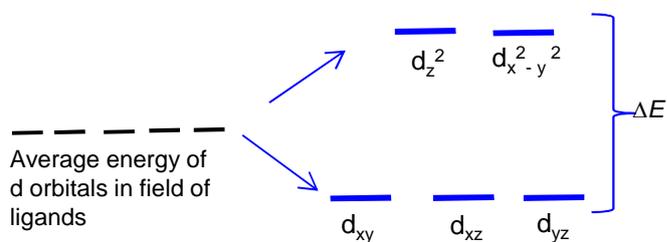# Colour in complex ions

How colour arises

Degenerate d orbitals split into two energy
levels in octahedral and tetrahedral complexes.
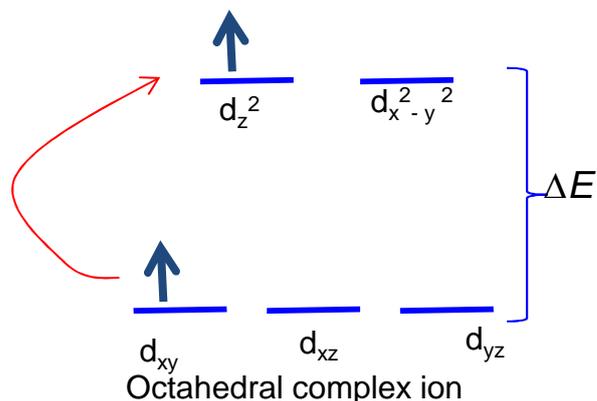(Degenerate means all orbitals have the same energy)

d_z^2 $d_{x^2-y^2}$
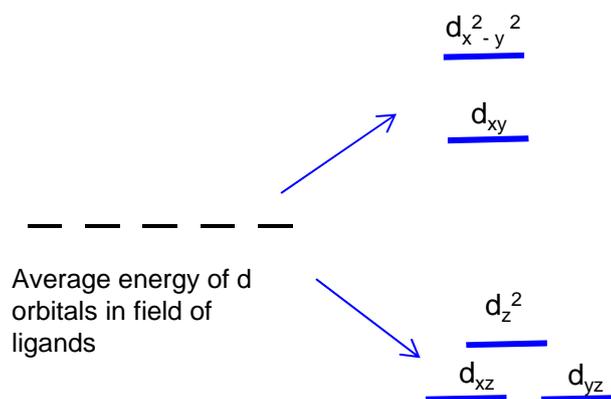
ΔE

Average energy of
d orbitals in field of
ligands

d_{xy} d_{xz} d_{yz}

Octahedral complex ion

Ligands cause the 5 d orbitals to
split into two energy levels.

