

Review Article

A Review on Macrocyclic Complexes

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Abstract

During the past few years there has been a great deal of activity in the field of macrocyclic complexes. It has been recognized that many complexes containing synthetic macrocyclic ligands may serve as models for biologically important species [1]. The discovery that the natural products, coenzyme B₁₂, is a cobalt (III) corrinoid complex containing a sigma bonded alkyl ligand (occupying an axial position) has led to lot of research in the preparation and study of synthetic analogues of vitamin B₁₂ (**Figure 1**) and its enzymes[2].

In the macrocyclic complexes metal ion is placed at the center of cyclic environment of the ligand .The extraordinary chemical and biological properties of molecules like cryptates, crown- ethers, macrolides cyclic peptides, and Schiff bases have triggered a great deal of interest in their synthesis, structure and reactivity. They have an ability to encapsulate metal ions with remarkable

specificity and stability. Now a days attempt have been made to promote considerable interest in the design and preparation of synthetic macrocyclic complexes to relate electronic properties and reactivity to those of naturally occurring macrocycles such as corrins and porphyrins. One of the interesting aspects of macrocyclic complexes is the influence of stereochemical preferences of a particular metal ion on ligand conformation and in turn, the capacity of metal ion to accommodate to the geometrical constraints imposed by the macrocycle. An important property of both naturally occurring and synthetic macrocycles having varying degrees of unsaturation is their ability to stabilize at both high and low oxidation states in the metabolic function of naturally occurring porphyrins.

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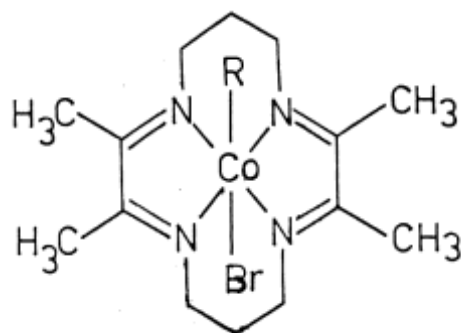


Figure 1 Synthetic analogue of vitamin B₁₂

Introduction

The macrocyclic complexes have wide spread applications-Macrocyclic polyamines, their salts and chelates with copper, nickel, iron, rhodium and thorium metal ions are useful as chemical sensitizers for photographic silver halide emulsions. Cobalt (II) macrocyclic complexes can be used to determine the concentration of oxygen dissolved in water and hence to increase the range of concentration and sensitivity and thus help to reduce the analytical time. The use of monocyclic complexes as extractants for the analytical separation of metals has been widely investigated [3]. The metal ions to be extracted undergo complexation with crown ethers and are further extractable into organic solvents. The crown ethers have been reported to be potential ligands for the transport of alkali and alkaline earth metal ions across natural and artificial membranes [4, 5]. Recently because of the possible use as therapeutic agents and also for other (non biological) applications a considerable interest has been developed in the study of macrocyclic complexes. A large variety of macrocyclic complexes are reported to have novel solid-state properties. Iodine doped macrocyclic complexes produced a new class of electrically conductive mixed valent metallic macrocyclic complexes. A pulse radiolysis and flash photolysis study of nickel (III) macrocyclic complexes reported it as a powerful oxidizing agent [6].

1.1 Crown type macrocyclic complexes

The macrocyclic complexes of crown type known as crown ethers or macrocyclic polyethers were first discovered by Pederson [7]. The crown ethers contain ethylene bridge, separated by oxygen atom. A central hydrophilic cavity of diameter ranging from 1.2-6.0 Å is also present in the crown ethers. The central cavity is ringed with electronegative binding polyether oxygen atoms surrounded by a collar of -CH₂ groups forming flexible hydrophobic framework. Inorganic cations can be extracted in the suitable organic solvents with the help of crown ethers. Cation under the investigation forms complex with crown ether. In this process cation is converted into lipophilic species. Crown ethers have received wide attention because of their unusual [8] behaviour towards a range of non transition metal ions. Few studies involving transition metal ions [9] have also been reported. It is evident that the majority of such polyether ligands show a limited tendency to form stable complexes with transition metal ions. The crown ethers now a day are widely used as extractants. The commonly used crown ethers for such purpose [10, 11] are 15-crown-5, 18-crown-6 and DB-18-crown-6. The alkali metal ions like sodium, potassium and alkaline earth metal ions like calcium strontium and barium formed extractable complexes in methyl chloride or nitrobenzene or chloroform with the crown ethers. In extractions the factors like size of the metal ion and its charge, nature of donor atom, diluents and counter ion plays a vital role. The nature of the extracting species for alkali metal complexes was metal: crown ether: picrate as 1:1:1 while for alkaline earth complexes it was 1:1:2. The extractions by crown ethers permitted sequential separation of alkaline earth metal ions. The s-block elements from biological, environmental and industrial samples have been also analyzed by the extraction with crown ethers. Apart from the extraction of alkali and alkaline earths, crown ethers were also used for the liquid-liquid extraction of complexes of lead, silver, thallium, gold, copper, zinc mercury, lanthanides and uranium metal ions [12].

