CHEM20018 – Chemistry: Reactions & Synthesis

Weeks 7-8

Stability of metal complexes: Quantifying Stability

Stepwise formation constants K_{f1} , K_{f2} ,...K_{fn}

We can define the stability of a coordinated metal compound in each ligand addition step:

$$M + L \rightleftharpoons ML, \qquad K_{f1} = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2, \qquad K_{f2} = \frac{[ML_2]}{[ML][L]}$$

… etc

We expect $K_{fn+1} < K_{fn}$ as each ligand is replaced.

The K_{fn}s are stepwise formation constants, with the **overall stability constant, β_n** defined as:

$$\beta_n = \frac{[ML_n\ ]}{[M][L]^n} = K_{f1} \cdot K_{f2} \cdot K_{f3} \cdot \ldots \cdot K_{fn}$$

Remember:

$$\Delta G^0 = -RT\ln(K) = \Delta H^{\circ} - T\Delta S^{\circ}$$

Stability of metal complexes: Trends across the first row transition metals

The Irving Williams series: low level of ligand exchange. high level of ligand exchange.

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

least reactivity
most stable

highly reactive
least stable.

Since:

Electrostatic Effects:

As we go across the row, the radius decreases (nuclear charge goes up).

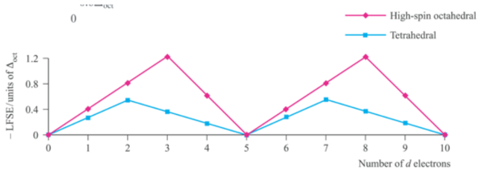
We know that there's stability is enhanced by a smaller size and larger charge. (since ∀charges=2+, ionic radii is the only thing that counts)

CFSE:

Greater stabilisation for electrons in the t_{2g} orbitals than the e_g ones.

Stabilisation for 2+ ions:

Mn	Fe	Co	Ni	Cu	Zn
0	0.4	0.8	1.2	0.6	0

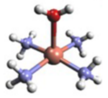


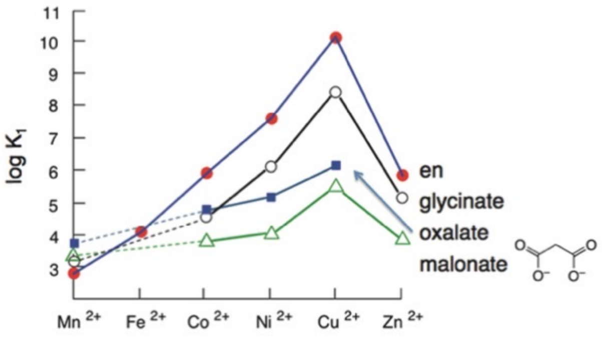
Jahn Teller Distortions:

Jahn-Teller Theorem: any non-linear molecule in a degenerate system will be unstable. (degenerate = same energy level)

Therefore, octahedrals will distort to create varying energy levels and thus become more stable.

Example: Cu^{2+} (a d^9 complex), will distort away from octahedral and gain stability:





Stability of metal complexes: The role of ligands

Chelate effect: a chelated complex will have greater stability than a comparable monodentate complex.

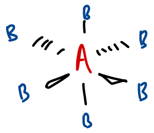
Enthalpic contribution: kinetically favourable as they favour bond reformation rather than recombination by the rings holding the ligand in place after partial disassociation.

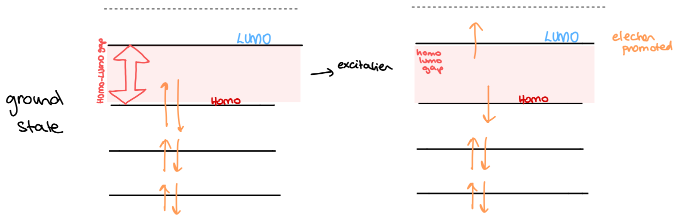
Entropic contribution: entropically favoured as we liberate more small ligands which then add to the chaos of the solution (more ΔS contribution)

5 and 6 membered rings are most stable.
3-4: tortional and steric strain of small rings make binding unfavourable.
7+: the steric and tortional strain of wrapping a larger molecule around itself; it'd rather bond with another metal than fold back onto itself.

HSAB principle: Definitions of Hard and Soft Acids and Bases

Acid: metal ion
Base: donor atoms in a ligand





HOMO: highest occupied molecular orbital
LUMO: lowest unoccupied molecular orbital.
HOMO is the highest energy molecular orbital that consists of electrons while the LUMO is the next highest energy orbital that is empty. The gap is the lowest energy excitation of electrons that exists in a molecule. Smaller HOMO-LUMO gaps correspond to better stability.

	Hard	Soft
	Large HOMO-LUMO gap Electrostatic in nature	Small HOMO-LUMO gap σ-donation with π-backbonding Covalent in nature Full d-shells more polarizable due to relatively inefficient shielding of $d^{>6}$ electrons (particularly d^{10})
Acid	• Small • High charge density • Not very polarisable (not squishy)	• Large monocations • Low charge density
Base	• Small • Electronegative • (slightly) not very polarisable	• Larger • Highly polarisable • Less electronegative