Electron Config, 18 Electron Rule, CF Theory and Coordination Numbers (W1)

Electron Configurations

- In the **elements** the 4s orbital is filled before the 3d orbital (gas)
  - Fe   [Ar]4s^2 3d^6
- In the **compounds** the **3d orbitals** are **lower** in energy than **4s** and therefore filled first
  - [Fe(CO)5]   Fe(0) [Ar]3d^8
- The number of d electrons from group number in compounds
  - [Cr(CO)6]   Cr(0) 3d^6 valence electrons
- Metals act Lewis acids (accept e-) and coordinate with Lewis bases (has electrons to share)
- Cr: [Ar]4s^1 3d^5 (special stability of half filled shell Cu: [Ar]4s^1 3d^10
- Cu+ and Zn2+ in complex state is isoelectronic ([Ar]3d^10)

18 Electron Rule

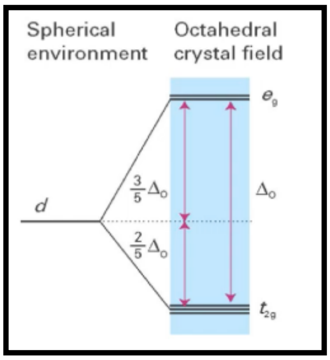
- Complex likely to be stable if 18 electrons are around the metal
  - Come from 4s, 3d and 4p orbitals
- Eg. [Fe(CO)5]
  - Fe(0)   d^8 = 8 electrons
  - 5 x CO -> 5x2 electrons = 10 electrons
  - Total of 18 electrons
- Works well for compounds in low oxidation state (0,+1), especially CO
- Doesn't explain colour paramagnetism of many transition metal compounds

Crystal field stabilisation energy

- Splitting of d orbitals leads to an overall lowering of energy and consequently the complex is more stable than before the splitting
- Accounting for the stability of most complexes

Octahedral environment

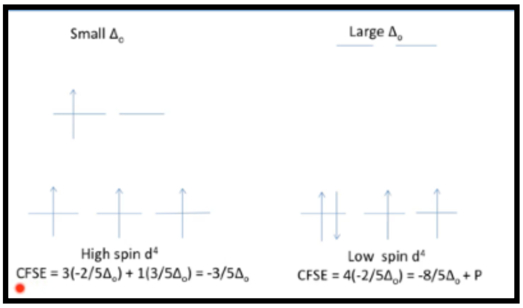
- eg > t2g
- Difference between eg and t2g is "delta oct"



Low or high spin?

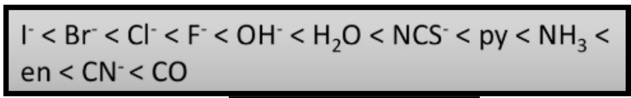
- Magnitude of delta oct can be small or large
- High spin d^4 -> 3 electrons in t2g and 1 in eg (small delta oct)
- Low spin d^4 -> 4 electrons in t2g with one full orbitals (large delta oct)
- When delta oct is large, more stable for electrons to stay in t2g and stay in low spin.
- "P" is extra pairing energy in low spin

- We can calculate the overall stabilisation energy using crystal field stabilisation energy, **CFSE**:

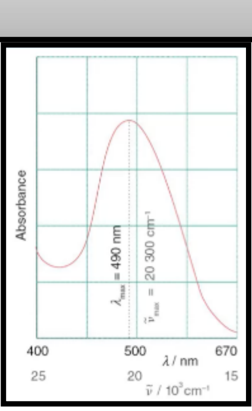


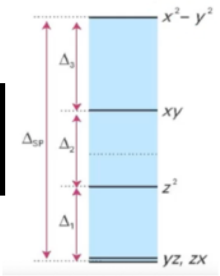
What effects size of delta oct?

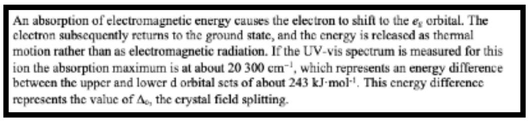
- **Identity** of metal
  - Down a group, delta oct INCREASES
- **Oxidation** state of the metal
  - When oxidation state increase, delta oct INCREASES as ligands are held more tightly
- **Number** of ligands
  - More ligands, delta oct INCREASES
- **Nature** of ligands (see image)
  - CN-, CO are high field ligands. I-, Br- are low field ligands
- Spectrochemical series: X- < O < N < C
- Ligands up to and including H2O usually give rise to **high spin** complexes