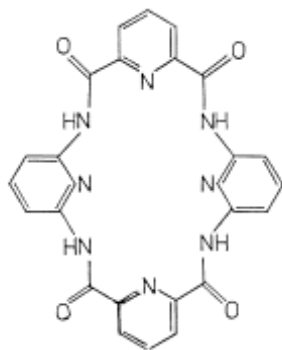


Figure 2 Polythioethers

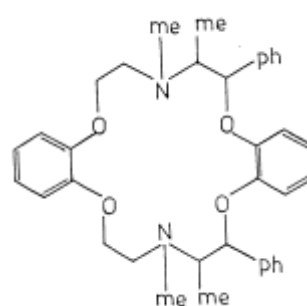


Figure 3 Crown aminoethers

Modified chromogenic crown ethers were also used for extractive spectrophotometry and flurometric analysis. Many of ethers were used for chromatographic separation and in fabrication of ion-selective electrodes. The stability constant [13] of macrocyclic complex with 18-crown-6-macrocyclic ligand is found to be enhanced by four figures than that of complex with linear ligand tetraglyme. The crown ethers containing oxygen atoms and nitrogen atoms are termed as polyaminoethers while those crown ethers with sulphur atoms and oxygen atoms are known as polythioethers as shown in the (Figure 2) with iron, nickel, silver, cadmium and gold were isolated [14] in crystalline form. Macrocyclic complexes of niobium pentachloride [15] with pentacyclic polythioethers were prepared and characterized as simple Lewis acid base adducts with the ligands functioning as bridges between niobium pentachloride units. Ligands displayed no reducing tendencies towards niobium pentachloride and all complexes were diamagnetic. Chiral crown amino ethers (Figure 3) were synthesized by Federico and coworkers[16] in three steps starting from amine. Macrobicyclic diaminopolyethers are reported to be useful in analytical and environmental studies.

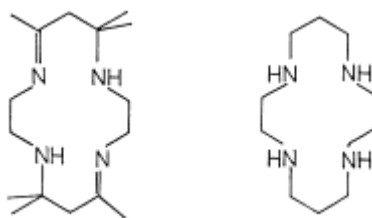


Figure 4 Quadridentate ligand

In macrocyclic complexes of 1,5,9,13-tetrathiocyclohexadecane ligand with copper [17], the ligand behaves as tetradentate in presence of copper(I) and copper(II) tetrafluoroborate. Whereas, when copper chloride is used instead of copper tetrafluoroborate the ligand behaves as bidentate. A phenomenon of host guest complexation is reported in macrocyclic polyethers by Helgenson and coworkers [18]. The identification of concentration of macrocyclic ligand as well as concentration of metal ion in the macrocyclic complexes can be carried out by thermometric titration [19]. A potentiometric method of analysis [20] can be used for the determination of stability constant. The stability constants of di and trivalent lanthanides complexes are reported to decrease with increase in ionic radius of lanthanide due to strong depressing effect of complexation on arm ring of macrocycle. The high stability constants of macrocyclic complexes of 'crown' type over a wide pH range minimize hydrolysis and subsequent polymerization problems.

'Curtis type' macrocyclic complexes

The macrocyclic complexes of this type were widely investigated by Curtis. Macrocyclic ligands of 'curtis type' usually form quite stable complexes with transition metal ions. A number of donor atoms mainly nitrogen or sulphur have been incorporated in such ligands. Macrocyclic complexes with transition metal ions often show special properties which in some instances are related to those of naturally occurring macrocyclic systems.

