

Review

Coordination chemistry and application of mono- and oligopyridine-based macrocycles



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Dedicated to Professor Pierre Braunstein for his pioneering contribution in the field of organometallic and coordination chemistry.

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ABSTRACT

This review gives an account of the coordination chemistry, metallo-supramolecular chemistry and application of mono- and oligopyridine-based macrocyclic ligands. For this purpose, recently reported ligands and their metal complexes possessing at least one pyridyl donor group in a cyclic structure as the metal binding site have been selected. The application and prospects of such compounds in different scientific areas have been delineated.

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1. Introduction

The term “*macrocycle*” refers to molecules having cyclic frameworks containing at least three donor atoms and the ring compris-

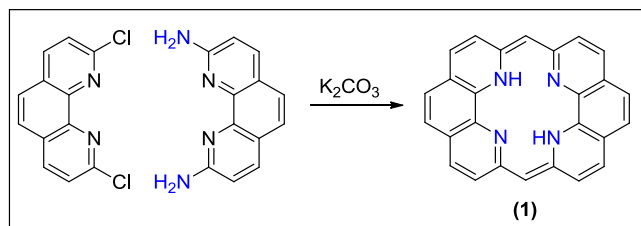
ing a minimum of nine atoms [1]. Some common examples of macrocyclic compounds encountered in everyday life include hemoglobin, porphyrins, chlorophylls, corrins, etc. Over the years, a wide variety of polydentate macrocyclic ligands having donor atoms incorporated in or attached to a cyclic backbone have been studied [2]. Several synthetic macrocyclic ligands and metal complexes mimicking their natural counterparts have been reported

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with application(s) in the field of biomedicine, catalysis and sensing [3–5]. While research in macrocycle chemistry dates back to 1950s [6], a resurgence of interest in macrocycles has been seen during last few decades. This is due to the rich coordination chemistry and multidimensional application offered by the macrocyclic compounds. Another interesting aspect of macrocyclic complexes is the unusual stereo-chemical arrangement that may be formed on coordination of macrocyclic ligand(s) to metal centers as with the macrocyclic ligands involving π -electron delocalization around the ring, a rigid stereo-chemical arrangement is often imposed on the metal, which would not occur in the absence of such ligand [7]. Furthermore, the redox properties of the macrocyclic complexes are of interest because electron transfer may be either at the ligand or at the metal center. The electrochemical properties depend on several factors including the denticity of the macrocycle ligand, the nature of metal ion as well as other co-ligands coordinated to the metal center, etc.

A wide variety of macrocyclic ligands having 3–6 donor atoms in the ring has been reported but the majority have 4, more or less evenly spaced around a ring of between twelve and sixteen atoms [6]. Among these, mono- and oligopyridine-containing macrocycles provide a versatile platform giving rise to a variety of structural motifs, including mono- and di-compartmental cycles, three-dimensional cages, and sterically enforced macrocycles, etc. [8]. The main interest in macrocycles incorporating pyridine sub-units is due to their ability to function as efficient coordinating ligands [9–13]. It is well established that transition metal ions bind more effectively to pyridine-incorporated macrocycles than their furan counterparts [14]. The enormous interest also stems from their excellent chemical-, photo-, and thermal stability. Their diverse areas of application include magnetism, catalysis, organic electronic, nonlinear optics, and biomedicine [3,4,15,16]. These outstanding features/qualities have inspired the study of different macrocycles with contracted, expanded or isomeric oligopyridine analogs [6]. Macrocyclic polypyridines such as cyclosexipyridine, azacalix[4]pyridine etc. constitute interesting, rigid supramolecular hosts for cations and H-bond donors, which provided the motivation for several earlier studies [6,7,17,18]. There are a number of review articles that chronicle the progress made in macrocycle chemistry during the past few decades [3,4,19–23]. During the preparation of this article, a review by Housecroft and Constable on oligopyridine systems has been published [24]. This review focused on the non-classical coordination (hypodentate) modes of oligopyridine and related ligand systems. Although several other reviews have also been published on one or more topics covered in this review, no review put together the coordination chemistry and application of mono- and oligopyridine-based macrocyclic ligands and their metal complexes in one place; hence the motivation for this review. Our very sincere apology to those peer researchers whose work have not been covered here due to the space constraint.



