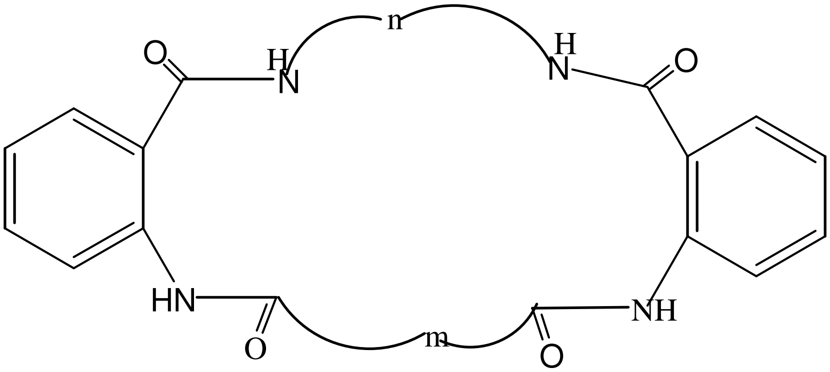
Polyaza macrocycles containing amide groups (**6-8**) possess two possible potential donor atoms (N and O) and hence deserve special interest. As a result synthesis of these macrocyclic complexes with a wide variety of tetraaza, hexaaza and octaaza macrocycles by template condensation reactions of dicarboxylic acids with di- or triamines and self-condensation of o-amino benzoic acid has been adopted very recently [47] (**8**).



(6)

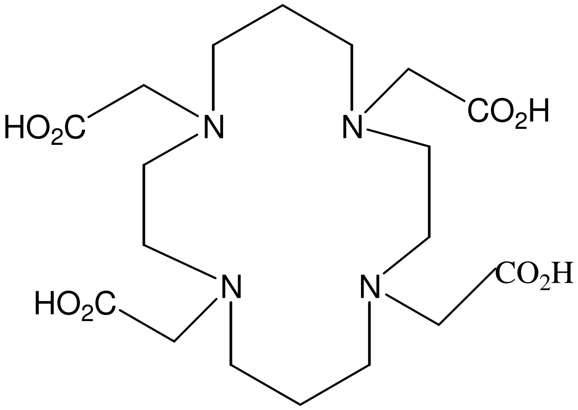


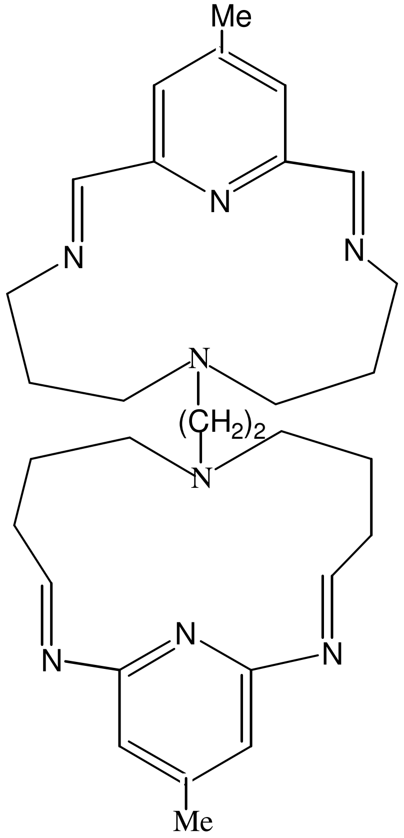
(7)



(8)

In an attempt to extend the field of macrocyclic chemistry, functionalized macrocycles (**9, 10**) that embrace binucleating macrocycles bis(macrocycles) [48] and macrocycles with pendent arm donor groups have been synthesized of which the latter are employed in the synthesis of metal chelating agents for medicinal applications [49].

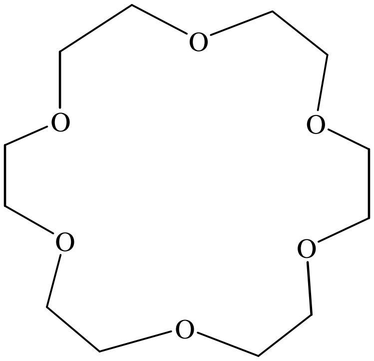




(9) **(10)**

2.2 Polyoxa Macrocycles

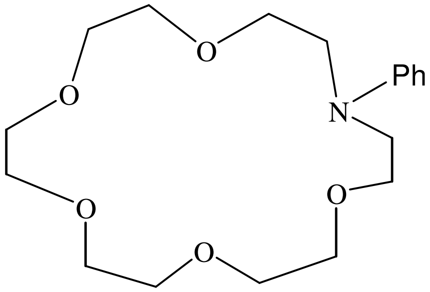
Polyoxa macrocycles, known more commonly as crown ethers, comprises of many types of oxygen donor macrocycles with predominant selective metal ion complexation. The 18-crown-6 (**11**) is one of the most common crown ethers with good ability to complex with alkali and alkaline earth metal ions [50].



18-crown-6

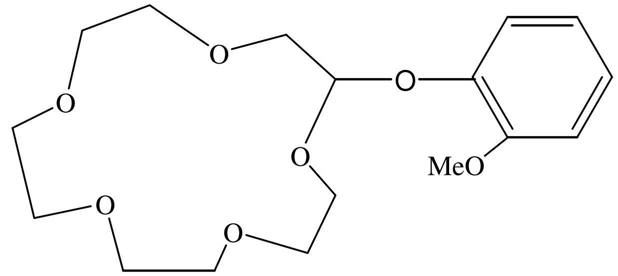
(11)

There is classification of polyoxa macrocycles as polycarbonyls [51], polyacetones [52], polylactones [53] and carcerands with functions other than complexing with metal ion. Some of the most commonly known polyoxa macrocycles, other than crown ethers, are lariat ethers, polyethers with pendent chains (**12-13)** (behaving as polyethers), spherands and hemispherand s (which contain arrangements of phenyl groups that provide preorganized cavity for complexation) [54], e.g. (**14, 15**) and calixarenes (**16**), which are results of condensation between phenols and aldehydes [55], have been referred to as the most easily accessible molecular baskets [56].



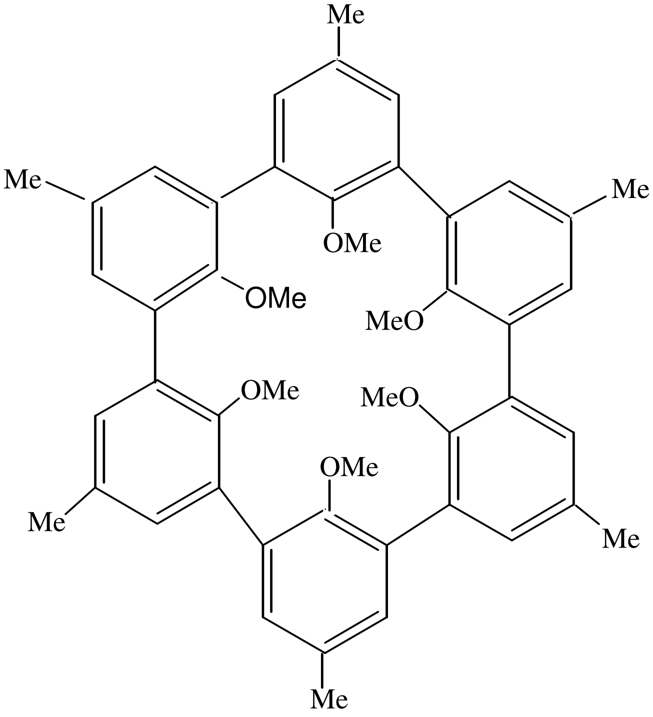
N-pivot

(12)

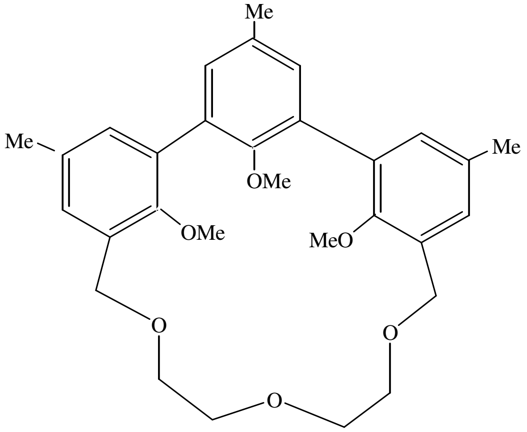


C-Pivot

(13)



(14)



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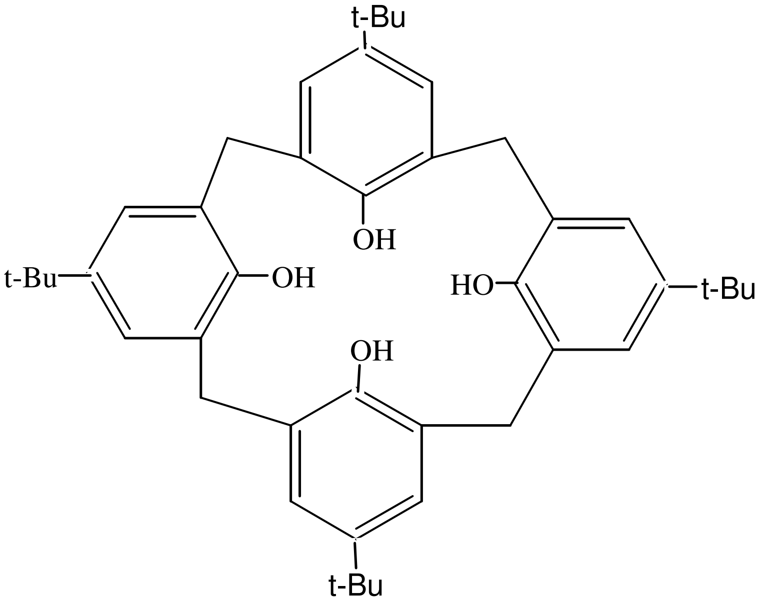
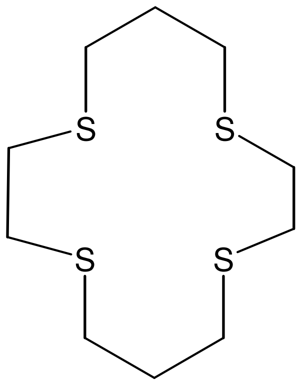


