Lecture 9 - Crystal field theory for octahedral, tetrahedral and square planar complexes.

- The order of ligands in the spectrochemical series
- Crystal field stabilization energies for octahedral complexes
- Four coordinate geometries – crystal field theory for tetrahedral and square planar complexes

1. The Spectrochemical Series

- We have seen that it is possible to arrange ligands into a series that reflects their ability to split the d-orbitals. This spectrochemical series is essentially the same no matter what the metal ion is. Thus, water not only splits the d-orbitals more than chloride for cobalt(II), but also for cobalt(III), iron(II), iron(III), nickel(II), platinum(IV), chromium(III), and so on:

  Remember the series is as follows:

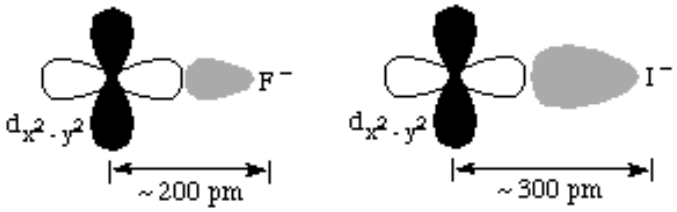
  $I^- < Br^- < Cl^- < SCN^- < NO_3^- < F^- < OH^- < H_2O < NCS^- < gly < py < NH_3 < en < NO_2^- < PPh_3 < CN^- < CO$

- The positions of some of these ligands can be explained, or at least the ligands can be classified according to their donor/acceptor properties.

We can consider the following three groups of ligands and rationalize their position in the spectrochemical series.

1. **I- < Br- < Cl- < F-**. The crystal field model looks at electrostatic repulsions between the ligands and electrons in d-orbitals on the metal ion.

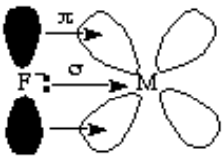
- The smaller the ligand, the closer it comes to the metal ion and thus the greater the repulsion.



2. **F- < OH^- < H_2O.** Fluoride and hydroxide lie below water in the spectrochemical series because they are both ***π-donor ligands.***

- That is, F^- and OH^- can rehybridize and donate a pair of electrons from their p-orbitals to d-orbitals on the metal, forming a π-bond as shown below.
- This reduces the negative charge on the fluoride and the positive charge on the metal, so in turn Δ_o is reduced.
- These orbitals can interact with the metal orbitals of the correct symmetry to give π-interactions

F^- is a π-donor ligand

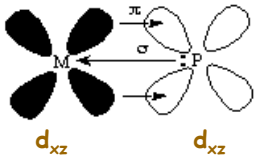


Fluoride (and hydroxide) can be pi-donors as well as sigma donors to the metal ion.

p_z in F^- d_{xz} in M

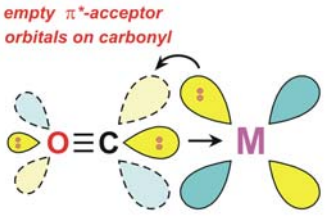
3. **PPh_3 < CN^- < CO.** It is astonishing to many chemists that not only do carbon monoxide and phosphine ligands bond readily to many transition metals, but that of all the ligands, they (together with cyanide) **have the greatest capacity to split the d-orbitals**.

- Let's consider what happens when a bond is formed between a metal ion and a phosphine ligand. The bond distance is relatively large (larger than the M-N distance in ammine complexes), so one would expect phosphines to fall lower in the spectrochemical series, as observed in the iodide-bromide-chloride-fluoride series.
- If the metal ion has electrons in its d-orbitals, it can donate them to the phosphine ligand through the empty d-orbitals on phosphorus:



P is a π-acceptor ligand – accepts electrons from the metal centre in an interaction that involves a filled metal orbital and an empty ligand orbital

Molecular orbital view of π-bond formation between metal d_{xz} and ligand π*-orbitals as for L = CO, an example of a π-acceptor ligand.