$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NCS^- < py < NH_3 <$ en $< CN^- < CO$

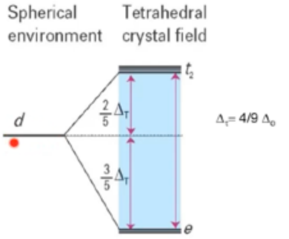





An absorption of electromagnetic energy causes the electron to shift to the e_g orbital. The electron subsequently returns to the ground state, and the energy is released as thermal motion rather than as electromagnetic radiation. If the UV-vis spectrum is measured for this ion the absorption maximum is at about 20 300 cm^{-1}, which represents an energy difference between the upper and lower d orbital sets of about 243 $kJ \cdot mol^{-1}$. This energy difference represents the value of Δ_o, the crystal field splitting.

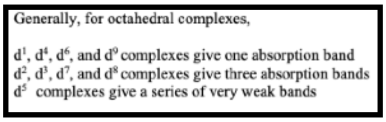
<u>How can we measure delta oct?</u>
- UV-vis spectroscopy
- Nm or wavenumber

<u>Selection rules</u>
- Laporte - change in subsidiary quantum number, l
  Allowed s->p, p->d, d->f
  Forbidden s->s, p->p, d->d, f->f
- Spin selection rule - no inversion of spin allowed
- Laporte's selection rule states there must be a change in the value of the subsidiary quantum number, l



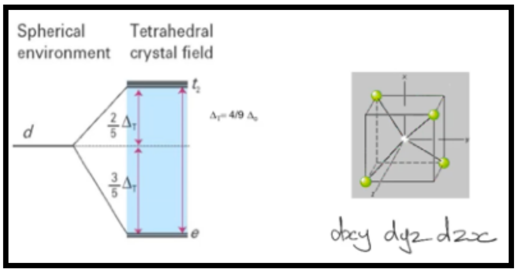
Rule 1: Laporte's selection rule only applies to molecules that have a centre of inversion. So, the rule is relaxed for tetrahedral complexes, which do not have a centre of inversion. This means that **tetrahedral** complexes are more **strongly** coloured than octahedral ones.
Rule 2: There is one more selection rule which determines which transitions are allowed or forbidden. This is the **spin selection rule** which states that a change in spin multiplicity is forbidden. In simple terms, this means that transitions which **change** the relative **orientation** of electron spins are forbidden.

Tetrahedral Environment
- t2 > eg
- Delta tet = 4/9 * delta oct
- 3 higher energy orbitals, 2 lower energy orbitals

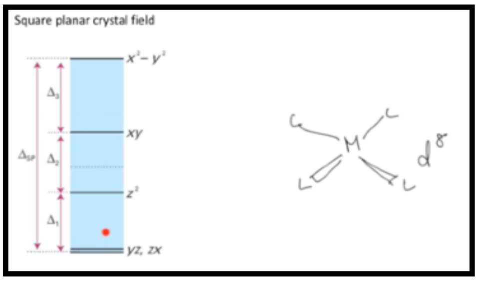

Generally, for octahedral complexes,

d^1, d^4, d^6, and d^9 complexes give one absorption band
d^2, d^3, d^7, and d^8 complexes give three absorption bands
d^5 complexes give a series of very weak bands

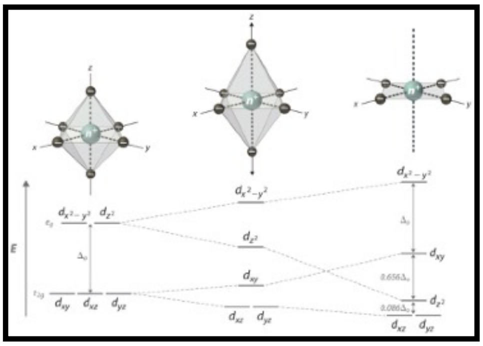
Square planar environment
- x^2-y^2 > xy > z^2 > yz = zx
- Maximum amount of electrons is d^8
- x^2-y^2 is very high in energy and is never filled



<u>**Effect of coordination number**</u>
Tetrahedral complex
- 4 ligands lie in between x, y z axes which means the d orbitals which lie between the **dxy, dyz and dzx experience greater repulsion** because they interact more strongly with the ligands and end up higher in energy (t2 > e)
- Orbitals that lie along the **dz^2 and dx^2-y^2 axes interact less strongly** with the ligand orbitals and are thus lower in energy
- 2 orbitals, e, and 3 orbitals in t2
- Opposite of octahedral complex
- Delta tet = 4/9 * delta oct because there are only 4 ligands interacting with the d orbitals, while 6 in an octahedral complex