d_z^2 orbital

$d_{x^2-y^2}$
orbital

d_{xy} orbital

d_{xz} orbital

d_{yz} orbital
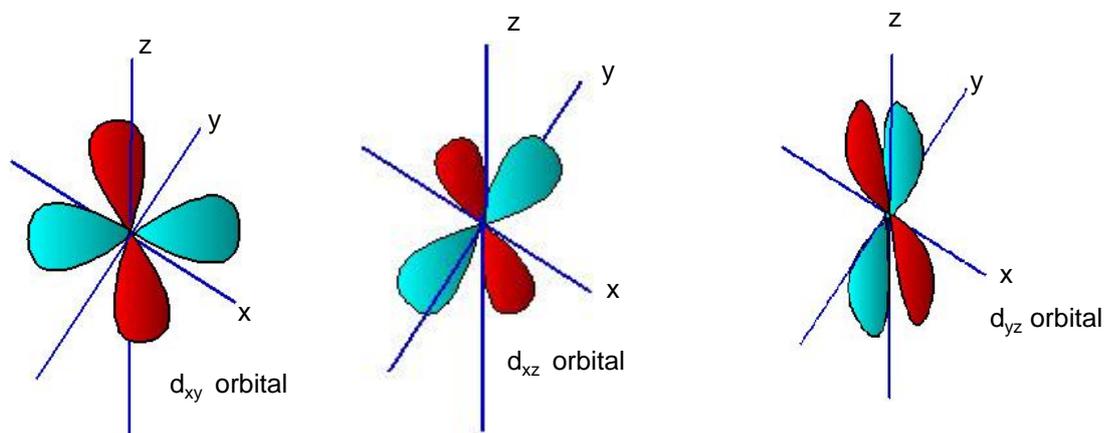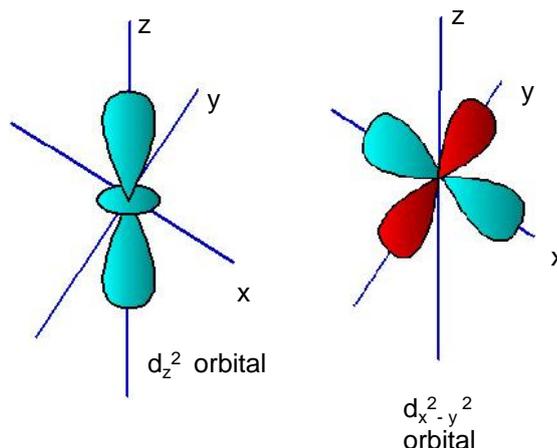
Colour arises from electronic transitions from the ground
state to excited states: between different d orbitals.
A portion of visible light is absorbed to promote d
electrons to higher energy levels. The light that is not
absorbed is transmitted to give the substance colour.

d_z^2 $d_{x^2-y^2}$

ΔE

d_{xy} d_{xz} d_{yz}

Octahedral complex ion

$$d_{x^2-y^2}$$

$$d_{xy}$$

— — — — —

Average energy of d orbitals in field of ligands

$$d_{z^2}$$

$$d_{xz} \quad d_{yz}$$

In a Square planar complex ion the orbitals split in a different way

Square planar complex ion

If one colour is absorbed then the solution will appear to be the colour on the opposite side of the colour wheel

In Copper(II) ions, yellow light is absorbed to promote the electrons in the d-orbital. This is because the frequency of yellow light supplies the correct energy gap.
 The remaining light is not absorbed and passes through the solution and the solution appears blue
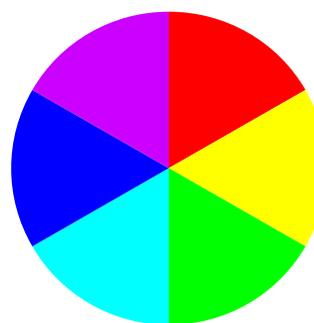
This equation links the colour and frequency of the light absorbed with the energy difference between the split d orbitals.
$\Delta E = h\nu$.
 ν = frequency of light absorbed (unit s^{-1} or Hz)
h= Planck's constant 6.63×10^{-34} (J s)
ΔE = energy difference between split orbitals (J)

A solution will appear blue if it absorbs orange light. The energy split in the d orbitals ΔE will be equal to the frequency of orange light(5×10^{14} s^{-1}) x Planck's constant
ΔE in a blue solution = $h\nu$

$$= 6.63 \times 10^{-34} \times 5 \times 10^{14}$$
$$= 3.32 \times 10^{-19} \text{ J}$$

Compounds without colour

Non-transition metals don't have partly filled d orbitals. Visible light is only absorbed if some energy from the light is used to promote an electron over exactly the right energy gap. Non-transition metals don't have any electron transitions which can absorb wavelengths from visible light.

Scandium is a member of the d block. Its ion (Sc^{3+}) hasn't got any d electrons left to move around. So there is not an energy transfer equal to that of visible light.

