LITTLE FLOWER COLLEGE
GURUVAYUR
DEPARTMENT OF CHEMISTRY

TOPIC : MICROCYCLIC AND MACROCYCLIC LIGAND

Presented by

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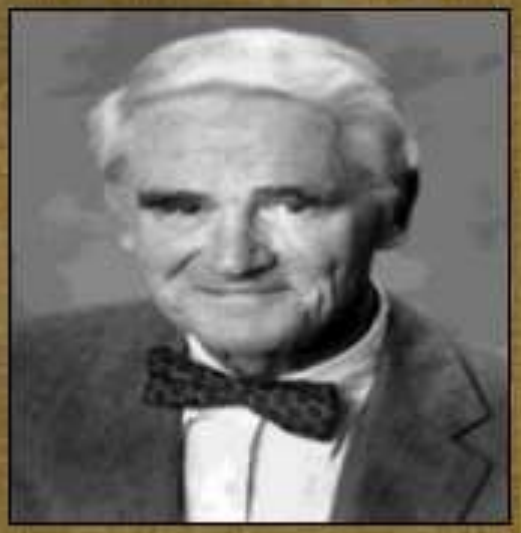
MACROCYCLIC AND MACROBICYCLIC LIGANDS

- CROWN ETHERS
- CRYPTANDS
- SPECIAL CROWNS



- The Nobel Prize for Chemistry in 1987 was given to Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen for their efforts in discovering and determining uses of cryptands and crown ethers.

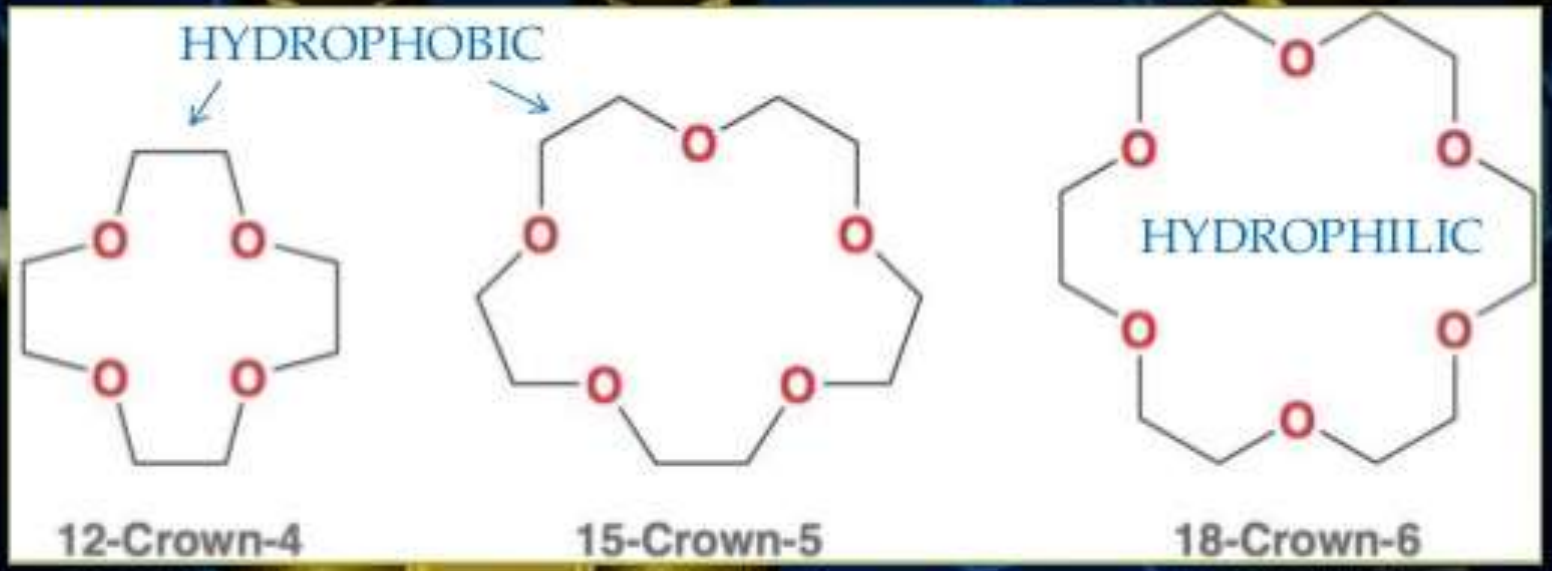
So, why we are interested about this types of molecules?