Scheme 1. An example showing synthesis of phenanthroline macrocycle by non-template method.

2. Synthetic strategies of pyridyl incorporated macrocycles

Macrocyclic ligands often include chelating nitrogen, sulfur, phosphorus, arsenic, etc. atoms which are separated by one or more methylene units [6,25,26]. In some compounds oxygen atoms are also present as donors; however, they are classified separately as crown ether. Due to the presence of electron-rich elements N/P/S/As in macrocycles, they show strong affinity for transition and other metal ions with, in some cases, also for alkali and alkaline earth metal ions [27]. Pyridine is an electron-deficient moiety and acts as a good Lewis base due to the presence of a lone pair of electrons on the nitrogen atom. Another advantage of pyridine sub-unit in the macrocyclic framework is that it imparts rigidity to generate highly stable metal complexes [16] and produce molecular helicity/chirality in inorganic complexes [28,29]. The strong affinity of pyridine nitrogen toward metal centers augments the formation of endo, or partial endo metal complexes [30]. A wide variety of saturated and unsaturated nitrogen donor macrocycle is currently available [22]. Since the recognition of the importance of complexes containing macrocyclic ligands, considerable efforts have been made for the development of reliable synthesis for this important and interesting class of coordination compounds. Recently, Rezaeivala and Keypour [22] with others [31–33] comprehensively reviewed the synthesis of different classes of macrocycles. Herein, we present prototypical macrocyclization reaction with representative examples. The synthetic protocol for macrocyclic compounds may be divided into two groups, both of which contain many representatives; those in which the ligand is prepared free of (non-template) and those in which it is prepared bound (template) to a metal or non-metal ions. In all cases of the synthesis of nitrogen donor macrocycle, the ring closing reaction involves either the formation of Schiff's base or the nucleophilic displacement by nitrogen of a halogen or its equivalent. Synthesis and functionalization of a macrocycle is also achieved by transient-template reaction and by organic ligand modification.

In the non-template or direct synthesis method, two components bearing appropriate functionalities are reacted in high, moderate or low dilution condition to achieve the desired macrocyclic product [6]. Non-template reaction methodology has been used mainly for the synthesis of S/As incorporated macrocycles with some examples of N donor macrocycles incorporating oligopyridines [6]. For example, macrocycle **1** (Scheme 1) was synthesized by Ogawa and co-workers [34] in high yield by heating 2,9-dichloro and 2,9-diamino-1,10-phenanthroline precursors under high dilution condition.

The concept of template reaction was introduced to the chemists by the seminal work of Busch [35] and Pedersen [36] in 1960s. According to Busch, a chemical template is “a species that organises an assembly of atoms, with respect to one or more geometric loci, in order to achieve a particular linking of atoms” [37]. In the template reaction, a metal ion, non-metal ion, or organic precursor assists the formation of free macrocyclic ligands and its metal complexes. Several examples of imine bridged mono-, oligo- and poly-pyridine macrocycles are available in the literature which have been synthesized by Schiff's base condensation of diamines with dicarbonyl precursors in the presence of transition and lanthanide metal ion as template (Fig. 1a). For example, Curry and Bush [38] reported the first example of 15- and 16-membered N_5 macrocycles and their Fe(III) complexes. Since the reaction uses metal ion as template, the size of the macrocycle formed significantly depends on the size of the metal ion. If the nitrogen atoms concerned are involved in bonding to a template ion, their nucleophilicity is removed unless they can be deprotonated or the reaction conditions are such that the M–L bond can be broken at a rate enough to allow the nitrogen an effective (if reduced)

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