(I) Macrocyclic complexes with nitrogen donors:

The majority of macrocyclic complexes obtained from nitrogen donor macrocyclic ligands have been studied are quadridentate (figure 4). Cyclic ligands have been prepared both directly by conventional organic syntheses [21,22] and by in situ [23,24] or template methods [25,26,27] which involves cyclization in the presence of metal ion. In the direct syntheses the cyclization is performed under conditions of moderate to high dilution in order to minimize the competing linear polymerization reactions. The quadridentate amine (cyclam) can be obtained by direct synthesis [28] using 1, 3-bis (2-aminethy-amino)propane and 1,3-dibromo propane in alcoholic potassium hydroxide under high dilution conditions. However the yield is small as compared to the 'cyclam' synthesized by in situ condensation [29,30]. Although a number of macrocyclic ligands can be synthesized by direct as well as by in situ procedure, it is nevertheless true that a large proportion of other cyclic ligands can only be obtained via in situ techniques. The Schiff base condensation between a carbonyl compound and organic amine to yield an imine linkage forms the basis of

many successful macrocyclic ligand syntheses. Bis (diaminoethane) copper (II) perchlorate reacts with dry acetone under reflux at 110°C for 6 hrs. to give blue violet coloured copper (II) macrocyclic complexes [31]. Similarly, yellow coloured Ni(II) macrocyclic [32,33] can be obtained. The nickel (II) complexes of the macrocycles (cis)-5,7,7,12,12,14-hexamethyl -1,4,8,11, tetra-azacyclotetra deca-4,14-diene and (trans)- 5,7,7,12,12,14-hexamethyl -1,4,8,11, tetra-azacyclotetra deca-4,14-diene [34] which have two secondary amine and two imine donor groups were synthesized by the reaction of diaminoethane -nickel(II) with acetone. This complex can be reduced step wise to give first the tri-amine-mono-imine Ni(II), cis and trans-triene nickel(II) and then the cyclic cis and trans Ni(II)tetra amine complexes[35]. The diene are oxidized by nitric acid to give the cyclic tetra imine complexes of cis and trans type (cis and trans tetene). These complexes may be partially reduced using hypo phosphorous acid to give monoimine-triimine complexes (cis and trans triene)-further reduction of which yields the diene ,starting material[36].

Now a day, instead of applying direct synthesis method or in situ method for the synthesis of macrocyclic complexes a new technique of demetallation of the complexes and replacing the metal ion in the macrocyclic ring by desired metal ion is being used. cyclic Schiff bases are reduced to form two isomeric cyclic tetramine nickel(II) complexes. Their reaction with cyanide releases the isomeric cyclic tetramine which can be used as macrocyclic ligand to form macrocyclic complex with other metal ions [37] (**Figure.5**). Stevens and coworkers [38] have reported the synthesis of the super structure Co (II) complexes by the same demetallation technique [39]. The macrocyclic ligand is removed intact from the Nickel (II) template of the macrocyclic ligand complex and then cheated around the more interesting (from bioinorganic stand point) Cobalt (II) without degradation and isomerisation .In the super structure ligands the bridge group $R' = (CH_2)_6(PF_6)_2$ provides a protective void or a 'dry cave', near the metal atom, which is intended to shelter small ligands from interactions with other cobalt centers or with solvent.

In order to develop certain class of metal for biological systems it is highly useful to have an access to functional groups provide points of attachment to superstructures designed to facilitate certain biometric properties in the metal complexes of the product ligands [40, 41]. The Ni(II)[MeOethi)₂-Me₂[14]tetraeneN₄]²⁺ macrocyclic complexes contain an unusual peripheral conjugated methyl vinyl ether functional group which readily undergo addition elimination reactions ,especially with amines[42] . With a view to relate electronic properties and reactivity of synthetic macrocyclic complexes with naturally occurring macrocycles a non template synthesis of (B-imioamines) macrocycles possessing 14,15 and 16 member rings is devised..This method is based on the electrophilic reactivity of 1-2 dithinium cautions and B-aminothioenes with primary amines. Tris (1,3-diaminopropanes)nickel(II) perchlorate on reaction with benzoin and aniso in methanol gives the orange coloured macrocyclic complexes [43].

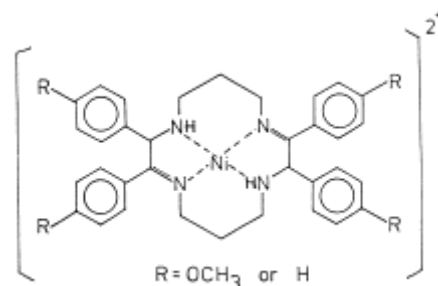


Figure 5 macrocyclic ligand

Takamoto and co-workers determined the chelate formation constants of newly synthesized macrocyclic complexes of ligand 1,2-di(1,4,7-triaza-1-cyclonyl)etane with Cd(II),Zn(II),Co(II) and Ni(II) at 25°C in potassium nitrate[44] . The macrocyclic complexes of Zn(II),Cd(II) and Mn(II) with macrocyclic ligands in which the 1-10 -phenanthroline group is incorporated are reported by Bishop and coworkers[45]. A new class of branched quadridentate Schiff base macrocycles [46] with an additional legating group in the side chain is also known as .Nickel(II) macrocyclic complexes of 'cyclam' and their [2,2,4,9,11-hexamethyl]and[2,2,4,9,11-hexamethyl-4,11-diene] derivatives can be very well oxidized electrochemically[47] on gold and platinum electrodes in aqueous disodium sulphate to give the nickel(II) corresponding complexes which have strong single electron oxidizing properties. Mononuclear