- They are exceptionally versatile in selectively bindig a range of metal ions and a varirety organic neutral and ionic species. Crown ethers are currently being studied and used in a variety of applications beyond their traditional place in chemistry.

CHARACTERISTICS

CROWN ETHERS

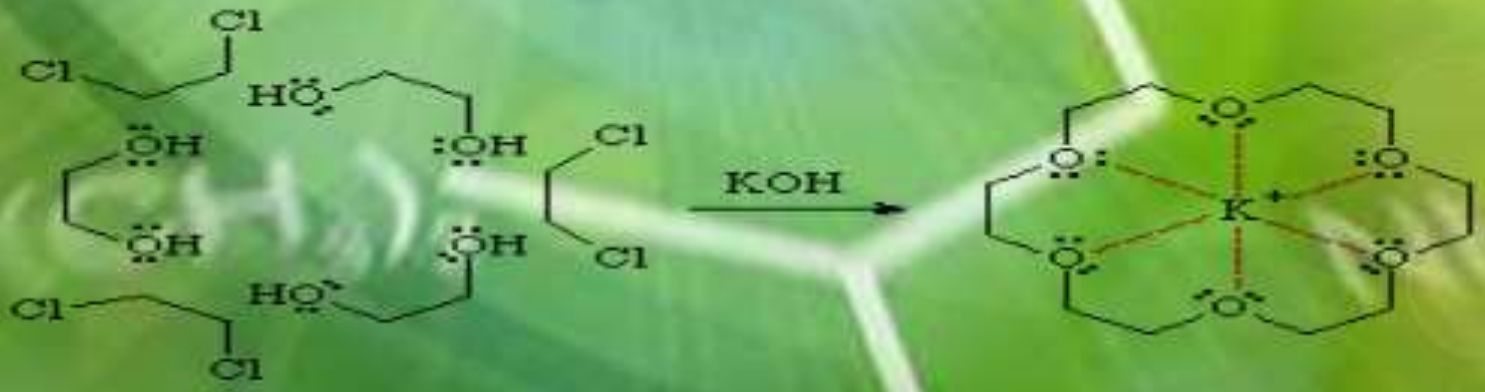
- The mono cyclic polyether i.e. Cyclic polymers of ethylene glycol $(OCH_2CH_2)_n$ are called the crown ethers.