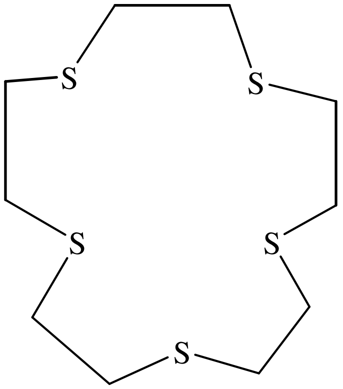
(16)

2.3 Polythia, Polyphospha and Polyarsa Macrocycles

Polythia macrocycles (**17,18**) such as the thioeter analogs of crown ethers have been known since 1930s [57] and hence they are the most extensively studied macrocycles after polyoxa and polyaza macrocycles. One of the reasons for the relative late blooming of the thioether macrocycles can be due to synthetic difficulties. While polyaza and polyoxa macrocycles often utilize template effects in controlling the critical condensations, polythia condensation has limitation in this area.



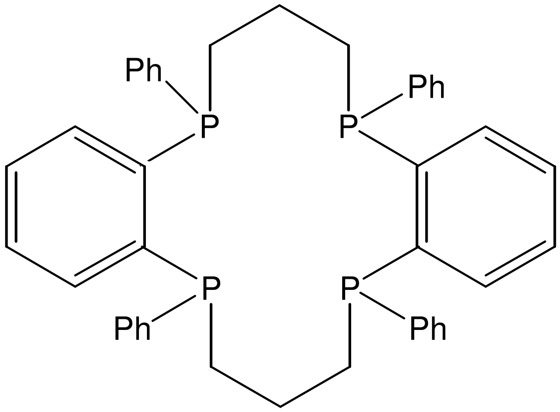
(17)



(18)

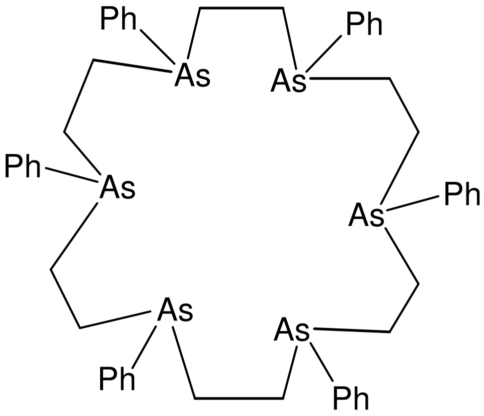
Polythia macrocycles can be synthesized from polythione and dibromoalkanes with high yields following high dilution technique [58, 59].

The polyphospha macrocycles like (**19**) were first reported in 1975 [30]. These macrocycles have been found to complex with a variety of transition metal ions, but have not received the same attention as the more readily accessible polyaza and polyoxa macrocycles.



(19)

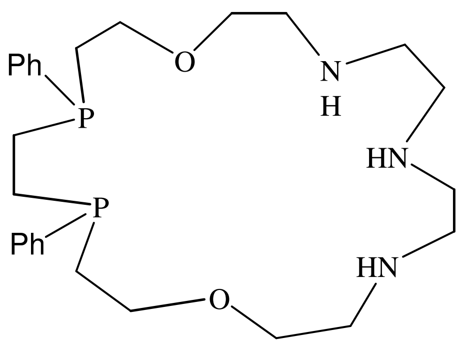
The polyarsa macrocycles like (**20**) comprise one of the least common types of macrocycles [60].



(20)

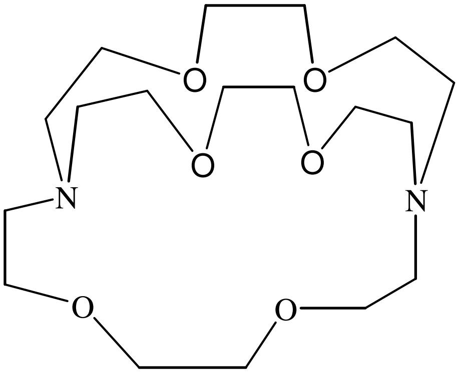
2.4 Mixed Donor Macrocycles

The mixed donor macrocycles are mainly used to stabilize higher oxidation states of metal ions for many chemical and biological processes. There are simple mixed donor macrocycles, e.g. (**21**). The major source of study of these macrocycles was the influence of the incorporation of ‘soft’ phosphorous and arsenic donor into macrocycles [61]. Mixed oxygen-nitrogen donor macrocycles have been studied quite extensively since they serve for examining the coordination tendency of the aza macrocycles and the oxo crown ethers [60].



(**21**)

There are other more complex mixed macrocycles such as cryptands [62], which are bicyclic macrocycles (**22**), which could contain a variety of donor atoms with bridgehead nitrogen atom [63]. This group of macrocycles is highly selective for alkali and alkaline earth metal ions. There are also other complex macrocycles (**23)** such as compartmental ligands, which contain compartments for housing more than one metal ion [64].



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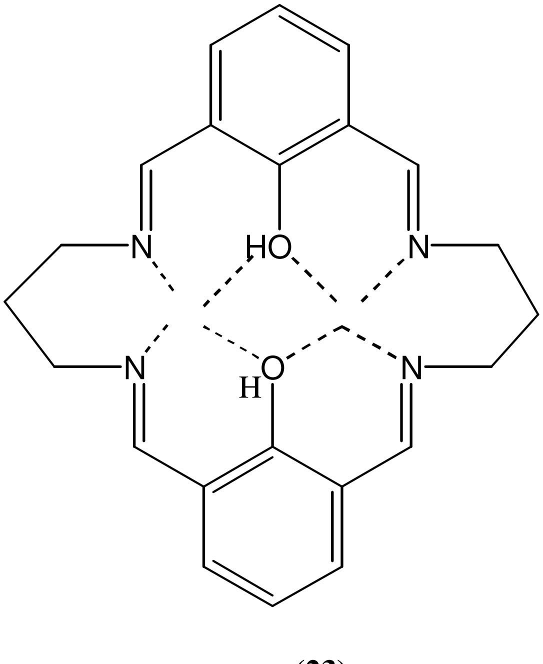


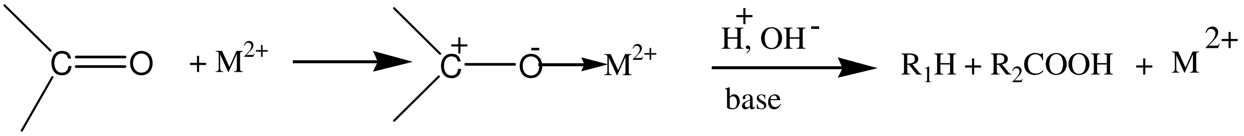
(23)

2.5 Models for Hydrolytic Metalloenzyme

There are a number of naturally occurring metalloenymes with various catalytic activities and very complex structure. Hydrolases, which catalyze the hydrolysis of organic and inorganic esters, is one of the major classes of these catalytic enzymes. Such enzymes usually contain Zn(II) ion in their active site. The Cu(II) and Co(II) can be substituted for Zn(II) even though their catalytic activity is much less than that of Zn(II) enzymes.

The basic role of Zn(II) in Zn enzyme is to act as a Lewis acid, i.e., to polarize a bond that is to undergo hydrolysis reaction. Unlike Cu(II) and Co(II), Zn(II) has a d^{10} electronic configuration and its polarizing effect is isotropic leading to flexible coordination. As a result, it is designed by nature to generate nucleophiles (e.g. OH^-, OR^-, or H^-) to attack at elctrophilic centers, such as carbonyl $C^{\delta+}$ and phosphate $P^{\delta+}$. Alkaline phosphatase is one of the many known Zn(II) containing hydrolytic enzymes that catalyze the hydrolysis of phosphate ester.

In order to explain the role of metal ion as Lewis acid, Bender and Turnquest [65] have studied the Cu(II) catalyzed hydrolysis of esters of α-amino acids. Based on oxygen-18 exchange data and kinetics studies, they have suggested a mechanism involving the formation of a complex in which the ester is chelated *via* the amino and carbonyl groups. Polarization of the carbonyl group then results in enhanced susceptibility of the carbon to nucleophilic attack by a base as shown in the following scheme.



