Supramolecular Chemistry-I

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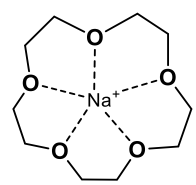
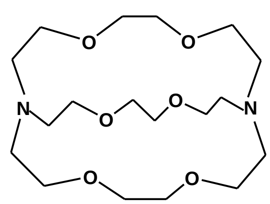
Week - 02

Lecture - 09

Good morning, from macro cycles and calixarenes, let me now introduce another supra- molecular synthon that is called Cryptands. In fact, cryptand molecules were first introduced by Jean-Marie Lehn for effective complexing of alkali metal ions. You already know that alkali metal ions can be complexed by crown ethers. So, let me draw a crown ether, a cartoon of a crown ether. Here is a crown ether, 15-crown-5 and this crown ether can accept a sodium ion inside. But what happens as I told you previously while discussing lariat ethers that reagents can react with the metal ion from top and from bottom.

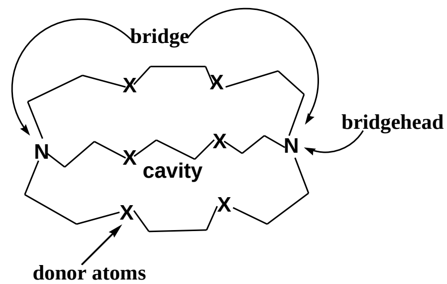


Lehn first envisaged that if we have a system where the metal ion will be completely surrounded then what happens. So, from 2D he went to 3D. So, let me write his molecule.

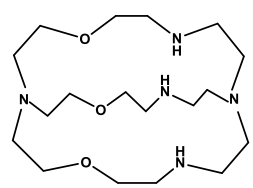


He said that if we have a molecule like this then what happen, when a metal ion is put inside ? Well, it will be completely surrounded from all directions. So, it is an isolated metal ion inside the cavity of this molecule and he told these molecules as cryptands.

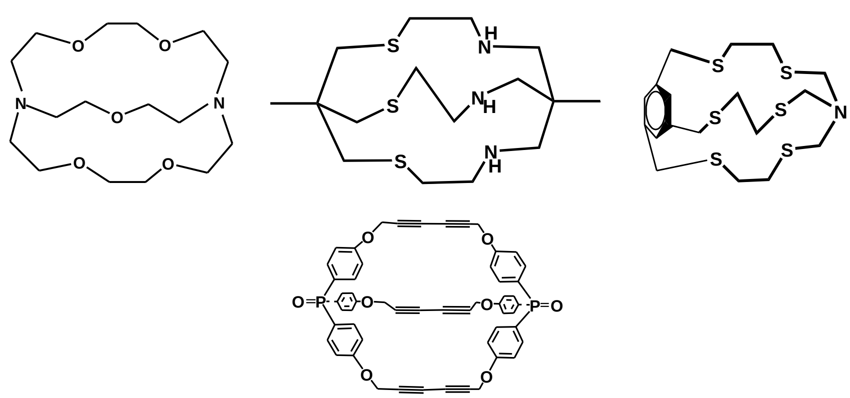
A metal ion inside the cage form a complex known as a cryptate and the cage without a metal is called a cryptand. Now beauty of this molecule is that we can put these donor atoms at different positions of the three bridges.



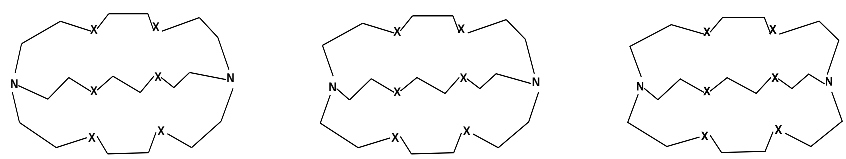
So, here is an example with nitrogen bridgehead and in bridges the donors can be O, N, S etc. Synthesis of these compounds are very complicated I am coming to that later, but right now I am discussing all these variations possible. Cryptands occupy an important place in supramolecular chemistry with a wide range of applications that cover most areas of chemistry and several fields of biological and material sciences as well.
Cryptands can not only accept a metal ion it can accept an anion a neutral molecule and so on it can accept a metal ion along with an anion or a neutral molecule. It can accept more than one metal ions or it can accept several water molecules connected. So, all are known. So, this is a very versatile ligand if you call it. So, this bridge there are 3 bridges and 2 bridge heads and this we will call laterally symmetric why this is laterally symmetric it is obvious is a symmetric structure.



What will be a laterally non-symmetric cryptand? If I replace this oxygen say I replace this oxygen with nitrogen I can do that I can put them with nitrogen then it is laterally non-symmetric. I can put one as sulphur or I can do anything I like during synthesis. Besides, I can put bridgeheads as carbon. So, let me write some of these structures.



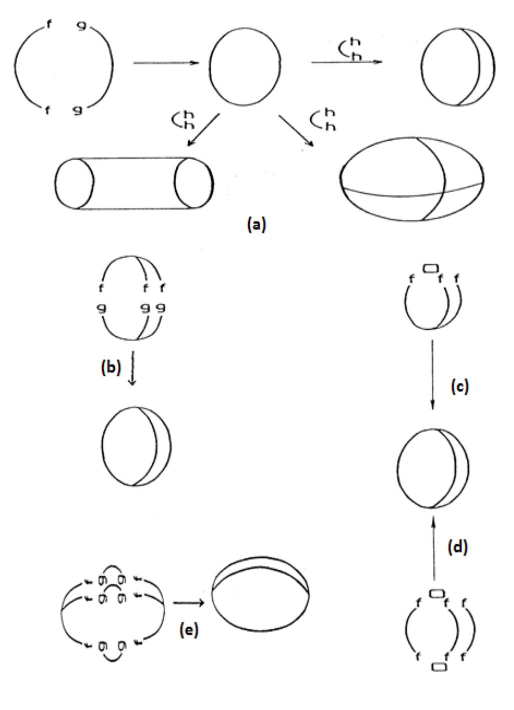
So, there is no dearth of tricks that we cannot apply. We can vary rigidity of these cryptand by including aromatic groups in the bridges. If we can put aromatic groups or cyclohexane groups as side groups, we can increase the organic layer. This not only changes solubility criteria of the cryptand but make the metal ion inside the cavity very isolated. Now, another point that is important to discuss. These molecules can exist in three conformational isomers as shown below:



exo-exo endo-exo endo-endo

When in exo conformation, the lone-pair of the bridgehead nitrogen is pointing outside. When in endo conformation, the lone-pairs are both are directed towards the center of the cavity. So, the endo-endo conformation is a very favored conformation for binding metal ions inside the cavity. It should be emphasized that cryptands with C-bridgeheads cannot show this conformations. Now I will talk to you about how to synthesize these molecules. The synthesis of these molecules has two aspects: one is strategy and the other is methodology. So, we will discuss both.

Let me discuss strategy first. In what follows I have collected the synthetic strategies:



All strategies will give cryptands but (e) will afford cryptands with long cavity useful for multi-metal cryptates. Strategy (a) is called stepwise synthesis that is quite cumbersome and time-consuming. We worked on cryptands for our research during my career and we synthesize these molecules by the strategy (b) that is called tripodal coupling. Tripodal coupling is the synthetic method we adopted first and since then all over the world is now being used. Now I will talk about tripodal mono-(c) bis-capping (d) where you can get a very rigid kind of cryptands. Strategy (e) is really amazing as here reactions at 12 points are taking place and instead of an oligomeric product a decent yield of the desired product is obtained.

Therefore, in a nutshell cryptands can be made by adopting the above strategies. Thank you very much for today.