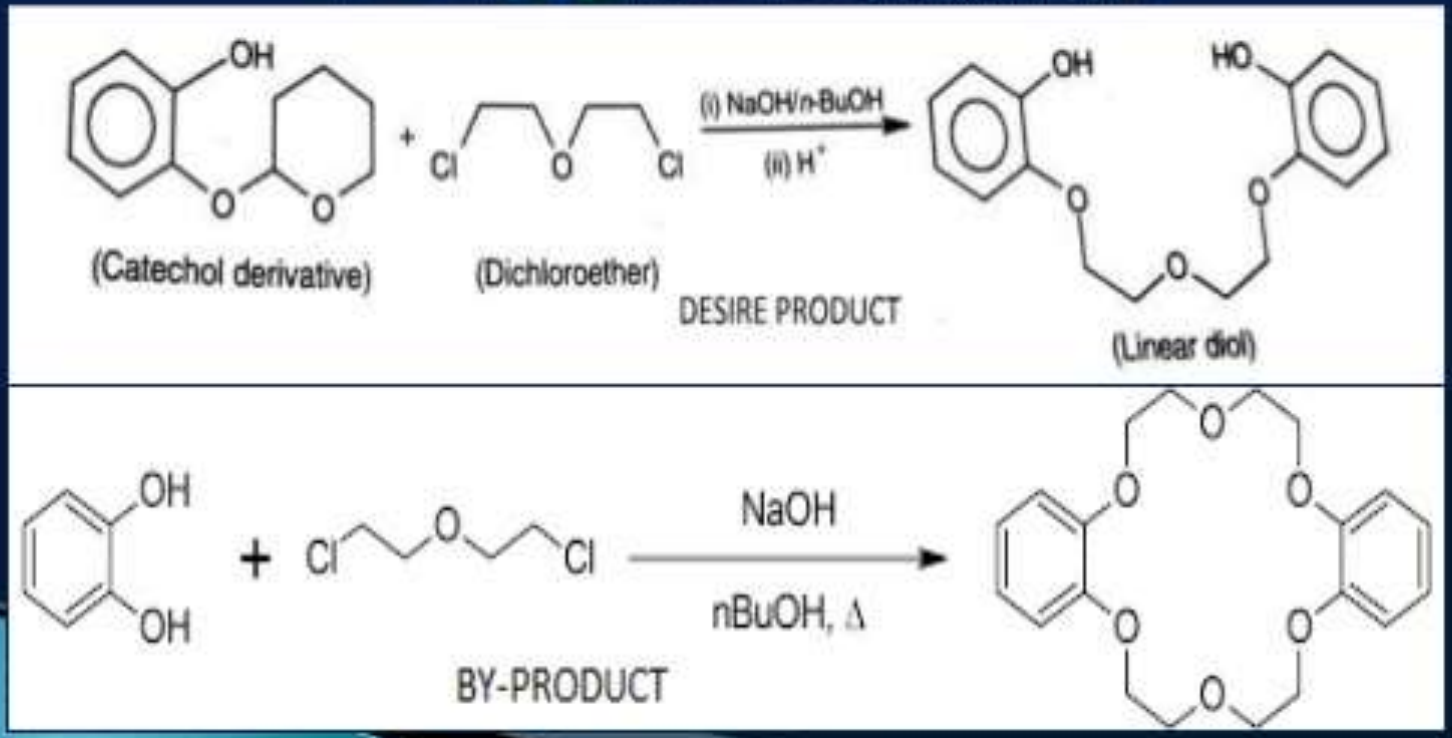
- It's inner side is hydrophilic
- And outer part is hydrophobic in nature.

SYNTHESIS OF CROWN ETHER AND THIA CROWN

- **CROWN ETHERS-** 18-Crown-6 can be obtained by reacting 3 ethylene glycol($HOCH_2CH_2OH$)with its corresponding dichloride in presence of aquous KOH. Actually, initially the K^+ - complex of 18-crown-6 is obtained and then from this complex, the free ligand may be isolated. If an organic base like NEt_3 is used instead of KOH, the crown ether is not produced.

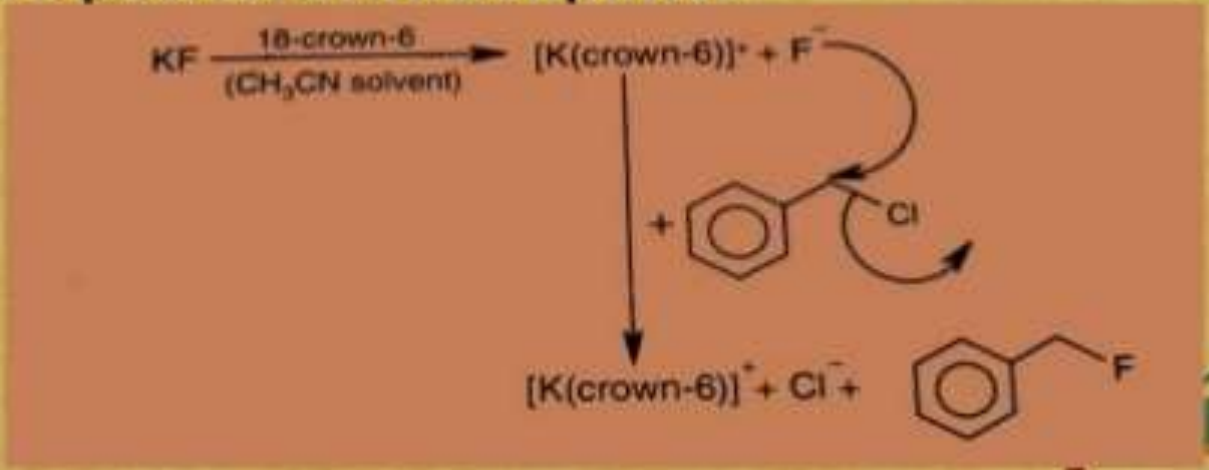


Pedersen's strategy entailed linking two catecholate groups through one hydroxyl on each molecule. This linking defines a polydentate ligand that could partially envelop the cation and, by ionization of the phenolic hydroxyls, neutralize the bound dication. He was surprised to isolate a by-product that strongly complexed with cations.