Scheme IV, General mechanism for the hydrolysis of ester by M^{2+} as Lewis acid

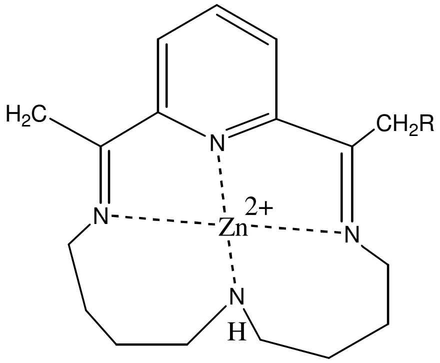
The complexity of the biological molecules and the associated problems in their study dictate the importance of examining the behavior of a model molecule that contain what appears to be the essential features of the original molecule, uncomplicated by other feature of that molecule. Such model molecules also possess greater solubility not possessed by the original molecule.

Most of the recent work on model compounds of alkaline phosphatase has been the synthesis of mononuclear Zn(II) or binuclear Zn(II) complexes with tri- or tetradentate ligands and often attached to hydroxo or aqua donor groups. These compounds are then studied for catalysis using phosphate esters such as 4-nitrophenyl phosphate or bis(4-nitrophenyl) phosphate as a substrate to test the ability of the model compounds to hydrolyze phosphate ester [66].

Macrocyclic polyamine ligands have been found to be quite advantageous in the synthesis of Zn(II) coordination environment as model of Zn enzymes because of enormous stability (macrocyclic effect) of the Zn(II) complex they form at a physiological pH [67].

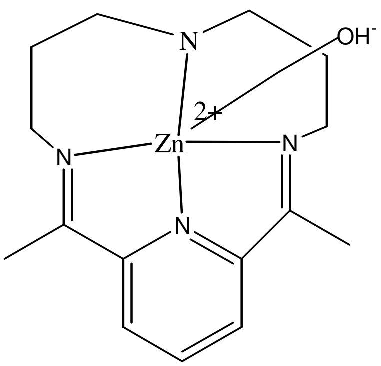
One of the problems in developing efficient Zn(II) based hydrolytic agent is the precipitation of polymeric hydroxide above neutral pH. Such alkaline condition is tolerated by few Zn(II) macrocyclic complex systems [15].

A zinc complex of tetraaza macrocycle is known to catalyze the hydrolysis of diphenyl p-nitrophenyl phosphate ester in aqueous acetonitrile (**24**) [16] whose hydrolysis reactions is related to the detoxification of some pesticides and chemical weapons [15]. Another tetraaza macrocyclic complex that hydrolyze methyl trifluoroacetate was also reported (**25**) [16]. But most of the so far developed tetraaza Zn(II) macrocyclic complex with hydrolytic nature contain imines not amides (**24, 25**).



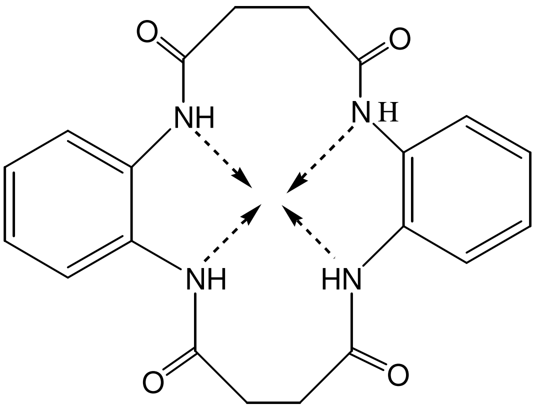
1 R=H
2 R=$C_{16}H_{33}$

(24)



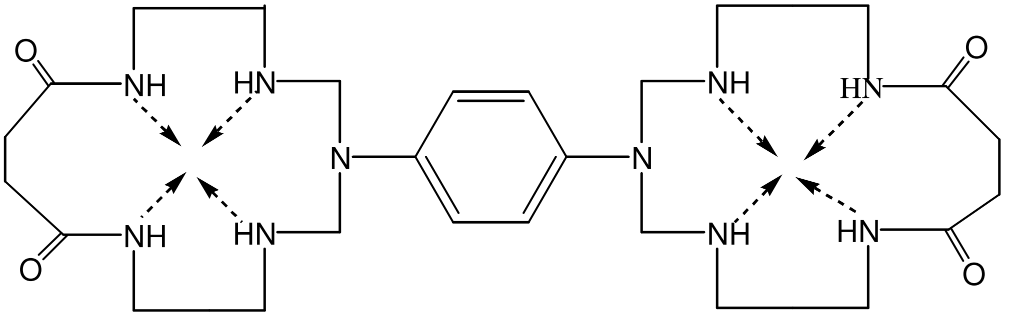
(25)

More recently a series of some new tetradentate pentaaza and octaaza macrocyclic complexes of transition metals, a few of which are bis(macrocycles) and contain amide groups have been synthesized by template condensation reaction in the Department of Chemistry, AAU [68-70]. But in most of these works the potential hydrolytic nature or other application part was not tested. The present work is a continuation of this and is aimed at synthesizing some other new transition metal macrocyclic complexes of tetradentate tetraaza and pentaaza macrocyclic ligands (**26**, **27**) containing amide groups with potential hydrolytic nature.



L

(26)



L`

(27)

2.6. Objective

The introduction and the literature survey parts revealed that synthetic macrocycles and their metal complexes in general and polyaza macrocycles in particular could play essential roles in diverse chemical and biological processes. Hence the objectives of the present research work are:

i. To synthesize some new series of quadridentate tetraaza and pentaaza macrocycles in the presence of divalent transition metal ions, i.e., Co(II), Cu(II) and Zn(II);

ii. To characterize the synthesized complexes based on some physico-chemical techniques.

iii. To assess the hydrolytic potential of the synthesized complexes.

3. EXPERIMENTAL SECTION

3.1 Chemicals and Reagents

Chemicals used in this study are $ZnCl_2$ (Riedel-dehaen), $CoCl_2.6H_2O$ (Aldrich), $CuCl_2.2H_2O$ (BDH), o-phenylenedimine (Riedel-dehaen), p-phenylenediamine (Aldrich), formaldehyde (39% solution, BDH), ethylenediamine (Fluka) and succinic acid (BDH). Methanol was used as a solvent for the synthesis of the complexes without further purification.

3.2 Physical Measurements

The IR spectra were obtained using a Pye-Unicam SP 2000 IR Spectrophotometer in the range of 4000 – 200 cm^{-1} and A Buck Scientific IR Spectrophotometer Model 500 in the range of 4000 – 600 cm^{-1} as KBr disks. UV-Vis spectrophotometer studies of freshly prepared $10^{-3}M$ solutions in water of the complexes in the range of 200 – 1100 nm were conducted using SPECTRONIC GENESYS 2PC Spectrophotometer at room temperature. The electrical conductivities of 1 mM solution in water and MeOH of the complexes were obtained from a

Philip Harris conductivity meter at about 25 ^{0}C. The ^{1}H and ^{13}C NMR spectra in D_2O solvent of Zn(II) complexes were determined by using BRUKER 400 NMR machine using TMS as an internal standard. The metal contents of the complexes were determined using Buck Scientific Model 210 VGP Spectrophotometer taking 0.001gm of each sample and digesting it in the presence of 2 ml of $HClO_4$ at high temperature using sand bath following known procedures [71]. The purity of some of the complexes was checked by dissolving the appropriate complex in MeOH solvent and using a mixture of 75% MeOH and 25% ethyl acetate as eluent. Only one spot was observed in each case after developing in an iodine chamber indicating the compounds were relatively pure. Chlorine content of the complexes was determined by precipitation from sodium fusion method.

3.3. Synthesis of Complexes

3.3.1. Synthesis of Monoaqua monochloro-5,8,13,16-tetraoxo-1,4,9,12-tetraaza-2:3,10:11-diphenyl tetradecane metal (II) monochloride, [ML(H_2O)Cl]Cl and 5,8,13,16-tetraoxo-1,4,9,12- tetraaza-2:3,10:11- diphenyl tetradecane copper (II) dichloride [CuL]Cl_2, where [M=Zn(II), Co(II)] and L is ligand

To each of 5 mmol solution of a metal chloride $ZnCl_2$ (0.6815 g), $CoCl_2.6H_2O$ (1.1896 g), and $CuCl_2.2H_2O$ (0.8527 g), dissolved in 20 mL methanol, 10 mmol (1.0814 g) of o-Phenylene diamine and 10 mmol (1.1823 g) succinic acid were added simultaneously while stirring. Each of the reaction mixture was stirred for about 7 hrs giving a solid material which was filtered, washed with methanol (50 mL), vacuum dried and kept in a desicator.

$C_{20}H_{20}N_4O_4Cl_2Zn$: Yield 50%; Elemental analysis: Calc. (Found) for Zn, 12.23% (12.70%); Cl, 13.28% (13.20%)., IR (KBr, cm^{-1}) ν(N-H), 3253; ν(C-H), 2920; ν(C=O), 1660; ν(C-N), 1200; ν(M-N), 460; ν(M-Cl), 260. ^{1}H NMR (D_2O, ppm): δ 2.5 (8H, *s*), δ 7.0 (8H, *md*). ^{13}C NMR (D_2O, ppm): δ 33.8, 119.0, 122.0, 134.7 and 182.8 (see page 30 for assignment).

$C_{20}H_{20}N_4O_4Cl_2Co$: Yield 54%; Elemental analysis: Calc. (Found) for Co, 11.20% (11.60%); Cl, 13. 44% (13.42%). IR (KBr, cm^{-1}) ν(N-H): 3200; ν(C-H), 2930; ν(C=O), 1710; ν(C-N), 1170; ν(M-N), 420; ν(M-Cl), 285.

