

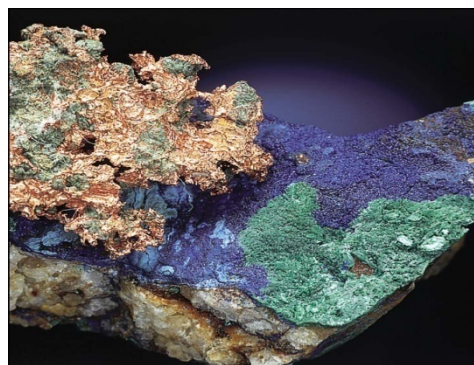
# CHEMISTRY 1000

## Topic #3: Colour in Chemistry

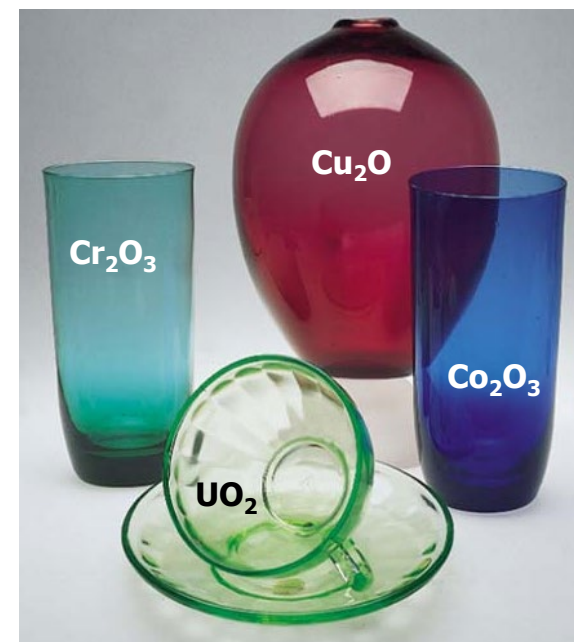
Fall 2020

Dr. Susan Findlay

See Exercises 12.1 to 12.3



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# Transition Metals

- Mercury (Hg) is the only transition metal that is not a solid.
- The transition metals all have valence electrons in a  $d$  subshell.
- Like other metals, transition metals form cations not anions.
- We shall see that many transition metals cations form beautifully coloured compounds (as shown on the previous page).



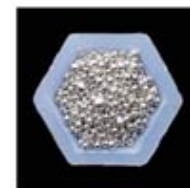
Fourth-period transition metals:  
left to right, Ti, V, Cr, Mn, Fe, Co, Ni, Cu



Group 8B: platinum (Pt)



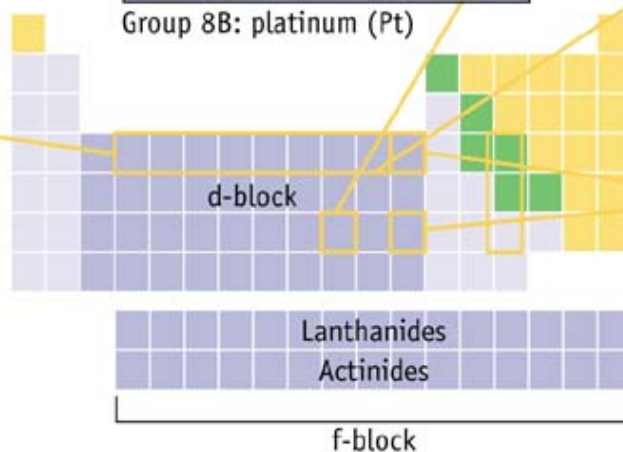
Group 1B:  
copper (Cu)



Group 1B:  
silver (Ag)



Group 1B:  
gold (Au)



Group 2B: left, zinc (Zn);  
right, mercury (Hg)