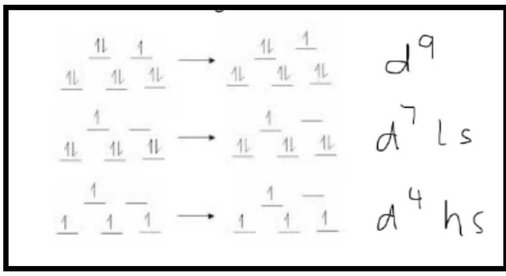
Square planar complex
- Exist in a d^8 configuration
- Quite stable (more than tetrahedral) because the crystal field splitting is quite large, so large that the x^2-y^2 orbitals are rarely filled
- Delta sp is larger than delta oct



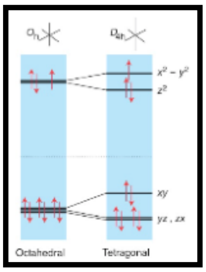
Jahn Teller, Macrocylic Effect and Ligand Field Theory (W2)

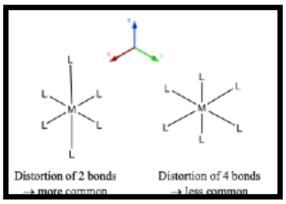
Jahn Teller

Jahn Teller Distortion



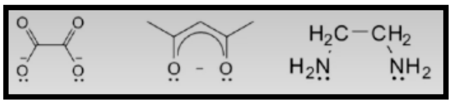
- Additional stability afforded by unsymmetrically filled eg orbitals
- Two of the ligands move away or go closer
- **Occurs when eg orbitals have unpaired electron**
- **x** and **y** component orbitals go **up** in **energy**
- Distortion gives stability to complex
- Oct complexes of **d^9**, **low spin d^7** and **high spin d^4** are often distorted due to unsymmetrically filled eg orbital
- Common for **Cu2+** complexes
- Distortion can lead to an **elongated** or **compressed** octahedron and is due to the unsymmetrically filled eg orbitals
- For d^4 if the **single** electron in the e_g orbital is in the **z^2 orbital** there will be **greater repulsion** in the z direction than the x or y directions and the complex will be **elongated**. If the single electron occupies the **d_{x2-y2} orbital** then the **extra repulsion** will be in the x and y directions and the octahedron will be **compressed**. Similar arguments hold for the **d^9** case. Which type of distortion happens is a matter of energetics but because **axial elongation weakens two bonds** and **equatorial elongation weakens four** bonds, **axial** is **more common**.

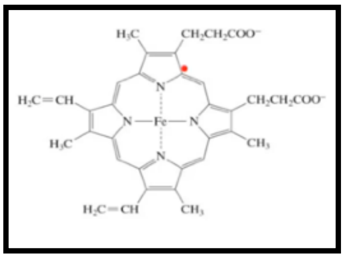




Macrocylic Effect

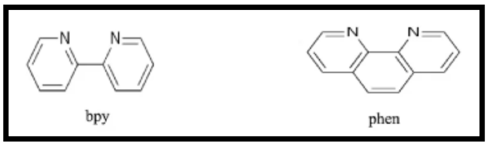
Chelate effects





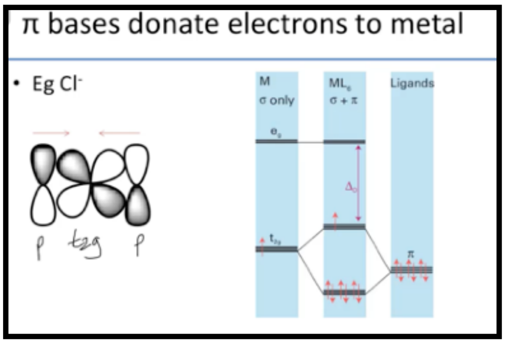
- More stable when theres **more donor atoms in the chelating molecule**
- **Increase** in **entropy** when in a cyclic form
- Organised in a way so the metal can bond easily with the donor atoms
- This greater stability of chelated complexes compared with their non-chelated analogies is called the **chelate effect**
- Chelating compounds have **more positive reaction entropy** and hence is **more favourable** process
- Once one ligating group of a polydentate ligand has bound to the metal ion, it becomes **statistically** more likely that its other ligating groups will bind, as they are now **constrained to be in close proximity** to the metal ion, thus chelate complexes are highly favoured
- The greater the number of donor sites the multidentate ligand has, the greater is the entropic advantage of displacing monodentate ligands
- This so-called **macrocyclic effect** is thought to be a combination of the **entropic effect** seen in the **chelate effect**, together with an additional **energetic contribution** that comes from the **preorganized nature** of the ligating groups, meaning **no additional strains** are introduced to the ligand on coordination.

