Małgorzata Ostrowska
Influence of the hydroxamate ligands' structure on the thermodynamic properties of metallacrown complexes with Cu(II), Zn(II) and Ni(II).
Supervisor: dr hab. Elżbieta Gumienna-Kontecka, Prof. UWr

In recent years one can observe a significant growth in research interest for the preparation of transition metal coordination compounds of high nuclearity, which possess very interesting properties allowing for their use as active components of molecular materials, new sources for luminescent or second harmonic generating (SHG) materials, and the core of functional metal-organic frameworks (MOFs) or large coordination polymers. Among the earliest identified self-assembled polynuclear complexes based on transition metal-ligand building blocks, metallacrowns (MCs) have attracted considerable attention. MCs are cyclic metal/organic compounds which are considered as crown ether analogs in their structure and function. The scaffold of MCs is conceptually obtained by replacing the methylene carbons of crown ethers with metal-heteroatom coordination units. As with crown ethers, they are characterized by the presence of an oxygen rich core cavity, which may encapsulate guest species. Due to their capacity to bind cations of almost any group – alkali, alkaline earth and transition metals, lanthanides and main group metals and metalloids, as well as anions or neutral molecules they have been recognized to be relevant compounds in a variety of research fields. Establishing the solution stability of MCs, their selectivity for metal ions and their guest recognition properties are essential for the design of functional compounds and materials based on MCs scaffolds. Therefore, detailed characterization of the thermodynamic parameters associated with the assembly of metallacrowns would be useful. This is particularly necessary in order to predict whether new metallacrown forming ligands that have been conceived to optimize magnetic or photophysical properties will serve as building blocks for desired metallacrown scaffolds. Optimization of ligands includes the development of chelators that have a high stability across a broad pH-range.

Despite the fact that the first MC was isolated and structurally characterized over 30 years ago, numerous aspects which regulate their stability in solution and the correlation between the species isolated in solid state and those present in solution still remain insufficiently explored. Extension of the knowledge on the thermodynamics of the MCs formation, and a deeper understanding of the relationship between the structure of the ligands and the type of metal ions in an aspect of stability of the MC species have significance in terms of a potential use of MCs as biomedical materials, such as contrast agents, selective metal ion chelators or fluorescent probes.

The aim of the study was (i) to examine the coordination properties of selected hydroxamate ligands functionalized in the α- or β- position, and their ability to form metalllacrown complexes of Cu(II), Ni(II) and Zn(II) ions and (ii) to understand the influence of ligand structure on the formation of metallacrown complexes, their structure and topology. To achieve the proposed aims, the use of a broad range of physicochemical methods was required: mass spectrometry, potentiometric studies, UV-Vis and EPR spectroscopies and isothermal titration calorimetry.

Group of aromatic hydroxamate derivatives with additional nitrogendonor atom in α-position with respect to the hydroxamate function – o-picolinehydroxamic,quinolinehydroxamic acid and pyrazylohydroxamic acid and β-functionalized hydroxamate derivative – ethylphosphonohydroxamic acid. It was shown that aromatic ligands are able to form stable MC complexes with Cu(II), Ni(II) and Zn(II) ions with different thermodynamic stability, pH range of self-assembly and topology, depending on the used metal-ligand pair. The fourth ligand, in in which the donor set was change from two nitrogen atoms to one oxygen and one nitrogen atoms forms 12-MC-4 complex only with Cu(II) ions.

A comparison of the thermodynamic stabilities of Cu(II), Ni(II) and Zn(II) MC species with the studied ligands reveal that by the modification of the ligand structure, one can tune the pH range of MC self-assembly and the thermodynamic stability of the complexes. Optimization of ligands leading to the development of chelators forming MCs that have a high stability across a broad pH-range is in particular interest in the perspective of a potential use of MCs when a specific pH conditions are required, i. e. selective binding of anions and cations. The use of a use of MeOH/H_2O mixture (80/20 w/w) has a significant influence on the thermodynamic stability of MCs.