Literature Survey on the Chemistry of Macromolecules

- Historical Back Ground

Macromolecular science was born in the middle of the last century and made a rapid progress in last several decades to fill the gap between traditional disciplines and to meet the practical needs of the new era. However, the macromolecular science is not a mere extension of chemistry or physics but stands at the crossroads of chemistry, physics, and life science. Especially, the macromolecular science has been regarded as an important field of science for understanding of biological phenomena at a molecular level. Macromolecules are known as a typical complex system and have recently attracted the great interest of many scientists in the field of chemistry and physics.

Before 1960 little work had been reported concerning the coordination chemistry of macrocyclic ligands. Since the early 1960s, the synthesis of a very large number of metallated heterocycles had been reported(1).

These synthetic endeavors had provided the raw material for a multitude of research projects in many areas including biological studies, metal-ion catalysis, and metal-ion discrimination. Some of these studies have resulted in industrial and medical applications(2). The macro molecules such as natural heme proteins, chlorophyll and vitamin B_{12}, reveal distinctive coordination chemistry and biological importance of complexes with macrocyclic ligand(3).

Supramolecular chemistry is a novel area of multi disciplinary chemical research that developed during the past few decades. It focuses on complex structures formed by the association (covalent or not) of several moieties and on the novel chemical properties resulting from this higher complexity. Supramolecular chemistry has two facts; one based upon the synthesis of complex organic structures by synthetic chemistry, and one in which the structural complexity is achieved by self-assembly and self-organization of smaller units without the help of covalent bonds.

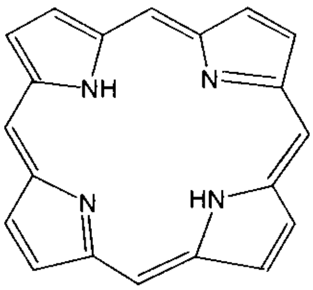
One of the major features of macrocyclic complexes is their remarkable thermodynamic stabilities and resistance to demetallation. Thus the macrocycle can be regarded as a protecting group for the metal ion, enabling unusual reactivity at other coordination.

Macrocycles are cyclic organic ligands which incorporate hetero atoms which may bind to transition metal and other guest ions within the ring. Several macrocycles occur in nature and perform important biological processes, e.g. heme proteins, cytochromes, vitamin B_{12}. Synthetic macrocyclic ligands incorporating O, N and S donor atoms have useful for applications including selective sites and/or stabilisation of unusual metal fragments oxidation states. There are different types of macrocycles involving phosphine, arsine, selenoether or telluroether functions, which are much less well known than amine or thioether macrocycles.

Macrocyclic ligand

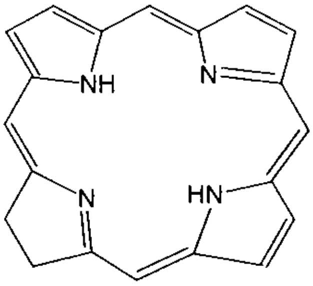
Monocyclic or polycyclic ligands with metal ligating groups incorporated into or attached to a cyclic back bone containing 9 or more atoms which contain at least 3 metal ligating groups. Examples for macro cyclic ligands are:

1- Macrocyclic ligand have biological importance such as porphyin (I) and chlorin (2,3-dihydro porphyin) (II).



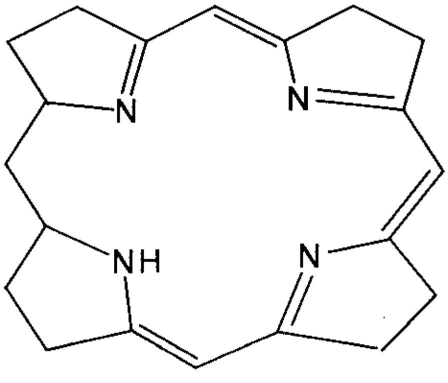
Porphin

(I)



Chlorin
2,3-DihydroProphin
(II)

2- Some macrocyclic ligand present in nature such as chlorophylls contain Mg^{2+}bound to a substituted chlorine system, protein, vitamin B_{12} contains Co^{3+} bound to a corrin ring system (III), hemes found in hemoglobin, cytochromes, catalase and peroxidase.



Corrin
(III)

3- Macrocyclic ligands containing mainly N, P, S as donor atoms prefer to bind to transition metals such as porphyrin and cyclam (IV).