

Summary

The submitted Ph.D. thesis concerns anion receptors based on symmetrically tetrasubstituted *cone* calix[4]arenes. These receptors are easily synthesized and display sufficient water solubility to function as receptors for tetrahedral oxoanions.

The thesis starts with a brief survey of literature on calix[4]arene anion receptors and sensors. The theoretical part of the thesis deals with a stereochemical investigation of calix[4]arenes from the Cambridge Structural Database (CSD) with emphasis on the influence of inter- and/or intramolecular interactions on the geometry and rigidity of the calix[4]arene scaffold. In order to describe the geometry of the calix[4]arene moiety, it was necessary to introduce new stereochemical parameters α , β and δ . The utility of these parameters in evaluating the geometry of the calix[4]arene base frame was confirmed. The stereochemical investigation formed the basis for design of new potential anion receptors based on symmetrically tetrasubstituted *cone* calix[4]arenes.

The experimental part of this work started with synthesis of symmetrically tetrasubstituted calix[4]arene derivatives containing 1-propoxy groups at the lower rim and synthesis of calix[4]arene derivatives with carboxymethoxy groups at the lower rim and enhanced water solubility. Identity and purity of prepared compounds was confirmed by ^1H and ^{13}C NMR, ESI MS, FTIR, FT Raman, melting point and TLC. Several crystal structures of the prepared calix[4]arenes were determined and the stereochemistry of the calix[4]arene platform was discussed. The stereochemistry of the prepared calix[4]arene structures followed the trends observed in calix[4]arene structures from the CSD.

Interaction studies of the prepared calix[4]arene derivatives with anions were performed. Interaction of the hosts with anions, preferably tetrahedral oxoanions in the form of tetrabutylammonium salts was studied by UV-Vis spectroscopy in a variety of solvents (acetonitrile, dimethyl sulfoxide and aqueous HCl). Measurement in aqueous solutions was complicated especially by aggregation caused by hydrophobic and π - π interactions, which was observed in concentrations 10^{-4} M and higher. Stability constants and stoichiometries were evaluated; interaction constant of $1770 \text{ mol}^{-1}\text{dm}^3$ (1:1 stoichiometry) was obtained for one of the prepared calix[4]arenes with sulfate in $5 \cdot 10^{-3}$ M aqueous HCl.