COMPUTATIONAL INVESTIGATIONS ON HOST-GUEST ADDUCTS BETWEEN METALLOCALIXARENES AND SUBSTITUTED DIBENZOTHIOPHENES

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Calixarenes are cyclic oligomers obtained by condensation reactions between \( p\)-tert-butyl phenol and formaldehyde. Calixarenes are like crowns in that they are pre-organized complexants, yet, unlike porphyrins, calixarenes are not fully conjugated and their three-dimensional structure leads to cavities. Calixarenes are conformationally mobile, and the extreme structures for the calix[4]arenes have been termed the cone (uuuu), partial cone (uuud), 1,3-alternate (udud) and 1,2-alternate (uudd) conformations. Each of these conformers can act as a host molecule to guests, and each has a cavity within both the wide and narrow rim. Because of the conical geometry of the calix[4]arene structure, the volume of the wide rim cavity is greater than that of the narrow rim.

Recently we reported the synthesis of a methylmercury(II) complexed calix[4]arene 1,2-ethoxythiolate, and we carried out our initial computational studies on its function as a host for sulfur containing macrocyclic and heterocyclic guests. These calculations have been carried out on systems where the guest is bound via its sulfur centers to the mercury(II) on the calix[4]arene host. For certain petrochemical applications it would be useful to have the ability to occlude sterically hindered sulfur containing heterocyclic guests into a molecular host. This represents a different challenge from unsubstituted heterocycles because hindered guest molecules may be sterically constrained from their being direct mercury(II)-sulfur bonds between the host and guest. We have now therefore carried out a series of computations between the methylmercury(II) complexed calix[4]arene 1,2-ethoxythiolate host and a series of four sulfur containing heterocyclic guests having functional groups appended that have different steric requirements. These guests are dibenzo thiophene, and both 2- and 2,9-substituted dibenzo thiophenes. The calculations are allowed to minimize freely without any constraint being introduced to favor mercury(II)-sulfur interactions. A further set of calculations have been carried out where a metal center other than methylmercury(II) is bonded to the ethoxythiolate sulfur of the substituted calix[4]arene. These are Ag, EuMe, UMe₃, FeMe, and CrMe. Each is uncharged, with the oxidation state being accommodated by methyl groups to make them comparable with the methylmercury(II) derivative. This group has transition metals, a post transition metal, a lanthanide and an actinide. These particular examples are chosen because they have a propensity to complex with unsaturated hydrocarbons or have high coordination numbers.