$C_{20}H_{20}N_4O_4Cl_2Cu$: Yield 49%; Elemental analysis: Calc. (Found) for Cu, 14.30% (14.75%); Cl, 13.80% (13.40%). IR (KBr, cm^{-1}), ν(N-H), 3200, ν(C-H), 2820 ν(C=O) 1525; ν(C-N), 1100; ν(M-N), 445.

3.3.2. Synthesis of tetraaquo [1,1`-p-phenylene bis (7,10-dioxo-1, 3,6,11,15-penta- aza cycloheptadecane) dimetal (II) ]tetrachloride, [ $M_2L`(H_2O)_4]Cl_4$, [M=Zn(II),Co(II) and Cu(II)] and L` is a second ligand

To each of the 3 stirred methanolic solutions (20 mL each) of p-pheneylenediamine (2.5 mmol, 0.2704 g) taken and added simultaneously to formaldehyde (39% solution) (10 mmol, 0.75 ml) and 1,2-diaminopropane (10 mmol or 0.60 mL). The mixture was stirred for 2 hrs. Following this, addition of a methanolic solution of metal salts (5 mmol) $ZnCl_2$ (0.6185 g), $CoCl_2.6H_2O$ (1.1896 g), $CuCl_2.2H_2O$ (0.8527 g) and succinic acid (5 mmol, 0.5904 g) was added to each where a change in color of the solution was noticed in each case. Furthermore, each of the reaction mixtures was refluxed for another 7 hrs. The solid obtained was filtered, washed with methanol (50 mL), dried in vacuum and kept in a desicator.

$C_{26}H_{52}N_{10}O_8Zn_2$: Yield, 53%; Elemental analysis: Calc. (Found) for Zn, 15.70% (16.10%); Cl, 16.34% (16.10%). IR (KBr, cm^{-1}), ν(N-H), 3450, 3250; ν(C-H), 2800; ν(C=O), 1635; ν(C-N), 1180; ν(M-N), 460; ν(M-O), 310.

$C_{26}H_{52}N_{10}O_8Cu_2$: Yield 30%; Elemental analysis: Calc. (Found) for Cu, 20.00% (19.60%); Cl, 16.41% (16.20%). IR (KBr, cm^{-1}): ν(N-H), 3442, 3240; ν(C-H), 2950; ν(C=O), 1678; ν(C-N), 1213; ν(M-N), 455 ; ν(M-O), 325.

$C_{26}H_{52}N_{10}O_8Co_2$: Yield, 57%; Elemental analysis: Calc. (Found) for Co**,** 17.30% (16.96%); Cl, 16.59% (16.24%). IR (KBr, cm^{-1}): ν(N-H), 3450, 3225; ν(C-H), 2850; ν(C=O), 1625, ν(C-N), 1200; ν(M-N), 460; ν(M-O), 310.

4. RESULTS AND DISCUSSION

Part A

4.1A Monoaquo monochloro-5, 8,13,16-tetraoxo-1, 4,9,12-tetraaza-2:3,10:11- diphenyl tetradecane metal (II) chloride, [ML(H_2O)Cl]Cl and 5,8,13,16- tetraoxo-1,4,9,12-tetraaza-2:3,10:11- diphenyl tetradecane metal (II) dichloride, [CuL]Cl_2, where [M=Zn(II), Co(II)] and L is a ligand

A new series of polyaza macrocyclic complexes of the form [ML(H_2O)Cl]Cl and [CuL]Cl_2 where [M= Zn(II), Co(II) and L= Ligand] have been prepared by template condensation reaction of metal ions, o-phenylenediamine and succinic in a 1:2:2 molar ratio, respectively.

4.2A Physical and Analytical Studies of the Complexes

The color, melting point, yield, conductivity and the metal and chlorine content in percentage of the complexes are summarized in **Table 1** below. All the complexes are polycrystalline powders obtained in a 49% to 54 % yield and are stable to atmosphere at room temperature.

The investigation of solubilities of the complexes in different solvents shows that they are slightly soluble in water, methanol, ethanol and DMF but insoluble in most organic solvents. All the complexes have high melting points or decomposition temperature.

Table 1 Physical property, yield, molar conductivity (Λ_m) and metal and chlorine content of the complexes where L is the first ligand.

Complex	Color	Yield (%)	M.P/Dec.Pt (^{0}C)	Λ_m(cm^2 Ω^{-1}mol^{-1})	Metal: Calc.(found) (%)	Chlorine: Calc.(found)(%)
[ZnL(H_2O)Cl]Cl	White	50	>250	80	12.23 (12.70)	13.28 (13.20)
[CoL(H_2O)Cl]Cl	Rose	54	216-218	98	11.20(11.60)	13.44 (13.42)
[CuL]Cl_2	Darkgreen	49	>300	146	14.30(14.75)	13.80 (13.40)

The molar conductivity (Λ_m) values for [ZnL(H_2O)Cl]Cl and [CoL(H_2O)Cl]Cl are in the range of 1:1 elctrolyte in water medium at room temperature, indicating that one of the chlorides is in the ionization sphere of the complexes. The relatively high Λ_m value of [CuL]Cl_2, which falls above the indicated range for 1:1 electrolyte, suggests that the complex is a 1:2 electrolyte with the chlorines in the outer sphere as chlorides [72].

The metal and chloride content of the compounds were analyzed by atomic absorption spectroscopy (AAS) and AgCl precipitate from sodium fusion respectively. The calculated and found values (**Table 1**) are close to each other, which is consistent with the suggested molecular formula of the complexes.

4.3A Infrared Spectral Studies

The major frequencies and their assignment in the IR spectra of the complexes are summarized in a **Table 2** below.

Table 2 IR data (cm^{-1}) of the complexes and their characteristic band assignments.

Complexes	ν(N-H)	ν(C-H)	Amid bands				ν(C-N)	ν(M-N)	ν(M-Cl)
			I	II	III	IV			
$[CoL(H_2O)Cl]Cl$	3308,3200, 3105	2930	1623	1500	1260	650	1170	420	285
$[CuL]Cl_2$	3209,3140, 3060	2820	1680	1350	1250	655	1100	445	-
$[ZnL(H_2O)Cl]Cl$	3253	2920	1660	1600	1300	660	1200	460	260

The absence of bands characteristic of primary amine or hydroxyl groups and the appearance of bands corresponding to secondary amide group suggest the formation of a macrocyclic product co-ordinated through the amide nitrogen. Normally ν(N-H) stretching of secondary amide display a single sharp band at lower frequency around the region 3200-3300 cm^{-1} for a solid sample spectrum due to the presence of hydrogen bonding [73, 74]. This is observed for $[ZnL(H_2O)Cl]Cl$, which show ν(N-H) stretching of the coordinated secondary amide at 3253 cm^{-1}. On certain occasion, where there is a possible existence of *cis*- and *trans*- conformation of an amide compound, a free ν(N-H) stretching is replaced by multiple bands in the range

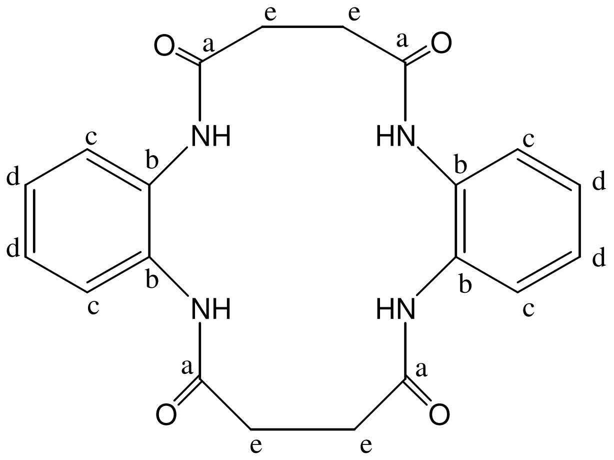
3300- 3060 cm^{-1} [74, 75]. This is actually what is observed for Co(II) and Cu(II) complexes, which exhibited about three bands in this region {i.e. for Co(II) complex ν(N-H) stretching of this amide are 3308, 3200 and 3105 cm^{-1} and for that of Cu(II) complex are 3209, 3140, and 3060 cm^{-1}}. Thus, the broadness of the band for the two complexes is due to the overlapping of this multiple of bands and their shift to lower frequency is due to the conjugation with the aromatic ring.

In general, the amide bands that were identified around the regions 1725 - 1620, 1550 - 1460, 1230 - 1270 and 800 – 650 cm^{-1} may be assigned to [74, 75] 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 that were observed in the region 1160 – 1200 cm^{-1} could be assigned to (C-N) stretching vibration [75, 76]. The medium to weak intensity bands observed in the range of 800 – 1,000 cm^{-1} and around 600 cm^{-1} are assignable to rocking and wagging modes of coordinated water molecules. The appearance of bands in the 410 - 450 cm^{-1} region in all the complexes corresponds to ν(M-N) vibration [77]. All the complexes except that of Cu(II) show bands in the region 280 – 350 cm^{-1}, which could be assigned to ν(M-Cl) and ν(M-O) vibrations [78].

4. 4A ^{1}H NMR and ^{13}C NMR Spectra of $[ZnL(H_2O)Cl]Cl$ Complex

The ^{1}H NMR spectrum of the above complex in D_2O and TMS as internal standard (**Table 3**) shows doublet signals in the aromatic region at 6.8 - 6.9 ppm, which could be assigned to the aromatic proton (8H) at position c and d (**28**). Signal observed at 2.4 - 2.5 ppm might be assigned to the methylene ($C-CH_2-C$) protons generated from succinic acid.

