

15.10: CROWN ETHERS

A “crown ether” is a cyclic ether containing several (i.e., 4, 5, 6 or more) oxygen atoms. It is possible to dissolve ionic compounds in organic solvents using crown ethers. Cyclic polyether with four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms., cyclic compounds with the general formula $(\text{OCH}_2\text{CH}_2)_n$. Crown ethers are named using both the total number of atoms in the ring and the number of oxygen atoms. Thus 18-crown-6 is an 18-membered ring with six oxygen atoms (part (a) in Figure 18.7.1). The cavity in the center of the crown ether molecule is lined with oxygen atoms and is large enough to be occupied by a cation, such as K^+ . The cation is stabilized by interacting with lone pairs of electrons on the surrounding oxygen atoms. Thus crown ethers solvate cations inside a hydrophilic cavity, whereas the outer shell, consisting of C–H bonds, is hydrophobic. Crown ethers are useful for dissolving ionic substances such as KMnO_4 in organic solvents such as isopropanol $[(\text{CH}_3)_2\text{CHOH}]$ (Figure 18.7.1). The availability of crown ethers with cavities of different sizes allows specific cations to be solvated with a high degree of selectivity.

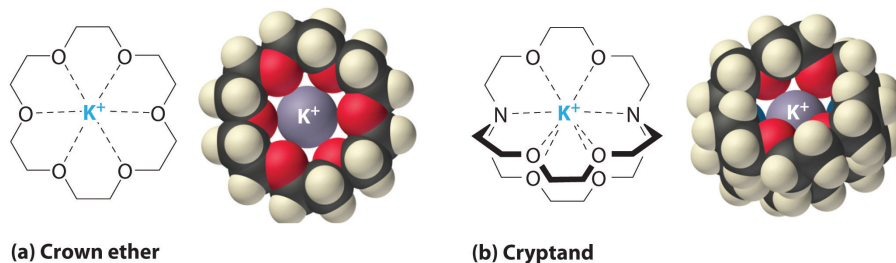


Figure: 1 Crown Ethers and Cryptands (a) The potassium complex of the crown ether 18-crown-6. Note how the cation is nestled within the central cavity of the molecule and interacts with lone pairs of electrons on the oxygen atoms. (b) The potassium complex of 2,2,2-cryptand, showing how the cation is almost hidden by the cryptand. Cryptands solvate cations via lone pairs of electrons on both oxygen and nitrogen atoms.



Figure 2: Effect of a Crown Ether on the Solubility of KMnO_4 in Benzene. Normally which is intensely purple, is completely insoluble in benzene which has a relatively low dielectric constant. In the presence of a small amount of crown ether, KMnO_4 dissolves in benzene as shown by the reddish purple color caused by the permanganate ions in solution.

Cryptands (from the Greek *kryptós*, meaning “hidden”) are compounds that can completely surround a cation with lone pairs of electrons on oxygen and nitrogen atoms (Figure 18.7.1b). The number in the name of the cryptand is the number of oxygen atoms in each strand of the molecule. Like crown ethers, cryptands can be used to prepare solutions of ionic compounds in solvents that are otherwise too nonpolar to dissolve them.

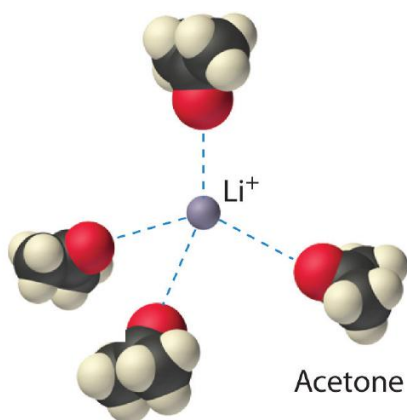


Figure 18.7.3: Ion–Dipole Interactions in the Solvation of Li^+ Ions by Acetone, a Polar Solvent

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