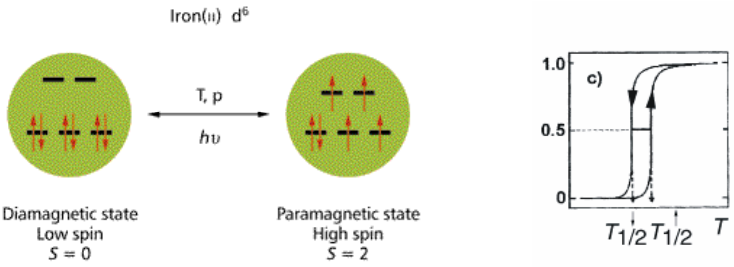


powerful π-acceptor ligand!
excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers

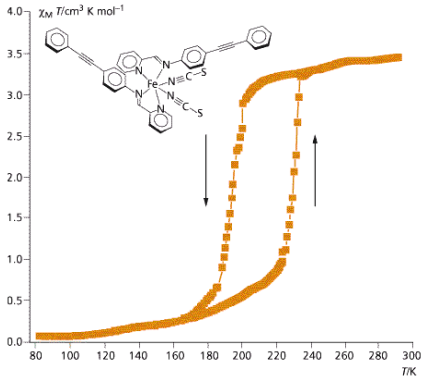
- Cyanide and carbon monoxide behave similarly to phosphine ligands, but they make use of their empty anti-bonding π-orbitals to accept electrons from the metal.
- "Normal" bonding occurs when a ligand donates electrons to a metal.
- When a metal ion donates electrons back to the ligand, this is called **back-bonding**.

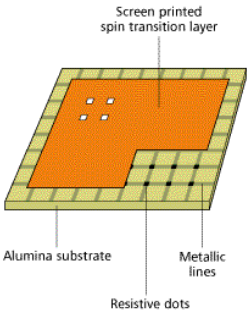
- The combination of normal bonding and back-bonding creates a **strong bond between the ligand and the metal**.
- The reason that phosphines, carbon monoxide, and cyanide are so poisonous is because they bond readily to iron in biological systems and cannot be displaced by the ligands (such as oxygen) which should bond to iron in normal metabolic processes.
- A π-donor ligand donates electrons to the metal centre in an interaction that involves a filled ligand orbital and an empty metal orbital: a π-acceptor ligand accepts electrons from the metal centre in an interaction that involves a filled metal orbital and an empty ligand orbital.
- What happens when the value of Δ_o is very close to that of the pairing energy P?

Spin crossover compounds



The choice between a low and high spin configuration for a d^4, d^5, d^6 and d^7 metal ion is not always unique and a spin crossover sometimes occurs; this maybe initiated by a change in pressure, temperature or light. A change in μ_{eff} accompanies the spin crossover.





When temp is above Tc, the material changes from violet to white.
To erase - cool material below Tc↓
Easily implemented as printed ink and deposited on any kind of substrate such as a plastic card.
Rewritable displays comprised of spin crossover copolymers bistable at RT

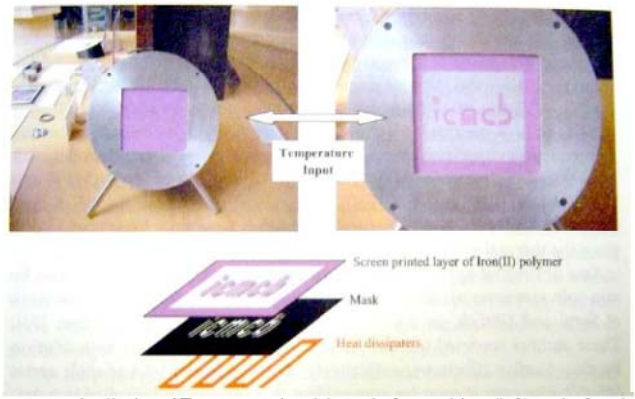
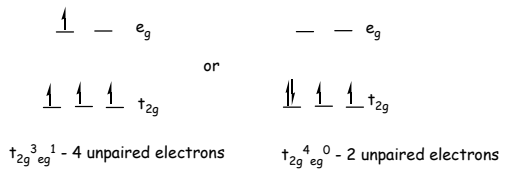