The ^{13}C NMR spectrum of the compound in D_2O and TMS internal standard (**Table 3**) shows one type of aliphatic carbon at 23.8 ppm at position e (**28**), which is confirmed to be the carbon of the methylene group by DEPT. The three aromatic signals at 119.0 ppm, 122.0 ppm and 134.7 ppm may be attributed to the two unsubstituted and substituted aromatic carbons at position d, c and b respectively (**28**). The signal at 182.9 ppm may be assigned to the carbonyl carbon at position a (**28**).



(**28**)

These results along with the fact that there is a 1:1 proportion of the aromatic protons to that of aliphatic methylene protons suggest that the proposed symmetrical macrocyclic framework is formed.

Table 3 ^{1}H NMR and ^{13}C NMR spectral data of the Zn (II) complex

C/H	^{1}H NMR δ ppm	^{13}C NMR δ ppm	DEPT indicate
a	-	182.9	C=O
b	-	134.7	C

c	6.9	122.0	CH
d	6.8	119.0	CH
e	2.5	33.8	CH_2

4.5A Electronic spectral analysis

The important band positions, and their corresponding assignment and geometries for Co(II) and Cu(II) complexes are summarized in **Table 4** below.

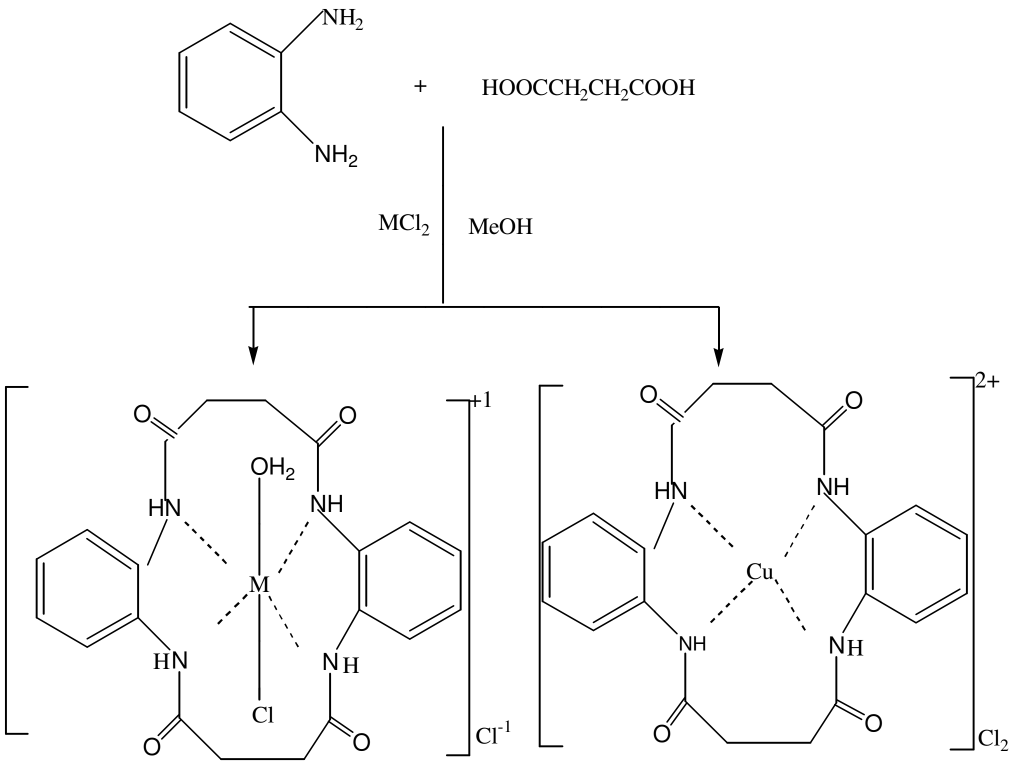
Table 4 Electronic spectral data λ_{max} (nm) of the complexes

Complexes	Band positions λ_m in Water (nm)	ethanol (nm)	Assignment	Geometry
$[CoL(H_2O)Cl]Cl$	254	308	$\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$	Octahedral
	428	422	$\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$	
	520		$^4T_1(F) \rightarrow {}^4T_1(P)$	
	740		$^4T_1 \rightarrow {}^4A_2$	
	960		$^4T_1 \rightarrow {}^4T_2$	
$[CuL]Cl_2$	284	443	$\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$	Square planar
	662		$^2B_1 \rightarrow {}^2A_1$	
	900		$^2B_1 \rightarrow {}^2E$	

Normally there are three or more d-d transition bands for the divalent cobalt and copper complexes. But in this work especially the Co(II) complex showed only one prominent band in the d-d transition probably due to the domination of the charge transfer spectral band as a result of high conjugation with aromatic ring. Thus, obscured bands at 520 and 740 nm (in water) and an observed band at 900 (in water) for $[CoL(H_2O)Cl]Cl$ may be assigned to $^4T_1(F) \rightarrow {}^4T_1(P)$, $^4T_1 \rightarrow {}^4A_2$ and $^4T_1 \rightarrow {}^4T_2$ respectively, suggesting octahedral geometry of the complex [79].

The bands at (443, 480, and 662 nm) and 900 nm for $[CuL]Cl_2$ may be assigned to $^2B_1 \rightarrow {}^2A_1$ and $^2B_1 \rightarrow {}^2E$ respectively, which suggest a square planar geometry of the complex [79]. The intense bands at 254 and 428 nm (in water solution) and 308 and 422 nm (in ethanol) for the $[CoL(H_2O)Cl]Cl$ and 284 nm (in water) for $[CuL]Cl_2$ may be assigned to [27] $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ inter-ligand or charge transfer spectra.

Based on analytical, conductance and electronic spectral data, octahedral geometry has been proposed for Co(II) and Zn(II) and a square planar for Cu(II) complex as indicated in a general synthetic scheme V below.



$[ML(H_2O)Cl]Cl$ M=Co(II), Zn(II)

$[CuL]Cl_2$

Scheme V, Synthesis of first series of complexes of tetraaza macrocycles containing amide groups by template condensation reaction.

Part B

4.1B Tetraaquo[1,1`-p-phenylene bis (7,10-dioxo-1, 3,6,11,15-pentaaza cycloheptadecane) dimetal (II) tetrachloride], [ $M_2L`(H_2O)_2]Cl_4$, [M=Zn(II), Co(II) and Cu(II)] and L` is a second ligand

A new series of quadridentate pentaaza bis(macrocyclic) complexes, formulated as $[M_2 L (H_2O)_4]Cl_4$, [M=Co(II), Cu(II) and Zn(II)], have been synthesized from the template condensation reaction of ethylenediamine, formaldehyde, p-pheynlenediamine, succinic acid and metal ions in a 1:4:4:1:2 molar ratio respectively.

4.2B Physical and Analytical Studies of the Complexes

The investigation of the solubility of the complexes shows that they are slightly soluble in water, methanol, DMF, but insoluble in most organic solvents like benzene. All complexes are stable to the atmosphere and are polycrystalline powder in nature. The color, M.Pt, Λ_m, yield and metal and chlorine content of the complexes are given in **Table 5**.

Table 5 the physical properties, Λ_m, yield, Metal and Chlorine content of the complexes

Complexes	Color	Yield (%)	M.P/Dec.P.t	Λ_m(cm^2 Ω^{-1} mol^{-1}	Metal: (%) calc.(found)	Chlorine:(%) calc. (found)
$[Co_2L'(H_2O)_4]Cl_4$	Dark brown	57	205-207^{0}C	491	17.30 (16.96)	16.59(16.24)
$[Cu_2L^\backprime(H_2O)_4]Cl_4$	Brown	30	182-184^{0}C	560	20.00 (19.60)	16.41(16.20)
$[Zn_2L'(H_2O)_4]Cl_4$	Cream	53	193-195^{0}C	505	15.70 (16.10)	16.34 (16.10)

The very high molar conductivity of the 1mM concentration of the complexes in water solution at room temperature suggests that the complexes are a 1:4 electrolyte with the four chlorines found as chlorides in the outer sphere of the complexes [72].

The metal and chloride content of the complexes are determined/estimated by AAS and by sodium fusion as AgCl precipitate respectively (**Table 5**) which are consistent with the molecular formula of the proposed complexes.

4.3B Infrared Spectral Studies

The major and important IR frequencies are given in **Table 6**. In all complexes two single sharp bands were observed in the regions 3450 – 3440 cm^{-1} and 3250 – 3225 cm^{-1}, which may be assignable to ν(N-H) of the secondary amine and coordinated amide groups respectively [73, 74]. The slightly higher values of the frequency of these series of complexes compared to that of the first series indicates that their amide groups are not conjugated with the aromatic ring. The medium to weak intensity bands observed in the range of 800 – 1,000 cm^{-1} and around 600 cm^{-1} are assignable to rocking and wagging modes of coordinated water molecule. Furthermore, the absence of bands assignable to primary amine or hydroxyl groups suggests the formation of macrocyclic framework.

Table 6 IR Spectroscopic data (cm^{-1}) of the complexes and their band assignment.