# Ligands and Co-ordination Complexes

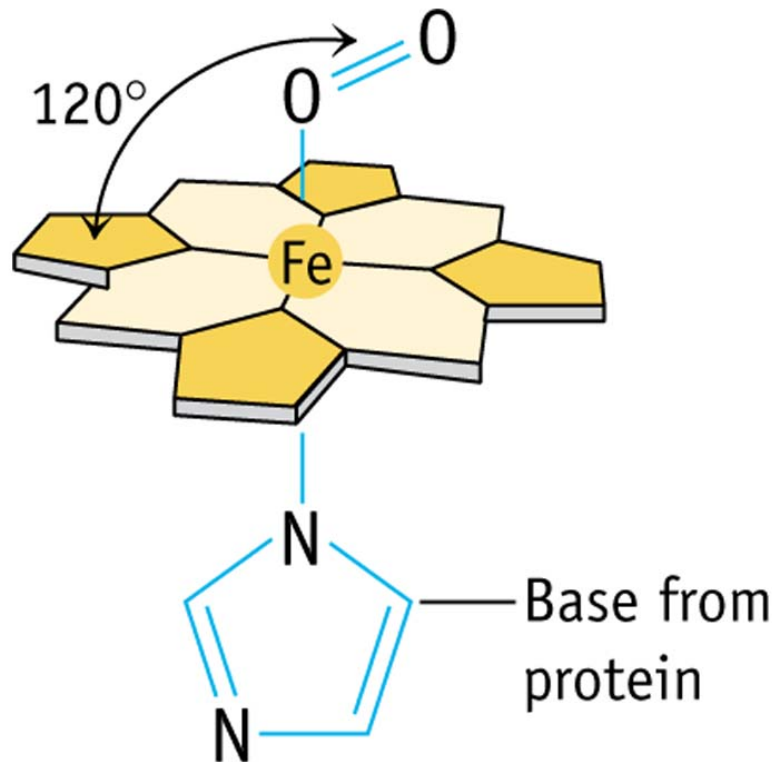
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- Co-ordination complexes are compounds in which several **ligands** are co-ordinated to a transition metal cation.
- A ligand is any substance (neutral or anion) which can act as a Lewis base, donating electrons to the transition metal cation (which acts as a Lewis acid).
- If the resulting complex has a charge, it is a **complex ion**.
- The number of atoms attached to the transition metal is referred to as the **co-ordination number**. It doesn't matter whether these atoms come from the same molecule/ion or from several different ones.

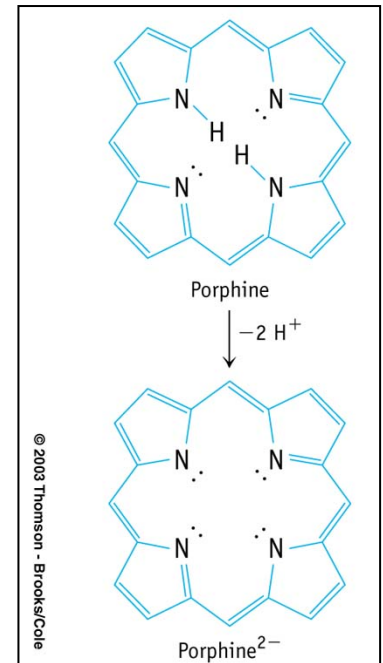


# Ligands and Co-ordination Complexes

- The ligands around the metal do not all have to be the same!
- A very important co-ordination complex is found in hemoglobin:



