

Selectivity for Cryptands

- Better selectivity than crown ethers - stability constants peak where cation size matches cavity size.
- More rigid cavity $\rightarrow$ less conformational flexibility
- Pre-organisation of binding sites.

(b) - Spherands: Pre-organised receptor sites

- 6 O-donor atoms arranged in rigid octahedral cavity.
- High binding constants to Li^+ and Na^+ .
- No unfavourable energy terms from ligand upon binding.
- K^+ not bound $\rightarrow$ cavity too small.

3. Selectivity via Choice of Ligand Donor Atoms

- Replacement of Oxygen (hard donor) with Nitrogen (softer donor) increases preference for soft metal (e.g. Ag^+).
- Other factors important for Transition Metal ions - e.g. Irving Williams series.

4. Selectivity by Directionality of Bonding

Ion-Dipole Interactions; Key to metal-ligand bonding, are not strongly directional.

Hydrogen Bonding; strongly directional - most effective with linear arrangement between H-bond donor and H-bond acceptor.

Bonding of $[\text{RNH}_3]^+$ to Crown Ethers

- Crown ethers can bind to ammonium $[\text{NH}_4]^+$ and alkylammonium $[\text{RNH}_3]^+$.
- Ion-dipole interactions can be reinforced by H-bonding but symmetry of crown ether important.