Complexes	ν(N-H)	ν(C-H)	Amide bands				ν(C-N)	ν(M-N)	ν(M-O)
			I	II	III	IV			
$[Co_2L'(H_2O)_4]Cl_4$	3450, 3225	2850	1625	1530	1280	620	1200	460	310
$[Cu_2L'(H_2O)_4]Cl_4$	3442, 3240	2950	1678	1617	1274	762	1213	455	325
$[Zn_2L'(H_2O)_4]Cl_4$	3450, 3250	2800	1635	1460	1230	650	1180	460	310

4.4B Electronic Spectral Studies

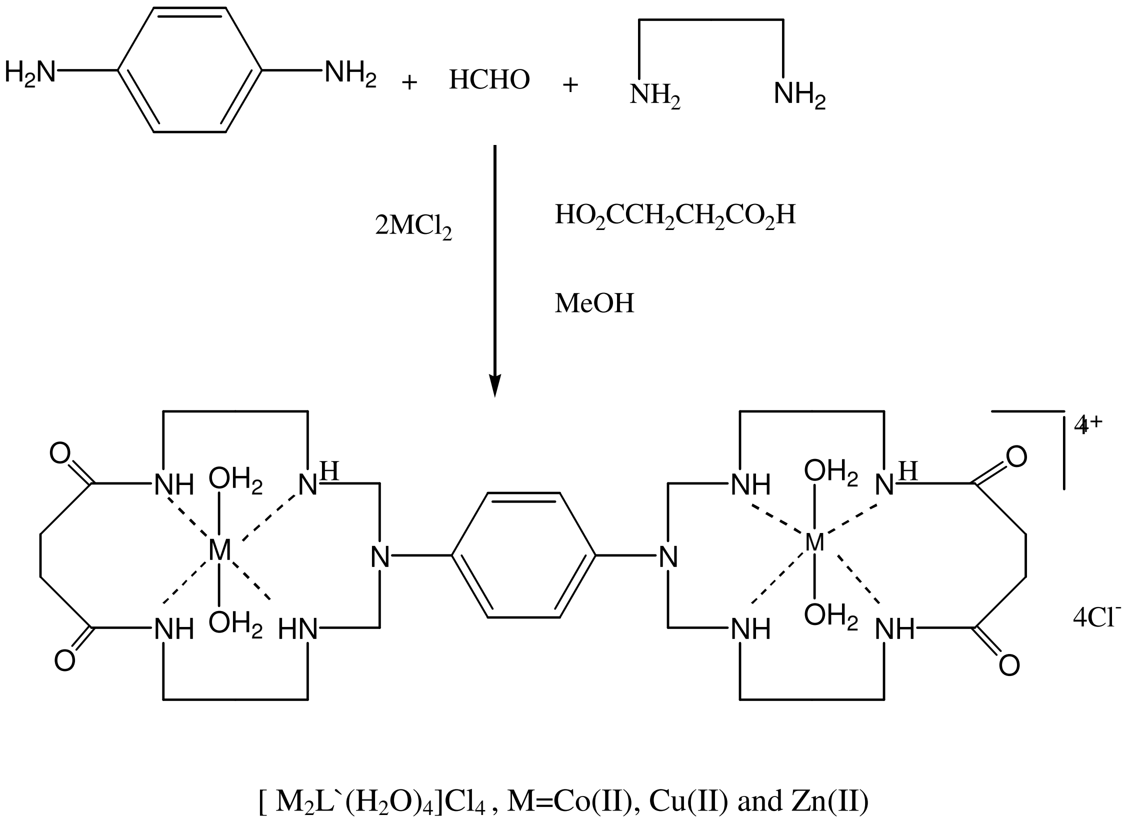
The spectral band positions in water and ethanol for the $[Co_2L'(H_2O)_4]Cl_4$ and $[Cu_2L'(H_2O)_4]Cl_4$ complexes with their corresponding assignment and geometries are given in **Table 7**. The assignments are consistent with the proposed geometries.

Table 7 Electronic spectral data λ_{max} (nm) of the $[Co_2L'(H_2O)_4]Cl_4$ and $[Cu_2L'(H_2O)_4]Cl_4$ complexes.

Complexes	Band positions λ_m in		Assignment	Geometry
	Water (nm)	Ethanol (nm)		
$[Co_2L'(H_2O)_4]Cl_4$	440	287	$\pi \rightarrow \pi^*$	Octahedral
	447	-	$^4T_1(F) \rightarrow {}^4T_1(P)$	
	714	-	$^4T_1(F) \rightarrow {}^4A_2(F)$	
$[Cu_2L'(H_2O)_4]Cl_4$	215	-	$\pi \rightarrow \pi^*$	Octahedral
	509	-	$^2B_1 \rightarrow {}^2E_2$	
	629	-	$^2B_1 \rightarrow {}^2B_2$	
$[Zn_2L'(H_2O)_4]Cl_4$	305	218	$\pi \rightarrow \pi^*$	-

The d-d transition bands at 447 and 714 nm (in water) for the $[Co_2L'(H_2O)_4]Cl_4$ complex may be assigned to $^4T_1(F) \rightarrow {}^4T_1(P)$ and $^4T_1(F) \rightarrow {}^4A_2(F)$ respectively suggesting an octahedral geometry of the complex. In case of $[Cu_2L'(H_2O)_4]Cl_4$ complex, there are d-d transition bands at 509 and 629 nm (in water), which may be assigned to $^2B_1 \rightarrow {}^2E_2$ and $^2B_1 \rightarrow {}^2B_2$, suggesting an octahedral nature of the complex. The observed intense bands at 440 nm (in water) and 287 nm (in ethanol) for the $[Co_2L'(H_2O)_4]Cl_4$, 215 nm (in water) for $[Cu_2L'(H_2O)_4]Cl_4$ and 305 nm (in water) and 218 nm (in ethanol) for the $[Zn_2L'(H_2O)_4]Cl_4$ may be assigned to an inter-ligand or charge transfer spectra.

Based on the conductance, analytical and electronic spectral values the proposed structures for the complexes are as indicated in the synthetic scheme VI.



Scheme VI, Synthesis of bis(macrocycles) by template condensation reaction

5. THE STUDIES OF HYDROLYTIC NATURE OF THE Zn(II) COMPLEXES

In order to examine the hydrolytic nature of the Zn(II) complexes, two p-nitrophenyl esters, namely p-nitrophenylacetate and tri(p-nitrophenyl)phosphate ester with higher rate of hydrolysis, are prepared, following the known synthetic procedure [80]. The products were confirmed by the melting point and other properties such as UV-Vis absorption bands.

5.1 Preparation of Ester Substrates

5.1.1 p-Nitrophenylacetate (p-NPA)

1 g (0.007 mmol.) of para-nitrophenol was dissolved in 5 mL of three molar sodium hydroxide solutions. 20 g of crushed ice were added followed by 1.5 g (1.5 mL) of acetic anhydride. The mixture was shaken vigorously for 60 seconds. The acetate separated was collected, washed with water, and recrystallized from dilute ethanol. M.Pt 75-76^{0}C ; literature M.Pt 77-79^{0}C [81].

5.1.2 Tri (p- Nitrophenyl) Phosphate (Tp-NPP) [80]

The preparation of this phosphate ester consists of two steps.

5.1.2.1. Sodium p-nitrophenoxide

11 mL of 10N sodium hydroxide was added with stirring to a suspension of 15 g p-nitrophenol in 70 mL of boiling water. To the resulting clear solution, a further 10 mL of 10N alkali was added and the mixture was rapidly cooled. The yellow sodium salt, which separated, was collected by filtration and washed three times with 60 mL portions of ice water. After drying thoroughly at 110^0 C and pulverizing, the anhydrous salt was obtained as a red powder (6 g, 40% and M.Pt >300^{0}C), literature M.Pt >300^{0}C [81].

5.1.2.2. Tri (p-Nitrophenyl) Phosphate (Tp-NPP)

Rigorously dried, finely powdered sodium p-nitrophenoxide (3.7 g, 0.023 mol.) was added slowly to anhydrous ethereal (THF) solution of 13 mL of phosphoryl choride (0.5 mL, 5.4 mmol). The mixture was stirred for 30 minutes at room temperature and then refluxed for two hours. The yield was 0.63 g (23%) and the m.p. 150-151^{0}C. Some physical properties and λ_m of the substrates and p-nitrophenol are summarized in the **Table** below.

Table 8 physical properties and λ_m of ester substrates and starting material.

Compound	Physical state	M.Pt(^{0}C) Exp.(Literature)	λ_m in aqueous acetonitrile (nm)
p-nitrophenol	Solid	110-112(113-115)	405
p-nitrophenyl acetate	Solid	75-76 (77-79)	271
Tri (p-nitrophenyl) Phosphate	Solid	152-153 (156)	310

5.2 Materials and Methods

5.2.1 Preparation of Buffer Solution

i. pH 1.0 was made by mixing 25 mL of 0.2 molar KCl and 67 mL of 0.2 molar HCl and making the final volume 100 mL.

ii. pH 7.4 was prepared by mixing 50 mL of 0.1 molar KH_2PO_4 and 39.1 ml of 0.1 molar NaOH and making the final volume 100 mL

5.2.2 Preparation of Solvents

i. pH 1.1 was prepared by mixing acetonitrile with buffer (pH 1.0)

ii. pH 5.76 was prepared by mixing 20 mL of water with 80 mL of acetonitrile

iii. pH 6.15 aqueous acetonitrile was prepared by mixing 10 mL of water with 90 mL acetonitrile.

iv. pH 7.4 were prepared by mixing acetonitrile , water and buffer (7.4).

5.2.3. Preparation of solutions

Solutions of esters (0.1 mmol) and Zn complexes (0.05 mmol) were prepared at a specific pH using the above solvents.

