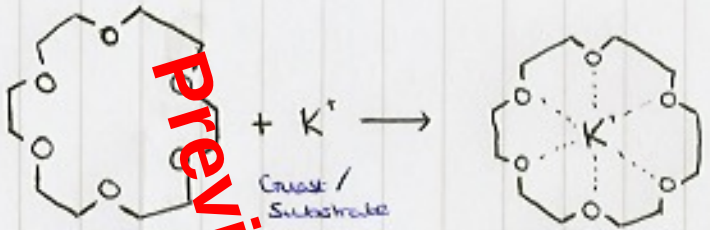
DIRECTIONALITY OF BONDING

Ion-Dipole;
- Key for M-L bonding
- not strongly directional.

H-Bonding;
- strongly directional.
- most effective in a linear arrangement of H-acceptor/donor.



- Complex formation requires strong binding and selectivity - design ligand to give selectivity

Guests for Molecular Recognition

Cations: Metals: Hard/Soft/Borderline Acids
Non-Metals: RNH_3^+

Anions: F^-, CN^-, SO_4^{2-}, $[Fe(CN)_6]^{4-}$

Neutral molecules

Non-covalent Interactions

Bind the guest to the host:
1. Electrostatic
2. H-bonding
3. π-π stacking

BONDING OF $[CeNH_2]^+$ TO CROWN ETHERS

- Crown ethers can bind
→ Ion-dipole interactions re-inforced by H-bonding but crown-ether symmetry important.

CHOICE OF LIGAND DONOR ATOMS

- Replacing Oxygen (Hard Base/Donor) with Nitrogen (Softer Base/Donor) increases preferences for softer metal. (Ag^+)
- Other factors important for Transition Metal Ions
  e.g. Irving-Williams Series.

MOLECULAR RECOGNITION: CATION BINDING

LIGAND DESIGN PRINCIPLES: Metal Cation Binding

1. Macrocyclic cavity size and configuration
2. Identity of donor atoms
3. Directionality of host/guest interactions
4. Cation binding: electrostatic ion-dipole.

LIGAND CONFIGURATION

Cryptates: Bound through 6 O-donor atoms giving higher binding constants than macrocyclic ethers.
- better selectivity → Hole-size fit.
- Rigid cavity

Spherands: - Pre-organised receptor sites
- 6 O-donor in an cavity
- High binding constants to Na^+ and Li^+.
- No unfavourable energy terms.

MACROCYCLIC CAVITY SIZE

To determine cavity size: r = r(hole) + r(donor)

Hole-Size Fit Concept: highest binding constants for best match between cavity diameter and cation diameter.

Limitations:
- crown ethers flexible so can modify configuration on binding
- most accurate measure of hole size where ligand conformation is in strain minimum.

Cation large: cation sits above ligand cavity.
Cation small: all donor sites don't connect to metal.