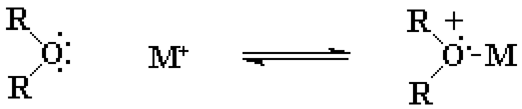
Crown Ether, Cryptands And Calixarenes

UNIT 2

MS.c 1 YEAR

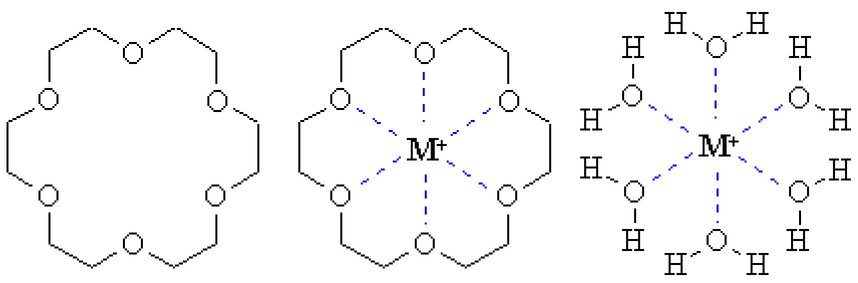
Crown Ethers

- Oxygen atoms are capable of acting as Lewis bases due to the presence of the lone pairs (*e.g.* in hydrogen bonding between water molecules or hydration of a metal ion in aqueous solution, see below).
- The interaction with metal ions with ethers is also important:



- In regular ethers, only weak complexes are formed.
- However, in certain *polyethers* (where mulitple interactions are possible) the complexes are much stronger.

- Crown-ethers are macrocyclic polyethers discovered by Pedersen in the late 1960s.[1]

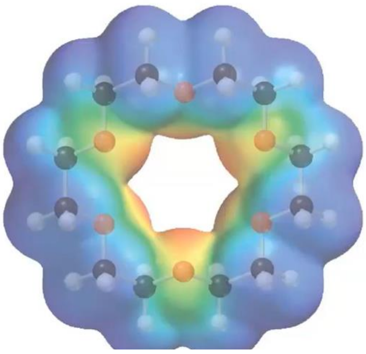


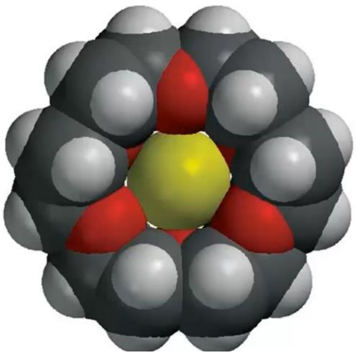
18-Crown-6 complex hydration of a metal ion

- These ethers are called "crown ethers" due to their shape.
- They are based on repeating -OCH_2CH_2- units, derived from ethylene glycol : **$HOCH_2CH_2OH$**

- The name **18-crown-6** indicates that there are 18 atoms in the ring, 6 of which are oxygen.
- These compounds are important co-solvents.
- The *interior* of the cavity is *water like*, whereas the *exterior* is *hydrocarbon like*.
- So a metal ion inside the cavity can be "carried" into an organic solvent.
- This allows ionic systems such as KF to be dissolved in organic solvents and used as reagents where the metal ion is in a complex, but the anion is unsolvated or *naked* and therefore quite reactive.
- Varying the size of the crown ether varies the cavity size and some metal ions fit better than others.
- For example, 18-crown-6 is an good fit for K+

- The **size of the metal must match the size of the crown** to form a strong attraction
- 18-crown-6 is the ideal size to trap a potassium cation



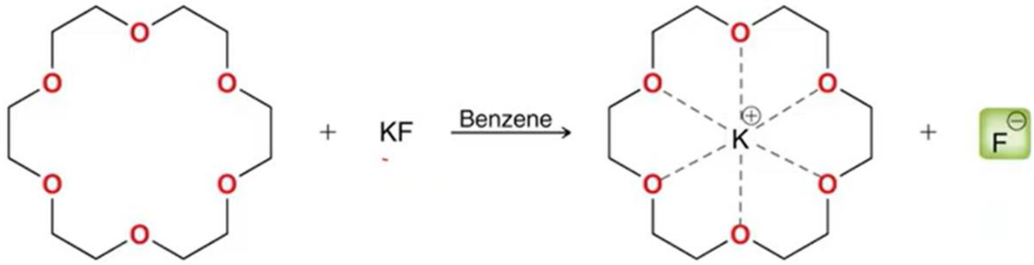


- Metal ions are not soluble in low polarity solvents.