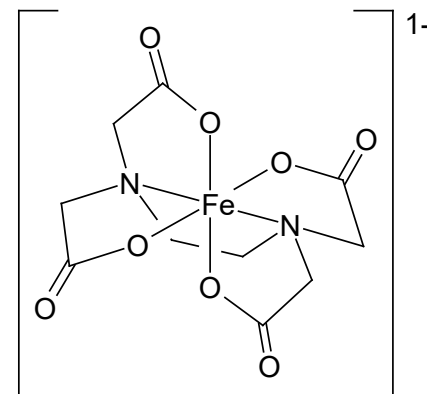
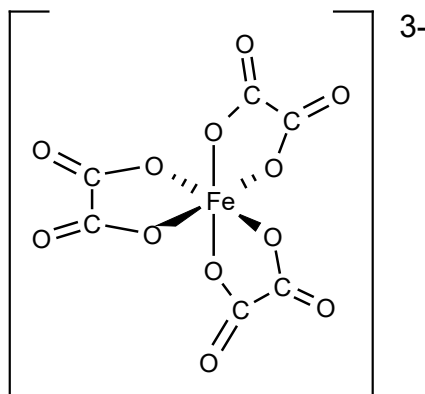
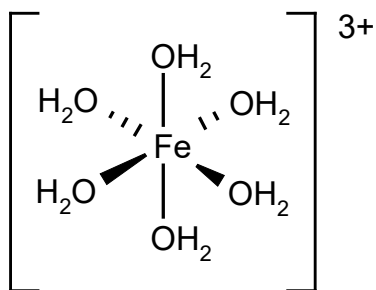
This is a cartoon!  
Heme (the porphyrin in hemoglobin) has chains branching off the porphyrin ring.



# Ligands and Co-ordination Complexes

## ■ Classifying Ligands

- Ligands co-ordinated to a transition metal through one atom are called **monodentate** ("one-toothed") ligands.
- Ligands co-ordinated to a transition metal through two atoms are called **bidentate** ("two-toothed") ligands.
- Polydentate ligands can also be called chelating ligands, or **chelates** ("claws"). Such ligands are able to "grip" a cation by co-ordinating to it with many different atoms!





# Ligands and Co-ordination Complexes

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- To make a neutral precipitate, charged co-ordination complexes (**complex ions**) need one or more counterions to balance the charge. This gives a **complex salt**.
- Some co-ordination complexes and complex salts contain extra water molecules which were trapped during crystallization. These complexes are also **hydrates**. Water of hydration can be removed by heating a complex salt in a dry oven.



# Ligands and Co-ordination Complexes

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- In the CHEM 2000 lab, you will make the bright green complex salt,  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  containing  $Fe^{3+}$ . Break this formula into a complex ion, counterion and water of hydration. Identify the ligands and their charge.





# Ligands and Co-ordination Complexes

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- If 5.00 grams of  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  is heated until all of the water has evaporated, what mass of solid ought to remain?