In the case of Zn^{2+} ions and Cu^+ ions the d shell is full e.g.$3d^{10}$ so there is no space for electrons to transfer. Therefore there is not an energy transfer equal to that of visible light.
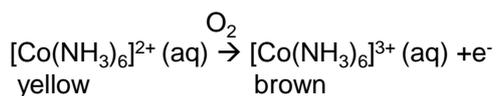
Formation of coloured ions
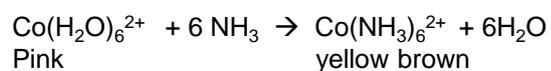
Colour changes arise from changes in
1.   **oxidation state,**
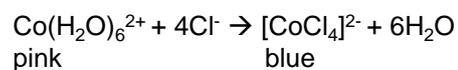2.   **co-ordination number**
3.   **ligand.**

Changing colour
Changing a ligand or changing the coordination number will alter the energy split between the d- orbitals, changing ΔE and hence change the frequency of light absorbed.

$$O_2$$
$$[Co(NH_3)_6]^{2+} (aq) \rightarrow [Co(NH_3)_6]^{3+} (aq) + e^-$$
     yellow   brown

In this equation only oxidation state is changing.

$Co(H_2O)_6^{2+}$ + 6 NH_3 $\rightarrow$ $Co(NH_3)_6^{2+}$ + 6H_2O
Pink   yellow brown

In this equation only the ligand is changing.

$Co(H_2O)_6^{2+}$ + 4Cl^- $\rightarrow$ $[CoCl_4]^{2-}$ + 6H_2O
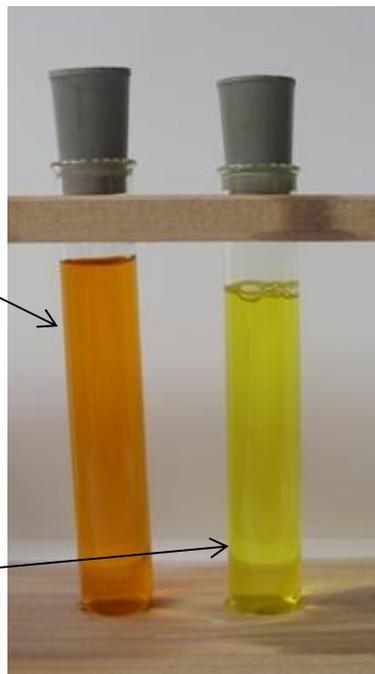pink   blue

In this equation both ligand and co-ordination number are changing.

Other coloured ions

Intensely coloured ions with the metal in its highest oxidation state (e.g. Mn(VII), Cr(VI), Fe(VI)) derive the colour from electron transitions between the metal and the oxygen atoms.

Eg . Deep purple of manganate (VII) MnO_4^-
Intense Orange of dichromate(VI) $Cr_2O_7^{2-}$

Yellow of chromate(VI) CrO_4^{2-}

Spectrophotometry

If visible light of increasing frequency is passed through a sample of a coloured complex ion, some of the light is absorbed.
The amount of light absorbed is proportional to the concentration of the absorbing species (and to the distance travelled through the solution).
Some complexes have only pale colours and do not absorb light strongly. In these cases a suitable ligand is added to intensify the colour.

Absorption of visible light is used in spectrometry to determine the concentration of coloured ions.

method
• Add an appropriate ligand to <u>intensify</u> colour
• Make up solutions of known concentration
• Measure absorption or transmission
• Plot graph of absorption vs concentration
• Measure absorption of unknown and compare

Spectrometers contain a coloured filter. The colour of the filter is chosen to only allow the wavelengths of light through that would be most strongly absorbed by the coloured solution.

Detailed method- measuring absorption of copper solutions
• Take nine 100cm³ graduated flasks and pipette 20cm³ of 2M ammonia solution into each one.
• Use the 0.05M solution of aqueous copper sulphate to make up solutions which are 0.005 to 0.04M $[Cu(NH_3)_6]^{2+}$
• Mix each solution thoroughly.
• Insert the red filter into the colorimeter.
• Use a cuvette with distilled water to zero the colorimeter
• Then put each prepared solution in cuvette and measure the absorbance of each solution.
• Plot graph of absorption vs concentration
• Measure absorption of unknown solution and determine its concentration from the calibration curve