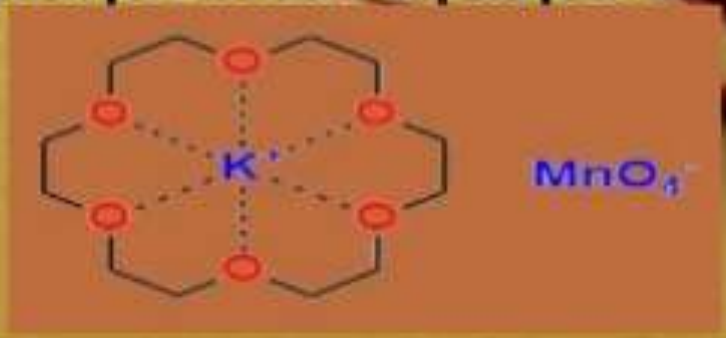


PHASE TRANSFER CATALYST:-

- **When KF is solubilized in the organic solvents in presence of 18-crown-6 or cryptand like C222, K^+ ion is stabilized as $[K(macrocycle)]^+$ and the unsolvated F^- ion acts as a powerful nucleophile.**



- **Similarly $KMnO_4$ solubilized in benzene in presence of crown-6 or suitable cryptand produces a purple solution called purple benzene.**



1.SIMPLE CROWN ETHERS

- 18- CROWN-6
- DIBENZO -18-CROWN-6
- 12-CROWN-4
- 15-CROWN-5

- **18-CROWN-6**

Reaction of triethylene glycol dichloride,triethyleneglycol and potassium hydroxide in tetrahydrofuran containing 10% water followed by precipitation of the crown-acetonitrilecomplex produced an overall yield of 25% of this.