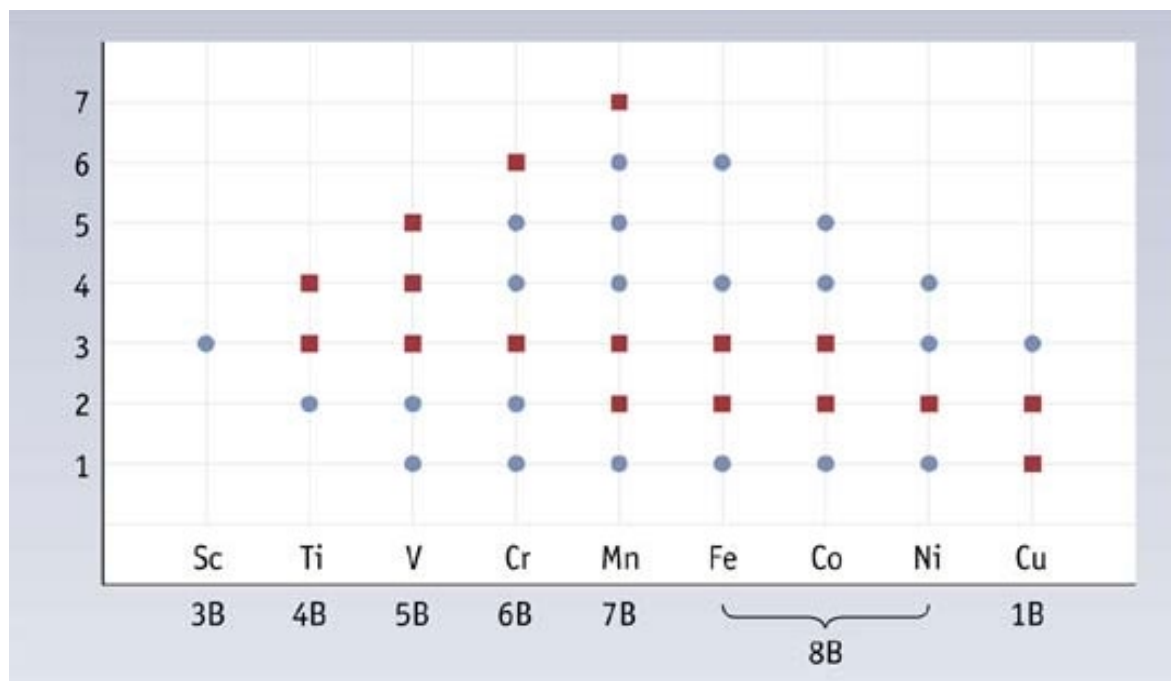
# Ligands and Co-ordination Complexes

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- A co-ordination complex *must* contain:
  - a transition metal cation
  - several ligands.
  
- A co-ordination complex *may* also have:
  - counterion(s) (to balance charge) and/or
  - extra water molecules (“water of hydration”)
  
- Co-ordination complexes can be charged or neutral.

# Why are Transition Metals Special?

- We have seen that main group metals are somewhat limited in what oxidation states they can adopt. Many transition metals, on the other hand, can take on a wide variety of different oxidation states. This distribution is not entirely random, as show in the graph below (common oxidation states in dark red):





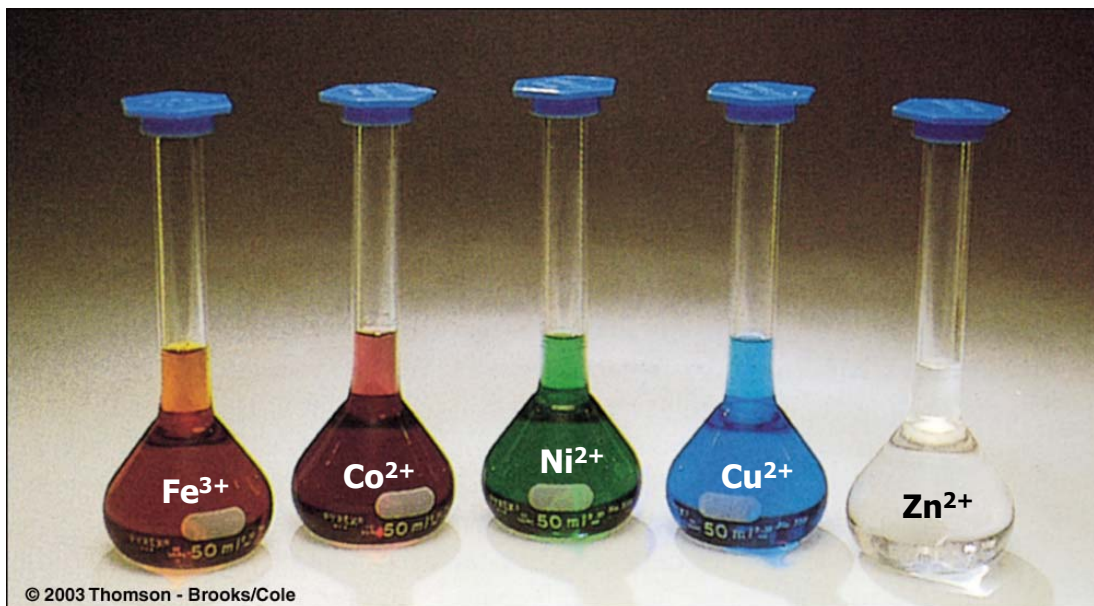
# Why are Transition Metals Special?

