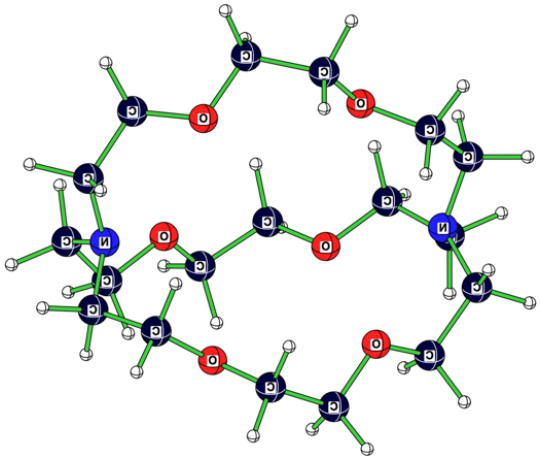
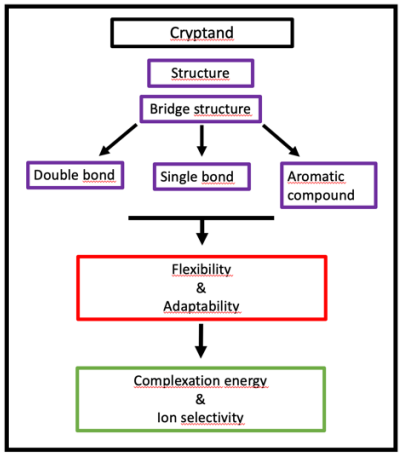
Quantum chemical analysis of structure and ion selectivity correlation of moieties derived from the [2.2.2] cryptand

Maximilian Dejori, Markus Walther, Ralph Puchta

Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany





A great impact in the field of supramolecular chemistry was made by J.-M. Lehn and his coworkers in 1967 by the discovery of 4,7,13,16,21,24-(hexaoxa-1,10-diazabicyclo-[8.8.8] hexacosane, better known as [2.2.2].[1] Today, [2.2.2] is the most prominent Cryptand and commercially available as Kryptofix 222. The outstanding complexation properties of [2.2.2] for alkaline and earth metal ions were immediately recognized. This discovery earned Lehn together with Pedersen and Cram the Nobel Prize in 1987.

The field of supramolecular encapsulation chemistry has thus been given the task of studying the [2.2.2] cryptand and its related systems in order to gain a better understanding and, if necessary, to carry out optimizations.[2][3] But what factors influence complexation properties and can these factors be modified to achieve a desired complexation behavior?

Based on DFT (B3LYP/LANL2DZp) calculations we designed derivates of [2.2.2]. At first glance, the structures of derivates differ significantly in their flexibility. In order to understand the effect of the flexibility of the structure on the ion selectivity, different descriptors were applied.
Specifically, complexation energies, bond lengths, dihedral angles and cavity volumes were investigated and correlated to each other, leading to some novel and interesting insight into the influence of cryptand cage flexibility and cryptand cavity volume on the depth and width of the ligand complexation energy curve relative to ligand type, size and charge.

[1] Dietrich, B.; Lehn, J.M.; Sauvage, J.P., Tetrahedron Letters, **1969**, *10 (43)*, 2889-2892.
[2] von Delius, M. et. al., Angew. Chem., **2017**, *56 (3)*, 776-781.
[3] Begel, S.; Scheurer, A.; Puchta, R., J. Coord. Chem., **2015**, *68 (17-18)*, 3374-3387.