- The crown ether complexes to the metal cation, and the resulting complex is soluble

- **Crown ethers are used to help ionic salts, needed for organic reactions, to dissolve in organic solvents**

- The F^- ion below is ready to react because the K^+ ion is "hosted" by 18-crown-6
- Without the crown ether, the solubility of KF in benzene is miniscule



- Choosing a crown ether depends on the metal cation present in a reaction:

12-Crown-4
Solvates Li^+

15-Crown-5
Solvates Na^+

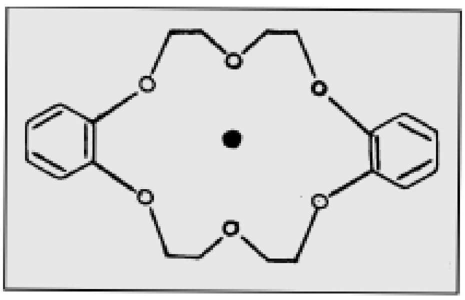
18-Crown-6
Solvates K^+

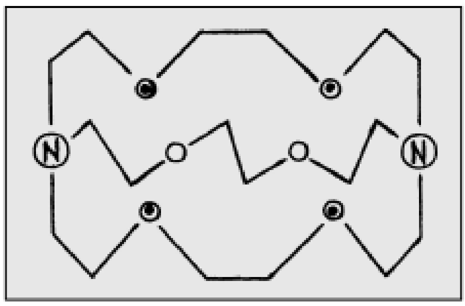
APPLICATION

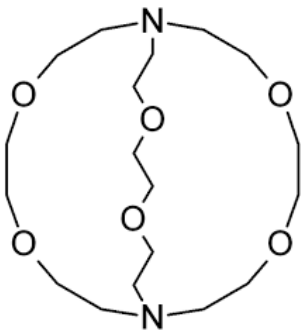
- Due to their strong ability to complex with cations and to solvate salts in aprotic solvents, crown-ethers have been used in phase-transfer catalysis, sensors, solvent extraction, analytical chemistry, biochemistry, and electrochemistry.

CRYPTANDS

- Many macropolycyclic ligands which are related to each other are also known to us and are called as ‘cryptates’ (or cryptands or simply, crypts).
- They are more potent, stronger and selective complexing agents for alkali metals.
- Crypts contain nitrogen, oxygen and sometimes phosphorus and sulfur atoms in their core structure.
- They are for the same reason considered as the 3D equivalents of crown ethers.
- The molecules are cross-linked appropriately with donor atoms correctly positioned in the bridging group in order encapsulate metal ions in structures having cage-like formations.
- A typical crypt is the molecule called Crypt-222 (222 denotes the no. of ethereal oxygen atoms in each N-N bridge) having the basic structure given in Figure .
- Cryptates (meaning hidden) are so called because they wrap around and hide the cation.
- It is because of the polyether bridges formed between the two N atoms which resemble the seams of a football – that this class of crypts is really known as 'football ligands'.
- Entire class of these ligands form complexes with very high formation constants.







✓The most common cryptand is [2.2.2]cryptand. (numbers indicate number of ether oxygen atoms

✓ formula- N[CH2CH2OCH2CH2OCH2CH2]3N
✓the systematic IUPAC name for this compound is 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane

✓which has two oxygen atoms per each of the three bridges between two nitrogen atoms in the molecule (see image above).