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- Compared to  $s$  and  $p$  electrons,  $d$  electrons can be added or removed relatively easily.
- The electron configuration of neutral vanadium is:
- The first two electrons lost from vanadium will be those in the  $4s$  orbital. After that, electrons are lost from the  $3d$  orbitals giving the three observed oxidation states:
  - vanadium(III)
  - vanadium(IV)
  - vanadium(V)

# Electronic Structure and Colour

- One of the more fun consequences of these partially filled  $d$  subshells is that the co-ordination complexes of transition metals are often brightly coloured.
- The flasks below contain aqueous solutions of nitrate salts. Since all nitrates are water-soluble, these solutions contain aqua complexes of the transition metal cation:  $[M(OH_2)_6]^{n+}$ .



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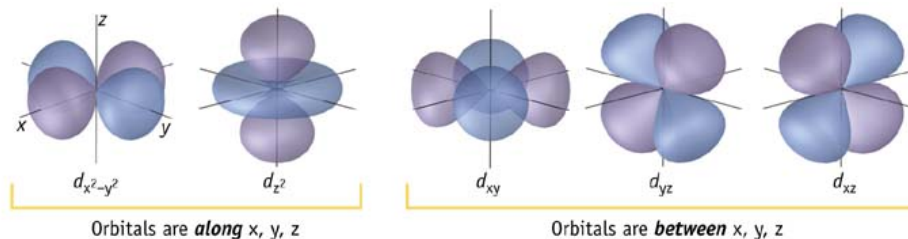
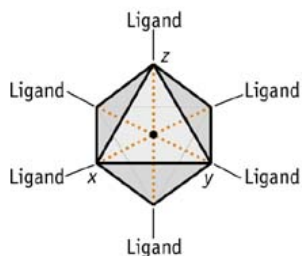
# Electronic Structure and Colour

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- Why is the  $Zn^{2+}$  complex the only colourless one?
  - Consider the electron configurations of the five cations:
    - $Fe^{3+}$
    - $Co^{2+}$
    - $Ni^{2+}$
    - $Cu^{2+}$
    - $Zn^{2+}$

# Electronic Structure and Colour

- Where does the variety in colour come from?
  - Many co-ordination complexes have octahedral geometry. This means that two of the  $d$  orbitals on the transition metal point directly at ligands while the other three do not:

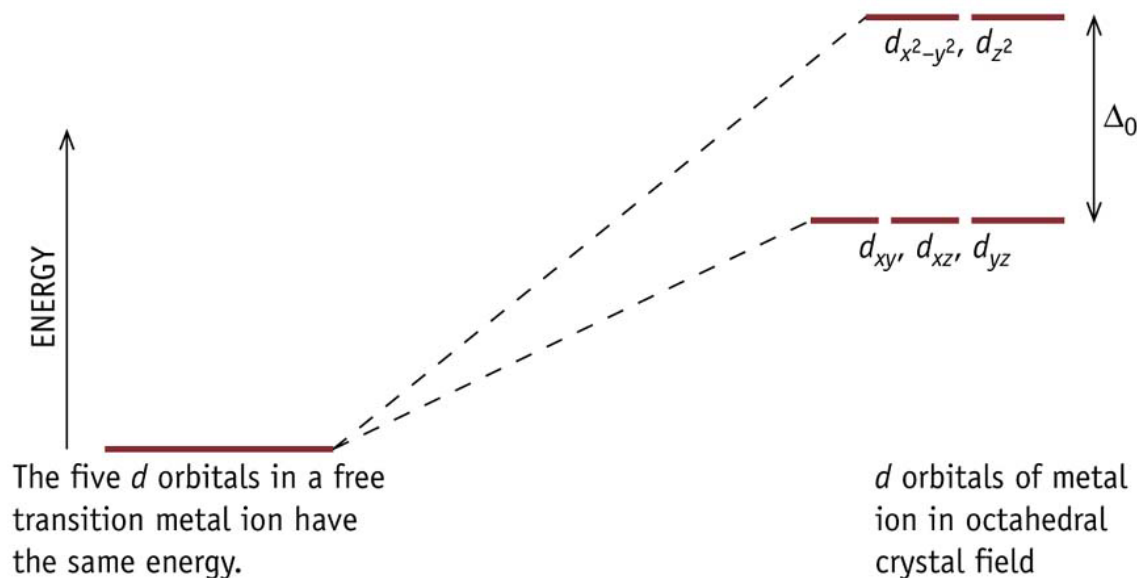


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- A simple electrostatic model, called the *crystal field theory*, assumes that there will be a certain degree of **electron-electron repulsion** between the electron pair a ligand donates and any electrons already in the metal's  $d$  orbitals. This repulsion is felt most strongly by electrons in the  $d$  orbitals pointing at the ligands.

