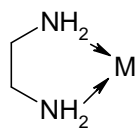
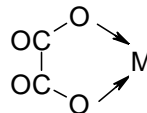


THE CHELATE EFFECT

Replacement of monodentate ligands by polydentate ligands produce ring structures called **chelates** (Gk, = crab's claws). *Chelate complexes are found to be much more stable than complexes of monodentate ligands.* This is called the '**chelate effect.**' Examples are oxalate, ethylene diamine (en), EDTA etc.

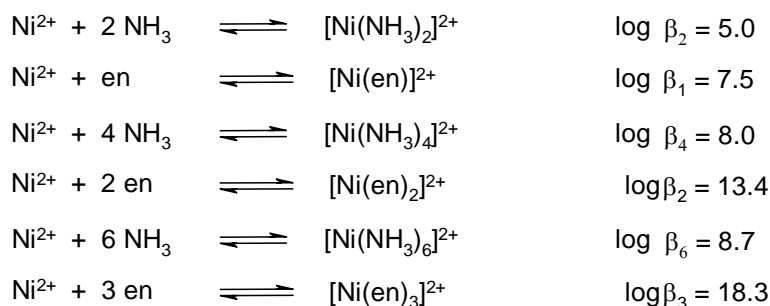


ethylene diamine (en)



oxalate

Comparison of the overall stability constants of some nickel complexes shown below should illustrate the point:



Note: Since 'en' is a bidentate ligand, each 'en' is equivalent to two NH_3 ligands. In each of the above pairs, we see that the $\log \beta$ value for complex with 'en' ligand is greater than that with NH_3 ligands, meaning that they are more stable.

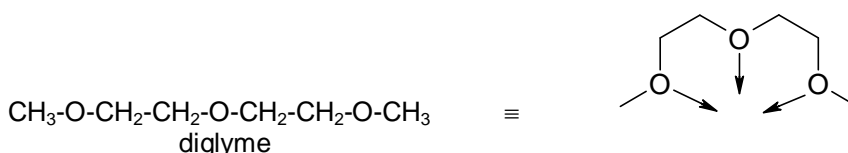
The reason for the extra stability may be attributed to both enthalpy and entropy effects. For example, in the replacement of NH_3 ligands by 'en',

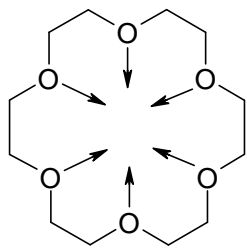
1. The basic nature of NH_2 group in 'en' may be larger than in NH_3 due to the +I effect of the alkyl chain. Thus the bond to the metal may be stronger leading to a lowering of enthalpy.
2. When one end of 'en' gets attached to the metal atom, the other end is locked in a position near the metal atom, favourable for attachment, compared to the random approach of an ammine ligand from the solution.
3. Substitution by one 'en' molecule releases two NH_3 molecules. Hence the entropy of the system increases. This factor also may favour chelate complex formation.

THE MACROCYCLIC EFFECT – Crown ethers and Cryptands

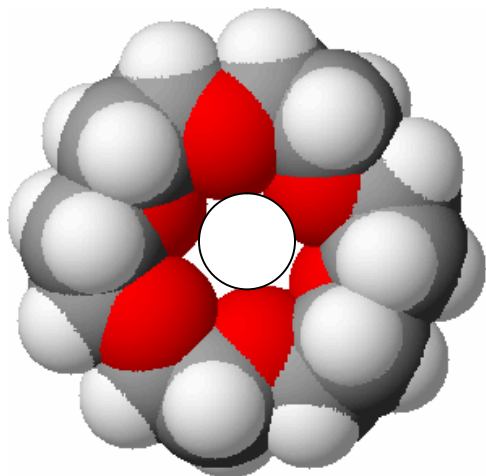
[Ref: (1) Sharpe AG. Inorg. Chem. Int. Stu. Edn. (2) Rodgers GE. Introduction to coordination, solid state and descriptive inorg. chem.]

Polyethers, especially cyclic polyethers are such strong ligands that they complex strongly even with alkali metal ions and are capable of extracting them into **organic solvents**. This is known as the **macrocylic effect** (macrocycles = large rings). Examples:





18-crown-6 or simply crown-6
(a **crown ether**)
[= 6 oxygen atoms in an 18-member ring]



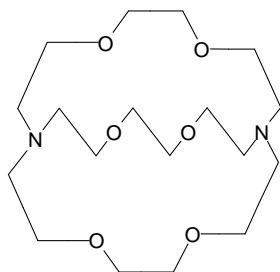
$[K(18\text{-crown-6})]^+$ (Space-filling model)

Note that all O atoms are pointing inwards, and the size of the central hole. The external alkyl groups make the complex more soluble in organic solvents than in water!

O atoms shown in red, C atoms in black and H atoms in light grey. K⁺ ion is shown in white at the centre.

The size of the ring in 18-crown-6 is such that a K⁺ ion can fit exactly, with the O atoms pointing inwards and acting as donor ligand atoms. The sequence of equilibrium constants for this ether is $Li^+ < Na^+ < K^+ > Rb^+ > Cs^+$. Other crown ethers which have cavities of different sizes give different sequences of equilibrium constants so that selective complex formation with a particular metal ion is possible.

