CHARACTERIZATION OF MICROSOLVATED CROWN ETHERS FROM BROADBAND ROTATIONAL SPECTROSCOPY

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Since they were first synthetized, crown ethers have been extensively used in organometallic chemistry due to their unparalleled binding selectivity with alkali metal cations. From a structural point of view, crown ethers are heterocycles containing oxygen and/or other heteroatoms, although the most common ones are formed from ethylene oxide unit. Crown ethers are conventionally seen as being hydrophilic inside and hydrophobic outside when the structures found for the metal cation complexes are considered. However, crown ethers are extremely flexible and in isolation may present a variety of stable conformations[a] so that their structure may be easily adapted in presence of a strong ligand as an alkali metal cation minimize the energy of the resulting complex.

Water can be considered a soft ligand which interacts with crown ethers through moderate hydrogen bonds. It is thus interesting to investigate which conformers are selected by water to form complexes, the preferred interaction sites and the possible conformational changes due to the presence of one or more water molecules. Previous studies identified microsolvated crown ethers but in all cases with a chromophore group attached to the structure.[b] Here we present a broadband rotational spectroscopy study of microsolvated crown ethers produced in a pulsed molecular jet expansion. Several 1:1 and 1:2 crown ether:water aggregates are presented for 12-crown-4, 15-crown-5 and 18-crown-6. Unambiguous identification of the structures has been achieved using isotopic substitution within the water unit. The subtle changes induced in the structures of the crown ether monomer upon complexation and the hydrogen-bonding network that hold them together will be also discussed.

[a] F. Gámez, B. Martínez-Haya, S. Blanco,J. C. Lòpez and J. L. Alonso, *Phys. Chem. Chem. Phys.* **2014**, *14* 12912-12918

[b] V. A. Shubert, C.W. Müller and T. Zwier, *J. Phys. Chem. A* **2009**, *113* 8067-8079