

In nature macrocyclic compounds - molecules of the shape of rings – are selected for use in several significant biological systems which include haemoglobin, chlorophyll and vitamin B₁₂. In such species the metal ion is bound firmly in the porphyrin macrocyclic cavity (**figure 1**). Such stability is characteristic of many synthetic macrocyclic complexes in comparison to their open-chain analogues complexed with metal-ions. Over the past half century, there has been a continuous and an extraordinary development in the field of synthetic macrocyclic chemistry. This is in part related to mimicking the unusual behaviour and properties commonly displayed by macrocycles occurring in nature.

Among the variety of macrocyclic molecules macrocycles containing nitrogen atoms are one of the most appealing ligands in coordination chemistry. Apart from the important tetraaza macrocycles such as porphyrins or cyclam (**figure 1**), which are able to bind a single metal ion in the centre, larger macrocycles are known, which can bind multiple metal ions. Simultaneous binding of several metal ions in close proximity by large macrocycles may result in attractive systems to study magnetic interactions, cooperative catalytic effects or to mimic metalloenzymes, which also utilize multiple metal ions.

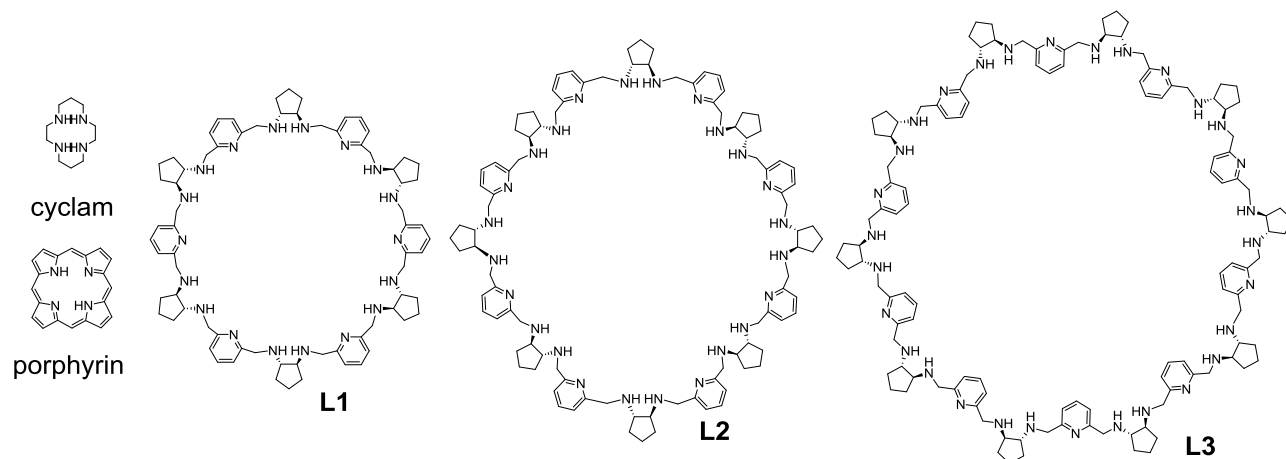


Figure 1. Small cyclam and porphyrin macrocycles vs. large macrocycles **L1**, **L2** and **L3** proposed in the project.

The main goal of our project is a synthesis and in-depth study of multinuclear metal complexes with large polyaza macrocycles capable of simultaneously incorporating several metal cations into their cavities. The synthesis of gigantic macrocyclic molecules is based on the unusual expansion reaction of small (2+2) macrocycle into its huge (6+6), (8+8) and larger homologues recently discovered in our laboratory (**figure 1**). The gigantic polyaza macrocycles, possessing many nitrogen donor atoms, but also cavities of strictly predefined sizes, are ideal candidates to serve as hosts to form different types of complexes with a variety of metal ions (**figure 2**). In the project in complexation reactions of large macrocycles transition metal and lanthanide^{III} ions will be employed. Using various metal salts will allow us to synthesize systems, in which metal ions will be additionally cross-linked by anions. Such complexes (clusters) should exhibit particular magnetic properties.

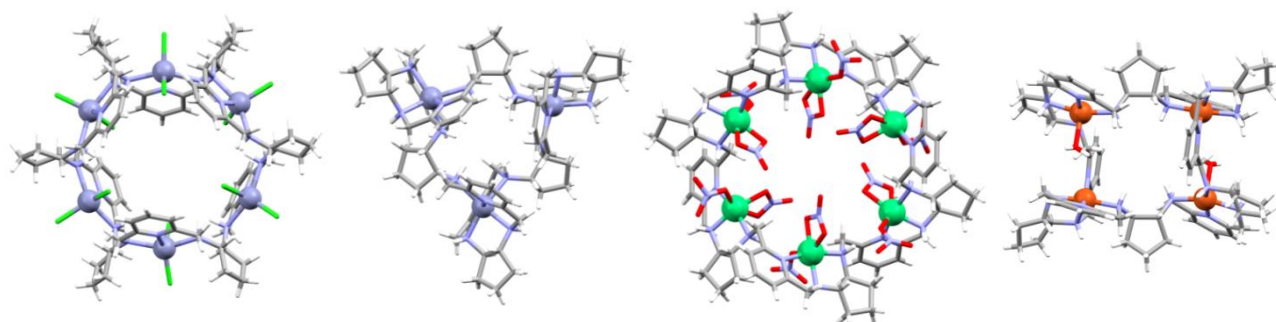


Figure 2. Crystal structures of multinuclear complexes with macrocycle **L1**. From left: [Zn₆(**L1**)Cl₁₂], [Zn₃(**L1**)](Cl)(NO₃)₅, [Ni₆(**L1**)(NO₃)₁₂] and [Cu₄(**L1**)(H₂O)₂](NO₃)₈. Uncoordinated anions and solvent molecules are omitted for clarity. Blue, green and orange balls represent zinc, nickel and copper cations, respectively.

A remarkable rise of interest in more and more complicated macrocyclic systems, is driven by their numerous applications in medicine, metal-ion discrimination, metal-ion catalysis, organic syntheses and analytical processes. Macrocyclic complexes exhibit uncommon thermodynamic, magnetic, spectral, catalytic and redox (including stabilisation of less common oxidation states) properties. It gives rise to the discovery and development of new multi-metallic catalysts, magnetic materials, materials for gas storage and selective sensing of chemical compounds.