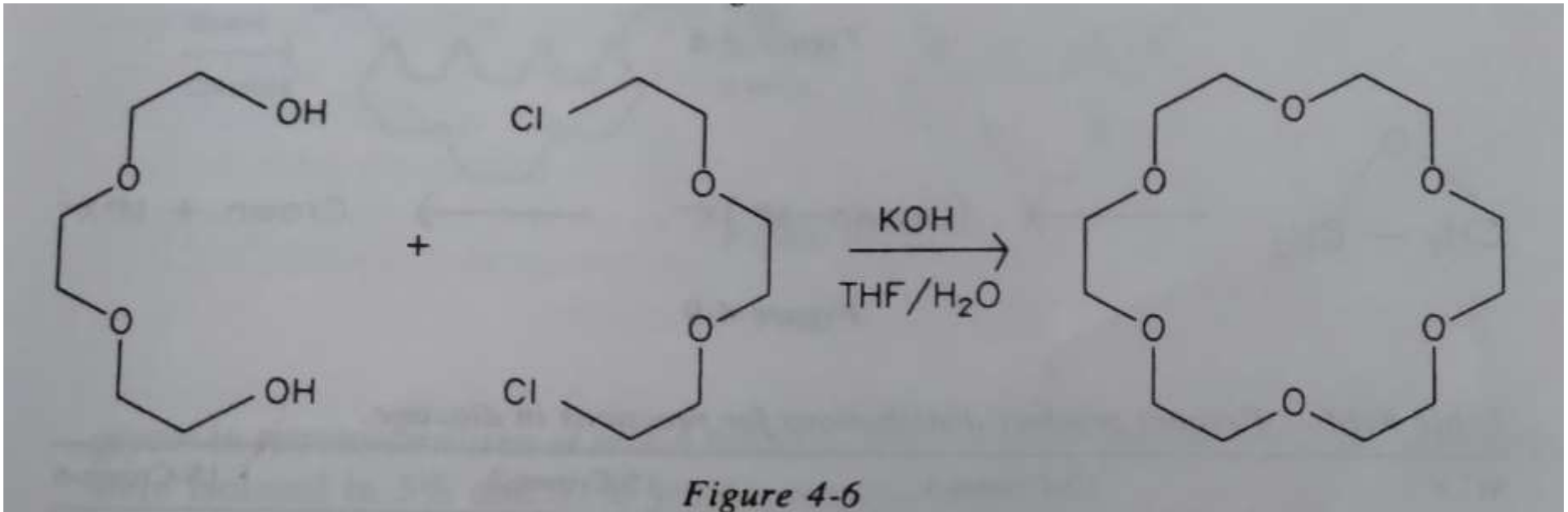


Figure 4-6

- **12-CROWN-4**

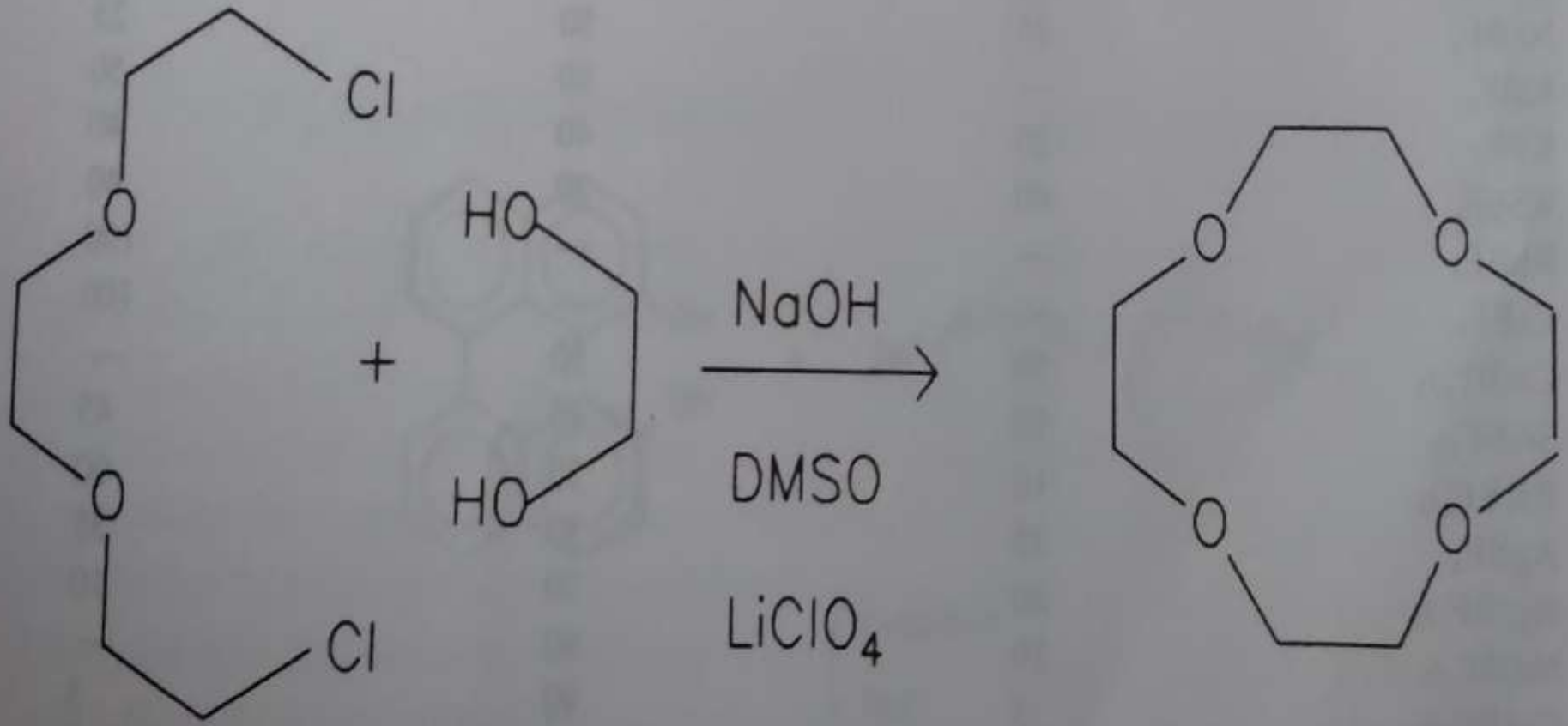


Figure 4-7