Electronic effects



- Act as pi acceptors - electrons from full metal t2g orbital to empty into antibonding pi*
- Electron density transferred from metal to ligand
- Complexes containing chelating ligands with delocalised electronic structures may be stabilised by electronic effects in addition to the entropy advantages of chelation

- The great stability of these complexes is probably a result of their ability to act as pi acceptors as well as s donors and to form pi bonds by overlap of the full metal d orbitals and empty ring pi* orbitals
- This bond formation is favoured by electron population in the metal t2g orbitals, which allows the metal atom to act as a π donor and transfer electron

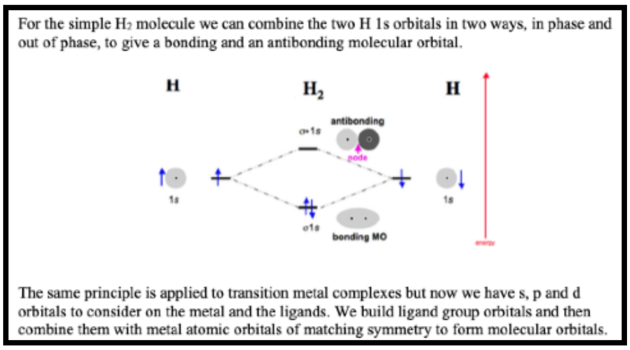

π bases donate electrons to metal

- Eg Cl^-

Ligand Field Theory

Molecular orbital approach
- Considers all metal and ligand atomic orbitals
- Combine to form molecular orbitals that extend over whole complex
- Fill with valence electrons from metal and ligands

Including Covalency
- **Ligands** are **Lewis bases**, so initially form a sigma-bond between the metal and ligand **(donate e-)**
- In some cases this is supplemented by pi-bonding, if the ligands have either filled or unfilled orbitals of the correct symmetry
- The molecular orbital model of bonding enables us to consider sigma and pi covalent interactions between the metal ion and the ligands. This is referred to as Ligand Field Theory


For the simple H_2 molecule we can combine the two H 1s orbitals in two ways, in phase and out of phase, to give a bonding and an antibonding molecular orbital.

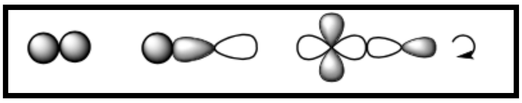
The same principle is applied to transition metal complexes but now we have s, p and d orbitals to consider on the metal and the ligands. We build ligand group orbitals and then combine them with metal atomic orbitals of matching symmetry to form molecular orbitals.

Molecular Orbital Theory
- Tells us why molecules are stable; i.e. they **combine atomic orbitals** to **form molecular orbitals** which extend over the whole molecule and only then populates them with electrons

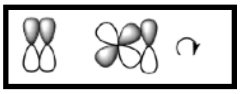
1. **N molecular orbitals** may be constructed from **N atomic orbitals**
2. The same rules that are used for filling atomic orbitals which electrons apply to filling molecular orbitals with electrons

Definitions

Sigma bonds:
- electron density appears along the **internuclear axis** and cylindrical symmetry around internuclear axis
- That means if we rotate the orbitals around the z axis there is no change of phase



Pi bonds:
- A **nodal** plane exists along the **internuclear axis**, lack of cylindrical symmetry
- That means if we rotate the orbitals around the z axis there is a change of phase



Sigma-donor ligands:
- If no pi-bonding is present the energy difference between the t2g and eg orbitals corresponds to the delta oct from crystal field theory
- Sigma donors donate electrons from lone pairs to the metal centre from their the s or p orbitals e.g. amines, water, nitrite
- For a first row transition metal the valence shell atomic orbitals are 3d, 4s and 4p
- Combinations of the metals and ligand orbitals generate six bonding and six anti-bonding molecular orbitals. Non-bonding for t2g set
- The MO theory of bonding in octahedral complexes gives a similar result to crystal field theory - this changes if there is also pi-bonding present

MO theory of pi bonding