✓Moreover, cryptands have a high affinity towards metal cations such as potassium ion. The interior cavity of the three-dimensional molecule is the binding site for cations. When the complex is formed, we call it a cryptate. More importantly, cryptands can bind with cations through both nitrogen and oxygen atoms.

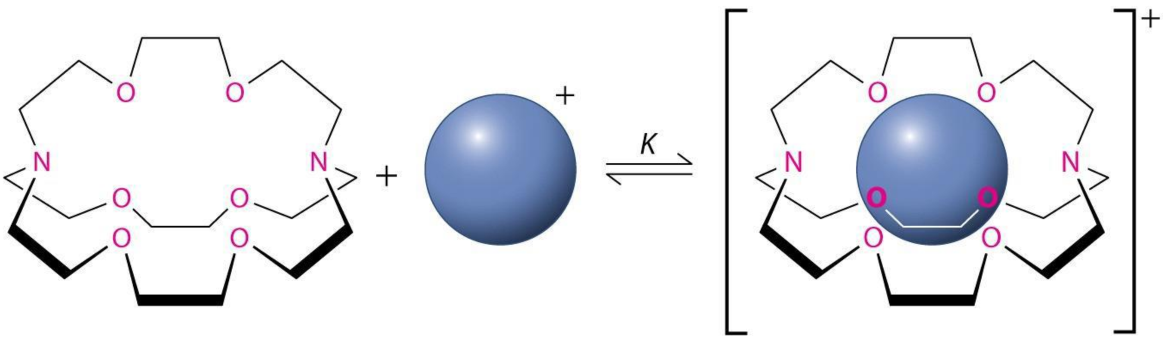
The three-dimensional interior cavity of a cryptand provides a binding site – or host – for "guest" ions.

The complex between the cationic guest and the cryptand is called a cryptate.

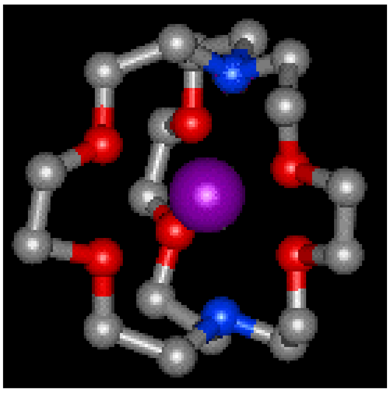
Cryptands form complexes with many "hard cations" including NH+4, lanthanoids, alkali metals, and alkaline earth metals.

In contrast to crown ethers, cryptands bind the guest ions using both nitrogen and oxygen donors.

Professor Jean Mary Lehn and his team gave the molecule cryptand its name after the Greek term crypto, which means "to hide"



A cryptand **A cation** **A cryptate complex**



Uses of Cryptands

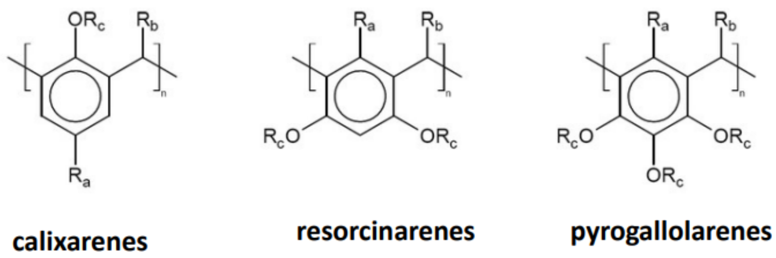
1. Cryptands are more expensive and difficult to prepare, but offer much better selectivity and strength of binding.
2. They are able to bind otherwise insoluble salts into organic solvents.
3. They can also be used as phase transfer catalysts by transferring ions from one phase to another.
4. Cryptands enabled the synthesis of the alkalides and electrides

- Crown ethers (or crowns) are known as a group of macrocyclic polyethers. Many macropolycyclic ligands which are related to each other are also known to us and are called as 'cryptates' (or cryptands or simply, crypts).
- The two rings of cryptand provide extra strength to hold the ion. In case a regular crown ether "surrounds" an ion, a cryptand "locks it up". This ion-capturing capability of a cryptand can reach upto a hundred thousand times more than that of 18-crown-6.
- Crowns and crypts find many important applications and uses. These include preparative organic chemistry, solvent extraction, phase transfer catalysis, stabilisation of uncommon or reactive oxidation states and the promotion of other improbable reactions.