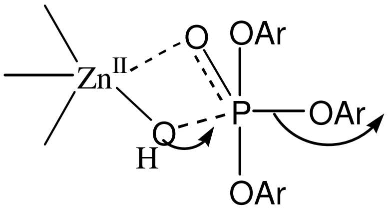
5.2.4. Method

The hydrolysis of the p-NPA and Tp-NPP esters were investigated by observing the change in an absorption maximum around 405 nm assigned to the p- nitrophenolate anion using SPECTRONIC GENESYS 2PC Spectrophotometer. PH measurement was done by using PW 9418 pH meter.

Rate measurement was started by running the ester solution before and after mixing with Zn (II) complex in a 2:1 molar ratio (ester solution to complex solution) at different temperature at a given pH. The progress of the reaction was detected as the instrument measures the absorbance at a wavelength of 405 nm at a preset interval of time.

5.3 Results and Discussion

Basically, in Zn(II) hydrolytic reaction, mechanistic investigation revealed that a Zn(II)-OH$^-$ intermediate formed from the deprotonation of coordinated water is the essential active species in ester hydrolysis [82]. Such intermediate may have dual roles as shown in the mechanism below (**29**).



(**29**) Proposed mechanism for Tp-NPP hydrolysis

But a preliminary kinetic investigation from UV-Vis spectra at varying pH (1.1, 5.76, 6.15 and 7.4) and varying temperatures (25 and 45^{0}C) indicate that the two ester solutions (p-NPA and Tp-NPP) showed no significant absorption band around the region 405 nm below pH = 7.4 in the presence and absence of the two Zn(II) complexes. This indicates that the rate, i.e., the change in absorbance per time taken (the time taken was varied from 8 minutes to 24 hrs) is nil and hence the two Zn(II) complexes exhibit no significant hydrolytic nature in the hydrolysis of the p-NPA and Tp-NPP esters. This may be attributed to the deactivation of the complexes by the carbonyl carbon on the macrocycles frame work, which compete for water coordination with the Zn(II) electrophilic site and the formation of polymeric hydroxide precipitate of the complexes at higher pH . There is an observed absorption at 405 nm for the two ester solutions in the presence and absence of the two Zn(II) complexes at pH=7.4, which is attributed the hydrolysis of esters by hydroxide ion of the slightly basic medium. There is an observed higher rate of hydrolysis of Tp-NPP ester compared to p-NPA, which is attributed to the relatively lower energy d-orbital of the phosphorous to accept the nucleophile compared to carbon p-orbital.

6. CONCLUSION

The synthesis of two series of tetradentate tetraaza and pentaaza macrocyclic complexes, the first series being $[M^{(II)}L(H_2O)Cl]Cl$ and $[CuL]Cl_2$ and the second series, $[M_2^{(II)} L'(H_2O)_4]Cl_4$, where M = Co, Zn and Cu and L and L′ are the first and second ligand, had been achieved by template condensation of o-phenylenediamine and succinic acid in the first and ethylene-diamine, formaldehyde, p-phenylenediamine and succinic acid in the second case. These were confirmed by the results of elemental analysis for metal and chlorine, IR, UV-Vis, ^1H NMR and ^{13}C NMR (400 MHz, D_2O), Λ_m and some other physical properties such as M.Pt and solubility data. Further analysis for the C, N, H, or the X-ray analysis may be required for complete description of the complexes. Finally the Zn(II) complexes showed no significant catalytic nature on investigation of their hydrolytic nature.

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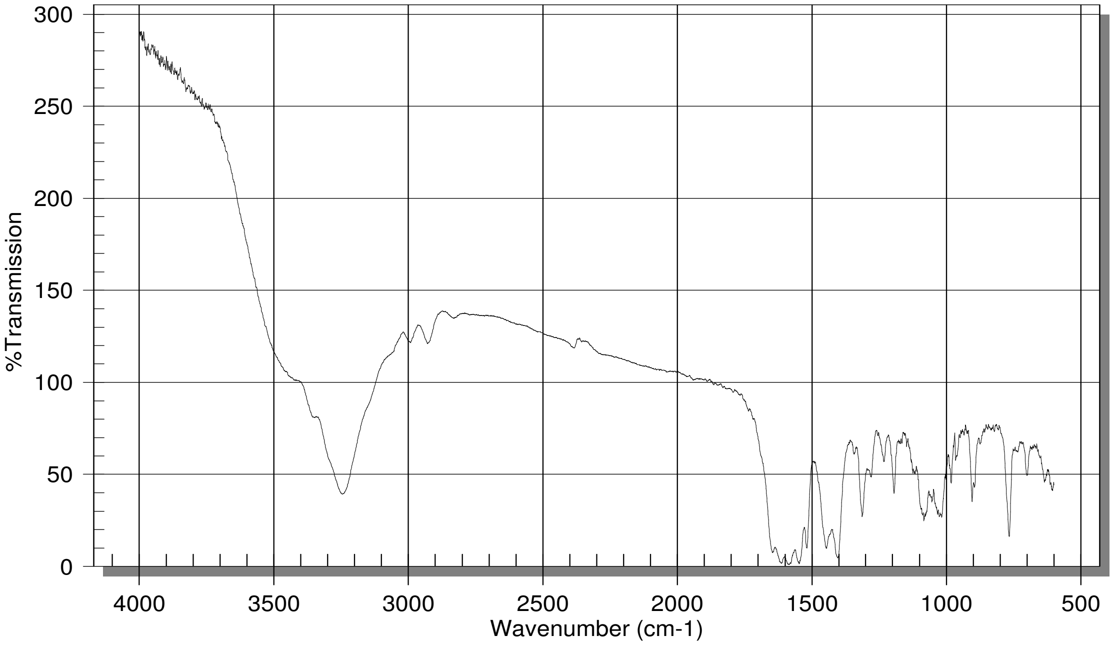
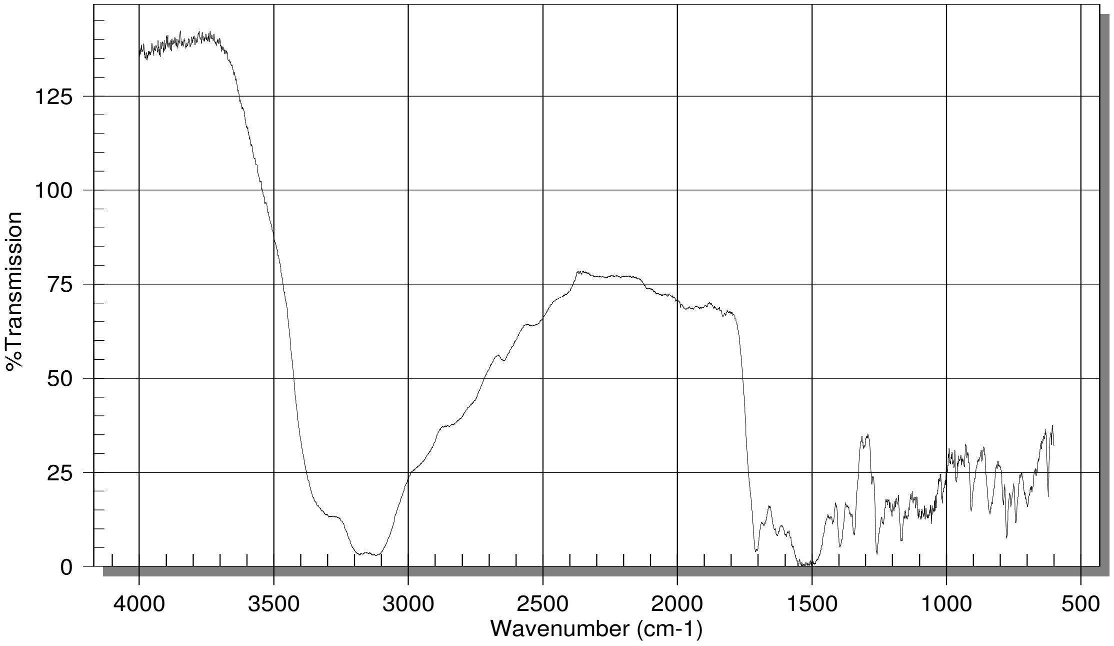
8. APPENDICES