Fig. 10. laboratory scale display. ST screens printed layer before writing (left) and after thermal writing (right). The display device involving the ST later, the aluminum plate containing the TCMCB logo and the heat dissipater resistance (bottom). When the temperature exceeds the critical "up temperature" the material transits from purple to white and the ICMCB information is addressed. (17)

2. CFSE's for Octahedral Complexes

Lets look at some specific cases of d-orbital splitting for octahedral metal ions, e.g consider a d^4 case e.g. Mn^{3+}

There are two possibilities:



$t_{2g}^3 e_g^1$ - 4 unpaired electrons

$t_{2g}^4 e_g^0$ - 2 unpaired electrons

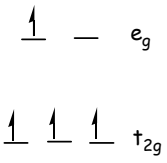
Remember it **costs energy** to put an electron into the **e_g orbital**, but it also **costs energy** to **pair up electrons in the t_{2g} orbital**.

For a given metal ion P (pairing energy) is constant, it does not vary with ligand, (but it does depend on the oxidation state of the metal ion).

P varies between 200-400 $kJmol^{-1}$ depending on the metal.

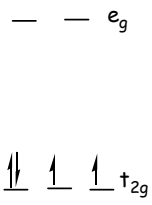
Δ_{oct} varies with liaand.

HIGH SPIN



small Δ_o
e.g. $[Mn(H_2O)_6]^{3+}$
d^4 metal ion
$\Delta_o < P$
i.e. it costs less energy to go to e_g than to pair.

LOW SPIN

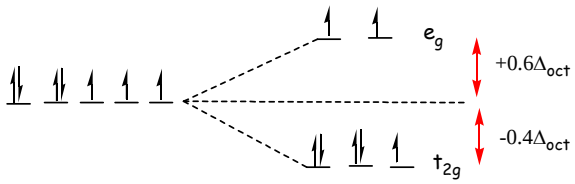


large Δ_o
e.g. $[Mn(CN)_6]^{3+}$
d^4 metal ion
$\Delta_o > P$
i.e. it costs more energy to go to e_g than to pair.

Δ_o varies between 100 to 400 $kJmol^{-1}$

- CFSE – the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands.
- Owing to the splitting of the d orbitals in a complex, the system gains an extra stability due to the rearrangement of the d electrons filling the d levels of lower energy.
- The consequent gain in bonding energy is known as crystal field stabilization energy (CFSE).

CFSE for a d^7 high spin case



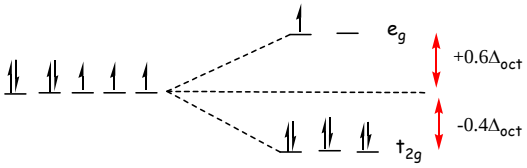
CFSE(7 electrons) = (5 electrons stabilised by $(-0.4\Delta_{oct})$ + (2 electrons destablized by $(+0.6\Delta_{oct})$

$= -2.0\Delta_{oct} + 1.2\Delta_{oct} = -0.8\Delta_{oct}$

since Δ_{oct} can vary between 100-400 $KJmol^{-1}$ a C-C bond is 350 $KJmol^{-1}$so this is significant. If we can determine the value of $\Delta_{oct}$from spectroscopic measurements then we can calulate the CFSE exactly for a particular complex.

Here pairing energy is not taken into account since the number of paired electrons is the same as that in the ground state of the free metal ion

CFSE for a d^7 low spin case



CFSE(7 electrons) = (6 electrons stabilised by $(-0.4\Delta_{oct})$ + (1 electrons destablized by $(+0.6\Delta_{oct})$ + P

$= -2.4\Delta_{oct} + 0.6\Delta_{oct} + P = -1.8\Delta_{oct} + P$

Now we add in the pairing energy since it will take some energy to pair up one extra group of electrons.