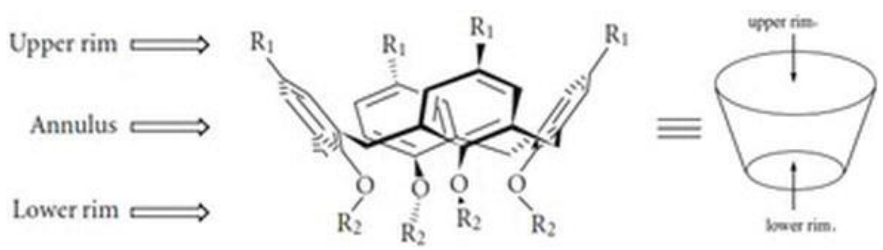
Calixarenes

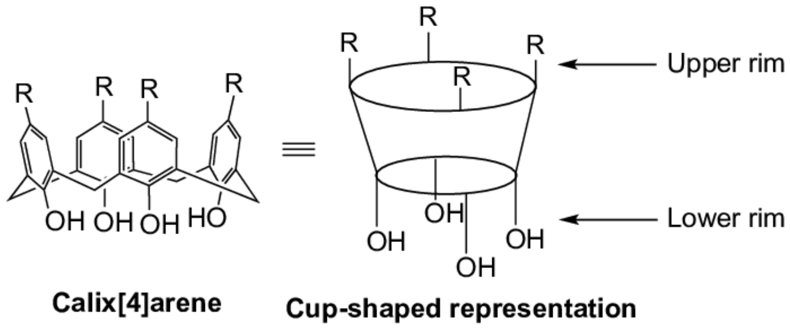
1. The molecule was first reported in 1872 by Baeyer as a reaction product of aldehyde-phenol condensation.

2. Calixarenes are cyclic oligomers obtained by condensation of suitable functionalised phenols with formaldehyde, or substituted aldehydes.
3. A calixarene is a cup-shaped supramolecule.
4. The name is derived from the calixarene is a cup-shaped supramolecule. The name is derived from the word "calix," which means a cup.
5. Calixarenes have hydrophobic cavities that can hold smaller molecules or ions and belong to the class of cavitands known in host–guest chemistry.
6. Calixarene nomenclature involves counting the number of repeating units in the ring and include it in the name
7. Eg :- calix [4]arene has 4 units
8. Eg :- calix[6]arene has 6 units



- The aromatic components are derived from phenol, resorcinol, or pyrogallol to give, respectively, calixarenes, resorcinarenes, and pyrogallolarenes.
- The basic structure of calixarenes consists of phenolic units or phenolic derivatives which are repeated and interconnected with Ar-C-Ar bridge to form a hollow cycle. The part with a broader hollow side is called the upper rim, and the narrow hollow part is called the "lower rim" as shown





- Calixarenes are air stable, therefore no precautions need to be carried out to exclude oxygen when they are synthesized and subsequently stored. In general, calixarenes are chemically very robust, and are stable to both strong acids and bases.
- The various conformations of calixarenes are caused by the free rotation of sigma bonds at methylene, Ar-C-Ar, bridges.
  Eg., calix[4]resorcinarenes have four prochiral centers on carbon atoms at the methylene bridges, causing the compound to form four different diastereoisomers.

APPLICATIONS

Calixarenes have been broadly used, as:

•Liquid crystal materials
•Sensors
•Catalysts
•Stationary phase of chromatography
•Host molecules (calix[4] arene and 4-tert-butylcalix[6]arene can be the host molecules for compounds such as trifluoromethyl-benzene contained in pesticide