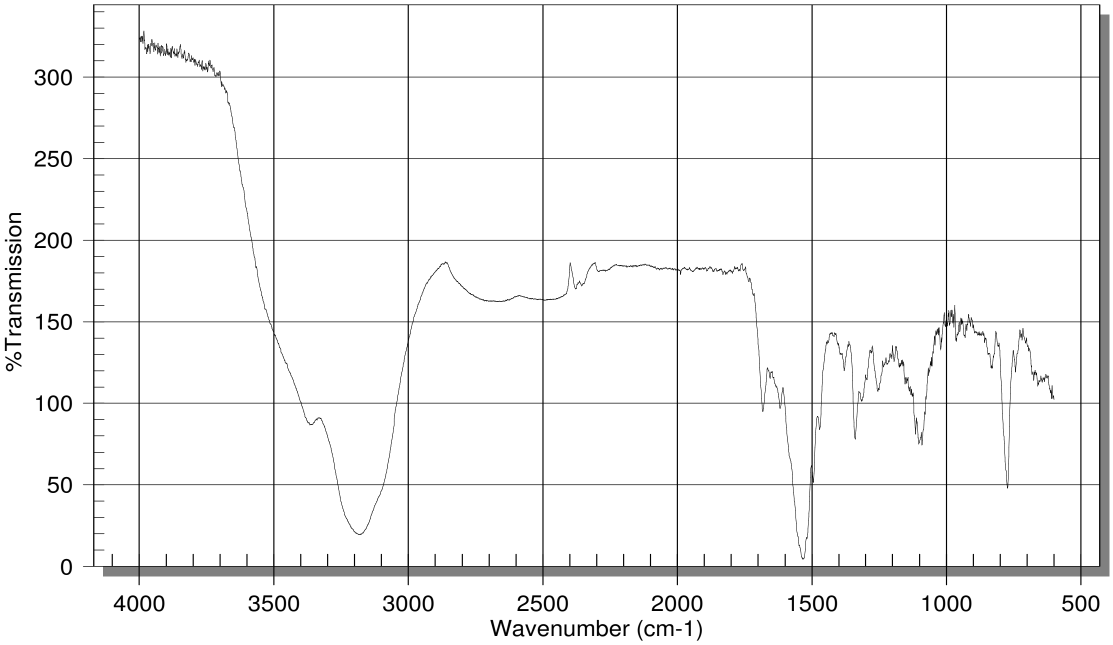
The IR Spectrum of [ZnL(H2O)Cl]Cl



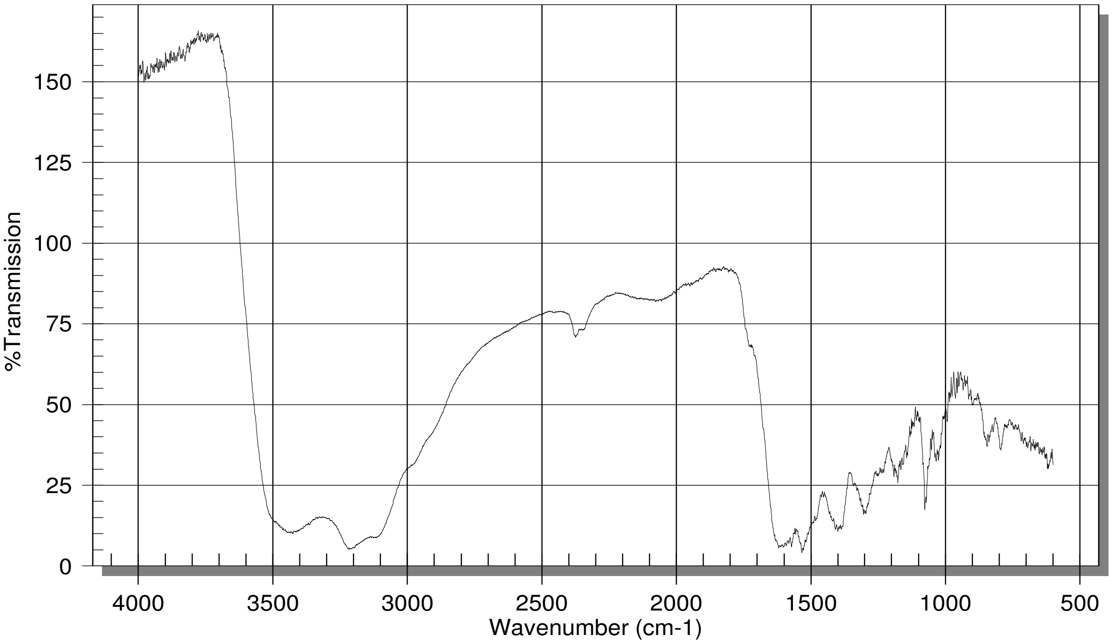
The IR Spectrum of [CoL(H2O)Cl]Cl



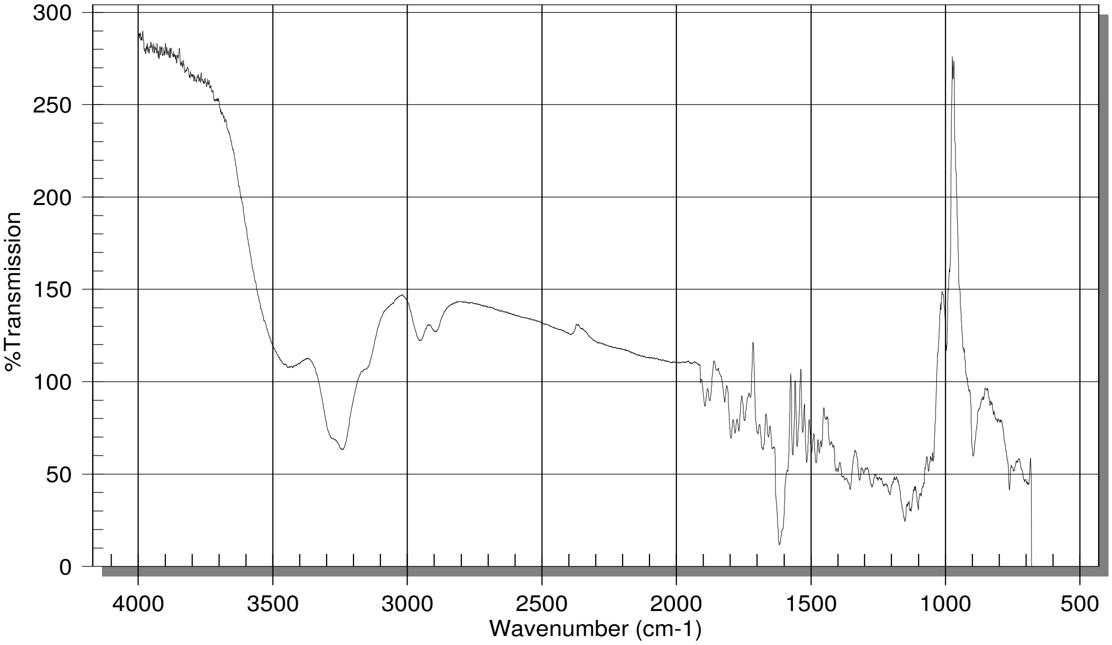
The IR Spectrum of [CuL]Cl2



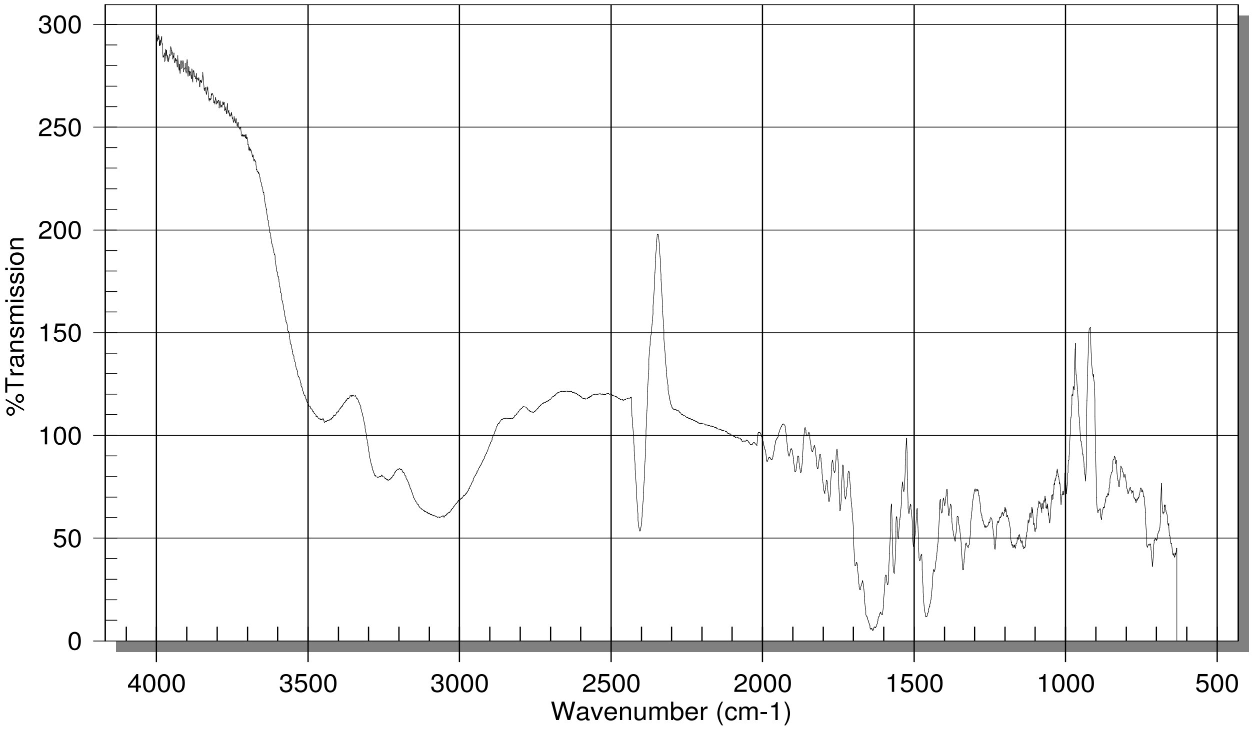
The IR Spectrum of [Co2L`(H2O)4]Cl4



The IR Spectrum of [Cu2L`(H2O)4]Cl4



The IR Spectrum of [Zn2L`(H2O)4]Cl4



The Proton NMR Spectrum of [ZnL(H2O)Cl]Cl

The Carbon-13 NMR Spectrum of [ZnL(H2O)Cl]Cl

The DEPT Spectrum of [Zn(H2O)Cl]Cl

The electronic Spectrum of [CuL] Cl2

The electronic Spectrum of [CoL(H2O)Cl]Cl