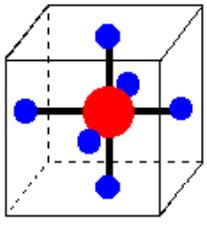
This looks the most stable configuration but we have then to take into consideration the Pairing energy P!

For many complexes, the perfect fit is for six ligands around the metal ion, but not always!

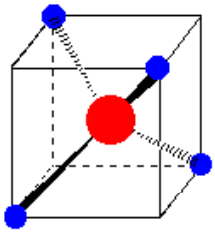
3. Four Coordinate Geometries

(i) Tetrahedral complexes

d-Orbital splitting for tetrahedral coordination. A cube, an octahedron, and a tetrahedron are related geometrically. Octahedral coordination results when ligands are placed in the centers of cube faces. Tetrahedral coordination results when ligands are placed on alternate corners of a cube.

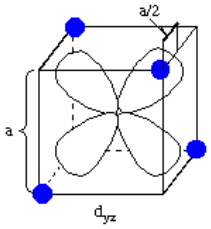


Octahedral complex in a cube. Ligands are on the centers of the cube faces.

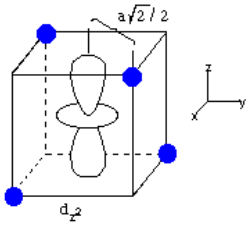


Tetrahedral complex in a cube. Ligands are on alternate corners of the cube.

- Now consider the effect of the ligands on the energies of the d-orbitals in tetrahedral coordination, with the **d_{yz}** and **d_{z2}** orbitals as examples. An electron in the d_{yz} orbital can approach the ligand to within a distance of a/2, where a is the cube edge length. However, an electron in d_{z2} only approaches the ligands at a distance of $a/2(2^{0.5})$, a distance 1.414 times as long as the distance in the d_{yz} case. This means that the d_{z2} orbital is lower in energy than the d_{yz} orbital, **exactly the opposite case** as in **octahedral coordination.**

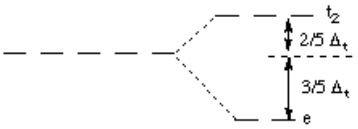


The d_{yz} orbital in tetrahedral coordination. Electrons in this orbital can approach within a distance of a/2 to ligand electrons.



The d_{z2} orbital in tetrahedral coordination: electrons in d_{z2} are further from the ligands than electrons in d_{yz}.

- The d_{xz} and d_{xy} orbitals behave the same way as d_{yz}, and d_{x2-y2} behaves the same way as d_{z2}. The resulting d-orbital splitting diagram for tetrahedral coordination is the inverse of the diagram for octahedral coordination, as shown below.



The d_{xy}, d_{xz}, and d_{yz} orbitals are the t_2 orbitals, and they are higher in energy than the e orbitals (d_{z2} and d_{x2-y2}) in tetrahedral coordination.

The energy difference between the t_2 and e orbitals is called the **tetrahedral splitting energy Δ_t.**

(Note that the orbitals are labelled t_2 and e, not t_{2g} and e_g; g refers to a geometry, such as octahedral, that has a center of symmetry. The tetrahedral geometry has no center of symmetry).

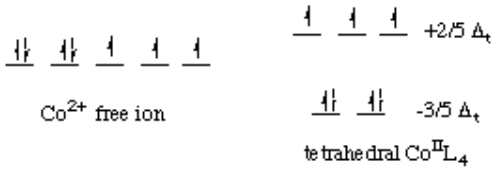
Crystal Field Stabilization Energy in Tetrahedral Complexes.

- The tetrahedral crystal field stabilization energy is calculated the same way as the octahedral crystal field stabilization energy.
- The magnitude of the tetrahedral splitting energy is only 4/9 of the octahedral splitting energy, or

$$\Delta_t = 4/9\ \Delta_o$$

- As a result of the relatively small size of the tetrahedral splitting energy, **there are no low-spin tetrahedral (ML_4) complexes.**
- It is always more energetically favorable to put an electron into a t_2 orbital rather than pair it in an e orbital.

