Supramolecular Chemistry-I

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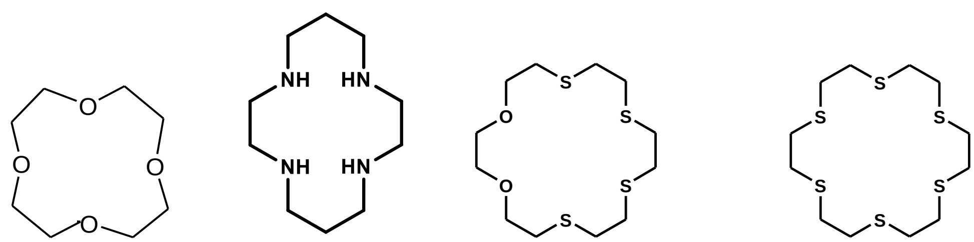
Lecture - 07

Okay, next in this class we will discuss few aspects of the macrocycles. Number one is macrocycles can have only one or different types of donors. In the simplest cases, let only one type of donor that we call X. So, when X is nitrogen, phosphorus, sulfur etc. they prefer to bind transition metal ions and when X is oxygen say like a crown ether, then they will prefer to complex alkali or alkaline earth metal ion. So, the macrocycle on the left should prefer to bind an alkali/alkaline earth metal ion. But which alkali metal ion?

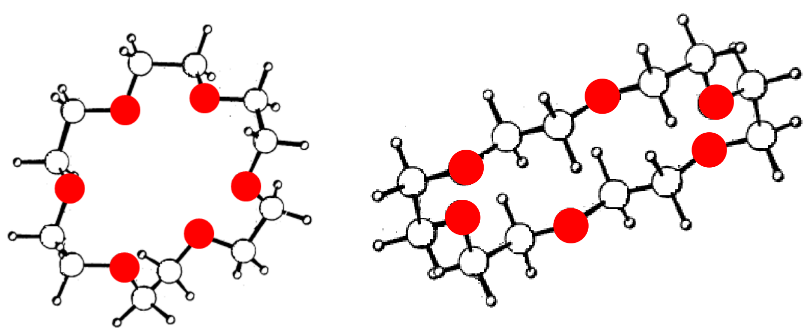


So, here the cavity size and the size of the alkali metal must match. What is this matching? Suppose, Li^+ ion sits in the middle of the cavity making Li^+-O bonds of normal length. In that case, if the macrocycle does not show any deformation then the size of the Li^+ ion matches with the size of the macrocyclic cavity. What happens with Na^+ ion ? Ionic radius of the Na^+ ion is still less than the cavity size of 12-crown-4. But, the Na^+-O bond length is greater than that of Li^+-O and so Na^+ ion cannot sit inside the cavity of 12-crown-4. So, the size of Na^+ ion and the cavity of 12-crown-4 do not match. So, when we say size matching or size mismatching this is what we understand. The cavity of 15-crown-5 matches with the ionic radius of Na^+ ion and so it will bind well. If instead of all oxygens we have sulfur, then it can preferentially bind heavy metal ions. If all oxygens are replaced with nitrogens then the macrocycle will preferentially bind transition metal ions. So, some ground rule exist but we have not been successful in having macro cyclic compounds which will specifically bind a particular metal and not any of the others. That is still not realized but we have understood few things about selectivity. Now, when we have a mixture of oxygen which is a hard donor and sulphur which is a soft donor, then the macrocycle can have interesting binding properties.

Now I will tell you another concept called the macrocyclic effect. A macrocyclic receptor compared to a linear compound with identical donors, will show greater stability and this extra stability is called the macrocyclic effect. Macrocyclic effect has both thermodynamic stability and kinetic stability. Let me explain with the important equation, $\Delta G = \Delta H - T\Delta S$.

Now, what happens to entropy when a metal ion enters the cavity of the cryptand? Entropy does not change very much upon metal complexation because the macrocycle is already arranged in solution before metal binding. So, once the metal ion goes inside the cavity, there is not that much of arrangement necessary. Only few solvent molecules bound to the metal are released to the bulk solution leading to a slight increase of ΔS. But change in ΔH is very highly negative as the bonds are very strong. Therefore, that extra stability comes mainly through ΔH thermodynamically. There is also a kinetic factor operating. Once the metal ion in the cavity, all metal-ligand bonds must be cut at the same time to dislodge the metal ion so the it can come out of the cavity which is difficult and this accounts for the kinetic barrier to the decomposition of the complex. Unlike this scenario, in case of open chain ligands. So, both thermodynamically and kinetically is favored over open chain compound and that is called macrocyclic effect.

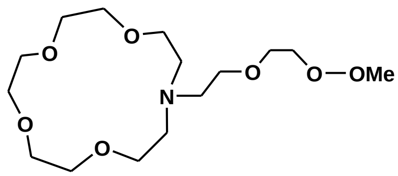
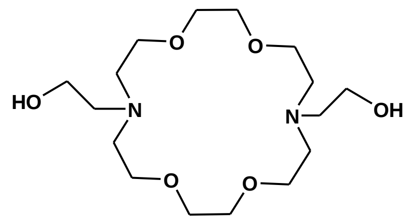
Another aspect of the properties of macrocycles should be kept in mind. Let me discuss with an example shown below.

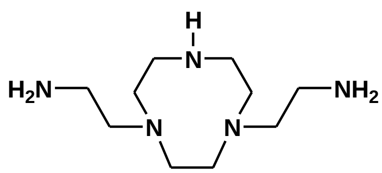
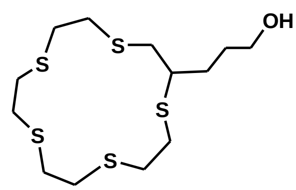


D_{3d} C_i

The macrocycle above is 18-crown-6. In absence of any metal ion, this macrocycle can exists in a number of conformations. Two prominent ones, D_{3d} and C_i are shown here. Complexes with K^+ ion is formed with D_{3d} symmetry but with smaller Na^+ and Li^+ ions, a conformer of lower symmetry for the macrocycle becomes more stable. For this change in conformation, energy must be expended.

We have said that when a metal ion enters the cavity of a macrocycle, it is very stable. However, even then there is a chance that it can be attacked from top and bottom because top and bottom are still available for attack. To avoid that something called lariat ethers have been synthesized as shown below:

With a lariat ether, the top and bottom coordination sites will be covered and the complex will be very stable.

So, this concludes the crown ether part. So, the first supramolecular synthon that I discussed are macrocycles and crown ethers. My second supramolecular synthon will be calixarenes. Thank you.