macrocyclic complexes of lead (II) with Schiff bases can be synthesized by template cyclocondensation [48]. The coordination number of lead (II) in these complexes varies from five to eight and it depends on the nature of the anions and the nature of the macrocyclic ligand. A tridentate macrocyclic ligand [49] is synthesized by reaction of 2,6-dipicolinic acid, hydrazide and acetyl acetone. Copper (II) complexes of this macrocyclic ligand are isolated and characterized as trigonal bipyramidal complexes on the basis of their chemical analyses. The pentadentate high spin nickel (II)[1,4,7,10,13-pentaazacyclodecane] are reported to have the distorted octahedron with folded macrocyclic ligands. The macrocyclic complexes of Lanthanum are also known. The eighteen member hexaaza macrocyclic complex is synthesized by template condensation of 2, 6-diacetyl pyridine with ethylene diamine in presence of lanthanum (III) perchlorate. Chelate macrocyclic compound by template condensation of pyrazole in the presence of transition metal ions at 130-160°C in organic solution also can be synthesized (**Figure 6**).

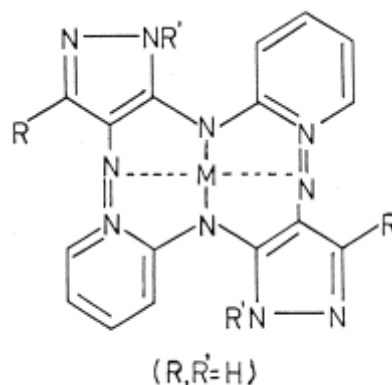


Figure 6 Template condensation of pyrazole

In the macrocyclic complexes with nitrogen donors usually the ligating atoms lie in a plane or nearly so, with the metal atom positioned either in the same plane or slightly above it. Thus most commonly encountered polyhedral are square planar, square pyramidal and octahedral (with distorted form also) This is the expected consequence of macrocycles having full or substantial degree of unsaturation. With fully saturated macrocycles, ring folding may occur. To fully encircle a first row transition metal ion, a macrocyclic ring size of between –thirteen and –sixteen members is required [50, 51] provided that the nitrogen donors spaced such that –five, six or –seven membered chelate rings are produced on coordination. The skeletal vibrations of the macrocycles reflect changes in the geometry of the macrocycles [52]. The stereochemistry of the macrocyclic ligand shows the possibility of configurationally isomers due to chiral carbon and chiral nitrogen centers. The distereo isomers, possible for other macrocycles have been isolated and identified on the basis of ^1H nmr, ^{13}C nmr, X-ray and electronic spectra [53].

(II) Macroyclic Complexes with nitrogen –sulphur donors:

Macrocyclic complexes containing both nitrogen and sulphur donors are widely known, some of them are illustrated in (**Figure 7**)

Bush and coworkers [54] investigated that for ligands incorporating sulphur donors require a ring size of greater than thirteen members to surround the metal ion in the macrocyclic complexes. Salts of diamagnetic complex ion can be isolated from the reaction in THF, of dihydrazine with formaldehyde in the presence of nickel ion [55], inherent in the synthetic strategy for this template reaction is the thought that the use of dihydrazine moiety may overcome the masking of the nucleophilic character of amines [56] which is usually observed when amines are coordinated to metal ions.

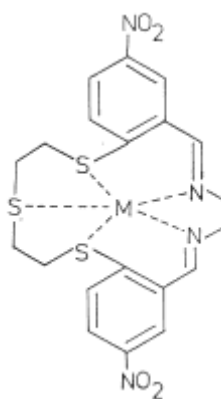


Figure 7 Macrocyclic complexes containing N-S donors

(III) Macrocyclic Complexes with nitrogen –oxygen donors:

A series of macrocyclic complexes having nitrogen oxygen donors containing cis-imine linkages are prepared by direct syntheses and in situ procedures in the presence of nickel salts. A template condensation [57] of 1,3-diaminopropane with dialdehydes yields the macrocyclic complexes in the presence of metal ion which can be isolated from the methanol reaction solution by the addition of water. A macrocyclic complex of lead (II) can be synthesized by template condensation [58]. X-ray analysis of crystal structure of the complex shows the position of lead(II) within the macrocyclic cavity and thiocyanate ions above and below the macrocyclic ligand gives the effective eight coordination of lead(II).

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