- Let's calculate the crystal field stabilization energy for a tetrahedral cobalt(II) complex. Cobalt(II) is a d^7 ion.
- The electronic configurations of the free ion and the tetrahedral complex are shown below.



Co^{2+} free ion

tetrahedral $Co^{II}L_4$

CFSE = (4 electrons)(-3/5 Δ_t) + (3 electrons)(2/5 Δ_t)
= -1.2 Δ_t

A table showing the crystal field stabilization energies for tetrahedral complexes with different numbers of d-electrons is given below:

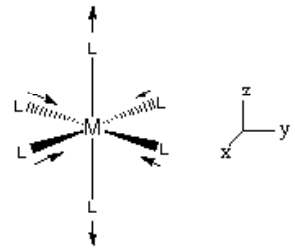
Crystal Field Stabilization Energies for Tetrahedral Complexes of d^1 - d^{10} Ions

# of d-electrons	Tetrahedral CFSE	# of d-electrons	Tetrahedral CFSE
1	-0.6 Δ_t	6	-0.6 Δ_t
2	-1.2 Δ_t	7	-1.2 Δ_t
3	-0.8 Δ_t	8	-0.8 Δ_t
4	-0.4 Δ_t	9	-0.4 Δ_t
5	zero	10	zero

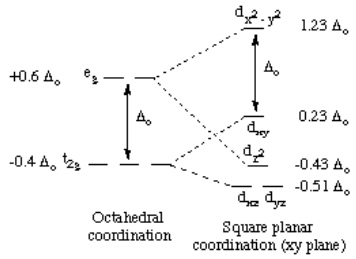
(ii) Square Planar Complexes

d-Orbital Splitting in Square Planar Coordination.

- Square planar coordination can be imagined to result when two ligands on the z-axis of an octahedron are removed from the complex, leaving only the ligands in the x-y plane. As the z-ligands move away, the ligands in the square plane move a little closer to the metal.
- The orbital splitting diagram for square planar coordination can thus be derived from the octahedral diagram.

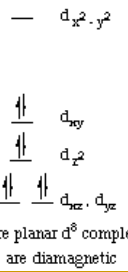


- As ligands move away along the z-axis, d-orbitals with a z-component will fall in energy.
- The d_{z2} orbital falls the most, as its electrons are concentrated in lobes along the z-axis.
- The d_{xz} and d_{yz} orbitals also drop in energy, but not as much.
- Conversely, the d_{x2-y2} and the d_{xy} orbitals increase in energy. The splitting diagram for square planar complexes is more complex than for octahedral and tetrahedral complexes, and is shown below with the relative energies of each orbital.

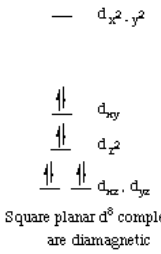


Crystal Field Stabilization Energy in Square Planar Complexes.

- Square planar coordination is **rare** except for **d^8 metal ions**. Among the d^8 metal ions exhibiting square planar coordination are nickel(II), palladium(II), platinum(II), rhodium(I), iridium(I), copper(III), silver(III), and gold(III). Copper(II) and silver(II), both d^9 ions, are occasionally found in square planar coordination.
- **All** known square **planar complexes** of **d^8 ions are diamagnetic**, because the highest-energy orbital (d_{x2-y2}) is greatly destabilized, and pairing in the d_{xy} orbital is more favorable than placing an unpaired electron in the d_{x2-y2} orbital.



Square planar d^8 complexes are diamagnetic



Square planar d^8 complexes are diamagnetic

The crystal field stabilization energy for a diamagnetic square planar d^8 metal complex is readily calculated by the usual method:

$$\begin{aligned} CFSE_{\text{square planar}} &= 4 \text{ electrons } (-0.51\,\Delta_o) + 2 \text{ electrons } (-0.43\,\Delta_o) \\ &\quad + 2 \text{ electrons } (+0.23\,\Delta_o) + P \\ &= -2.44\,\Delta_o + P \end{aligned}$$

The pairing energy correction is included because a free d^8 ion has 2 unpaired electrons, but a square planar d^8 complex has no unpaired electrons