Using 18-crown-6 and Cs in liquid NH₃, a paramagnetic solid of formula $[Cs(18\text{-crown-6})]^+ e^-$ is obtained (an **electride!**). $[K(\text{crown-6})]OH$ and $[K(\text{crown-6})]MnO_4$ in toluene and benzene respectively find much use in preparative organic chemistry.

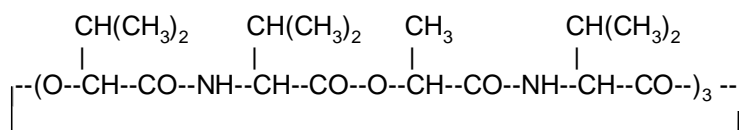


Cryptand-222 (a **cryptand**)

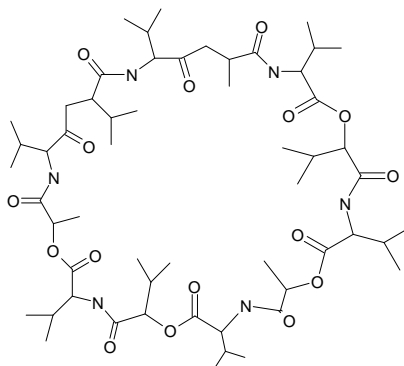
[222 = three chains, each containing two CH₂-O-CH₂ groups]

3-D equivalents of crown ethers containing N atoms provide extra donor sites. They are called **cryptands** (encrypt = hide). A typical cryptand is cryptand-222 in which all N atoms and O atoms act as donors. The conformations at the N-atoms are 'endo', meaning that the lone pairs point inwards. Cryptands shield the cations even more effectively than crown ethers, and show selectivity. Cryptand-211, cryptand-221 and cryptand-222 form their most stable alkalimetal complexes with Li⁺, Na⁺ and K⁺ respectively. From sodium metal dissolved in liquid methanamine, 222-crypt recovers a compound of formula $[Na(222\text{-crypt})]^+ Na^-$ (a **sodide!**)

Sodium and potassium cryptates are interesting models for biologically occurring materials involved in the transfer of ions across cell membranes. One of these is the polypeptide **valinomycin**, commonly formulated as:



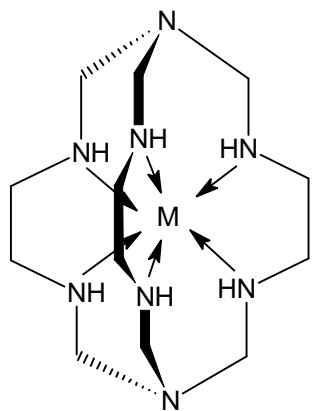
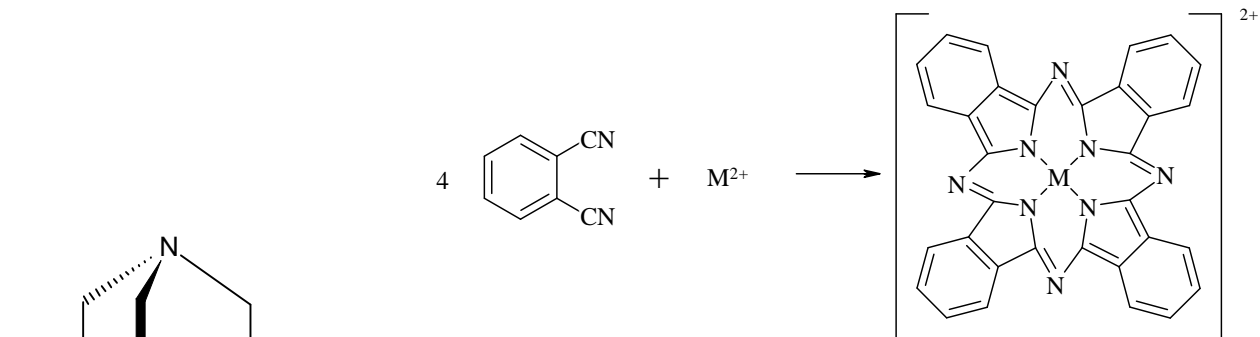
but more faithfully represented by the symmetrical cyclic structure:



In this molecule, the polar interior groups bind the cations and the non-polar exterior groups enable the ligand to transport the whole complex across cell boundaries.

The Template Effect: [Ref: Shriver & Atkins, Inorganic Chemistry, 3rd edn., Oxford, 1999]

A metal ion such as nickel may be used to assemble a group of small ligands around it by coordination. Members of the group then may undergo condensation reactions among them, if they have suitable reactive functional groups, to form a macrocyclic ligand. This is called the template effect since the coordination of the small ligands with the metal atom acts as a template to bring them into correct positions and suitable interatomic distances for bond formation. This type of reaction is used in the synthesis of several macrocyclic ligands. An example is given below:



A hexadentate sepolchrate ligand

[Ref: S.F.A.Kettle, Physical Inorganic Chemistry – A Coordination Approach. Spektrum Academic Publishers (1996)]

The (minimum) distance between two donor atoms in a didentate ligand is sometimes referred to as the **bite** of the ligand and the angle subtended at the metal atom the **bite angle**.

Complexes in which the metal atom is totally encapsulated is called **sepolchrates**. Those in which it is surrounded by two ligands which interleave each other are called complexes of **catenands**. Those in which it is at the centre of a stockade-like ligand are called **picket-fence** complexes.