# Electronic Structure and Colour

- Thus, in an octahedral complex, the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are pushed to higher energy than the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals.
- This separation in energy is referred to as **crystal field splitting**, and the crystal field splitting energy is  $\Delta_o$  ('o' is for 'octahedral'):







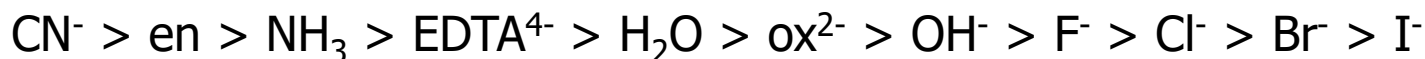
# Electronic Structure and Colour

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- In co-ordination complexes with crystal field splitting, there are two ways to distribute  $d$  electrons. Which one is favoured depends on the size of  $\Delta_o$  which, in turn depends on where the ligands fall on the **spectrochemical series**:

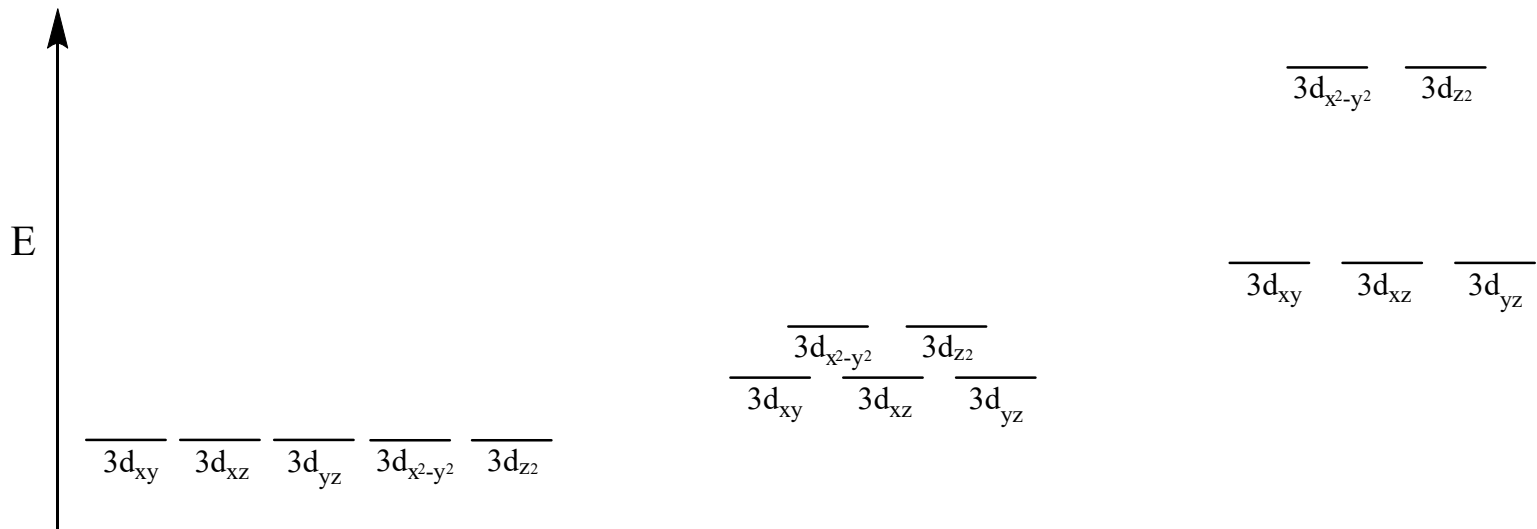
strong field

weak field



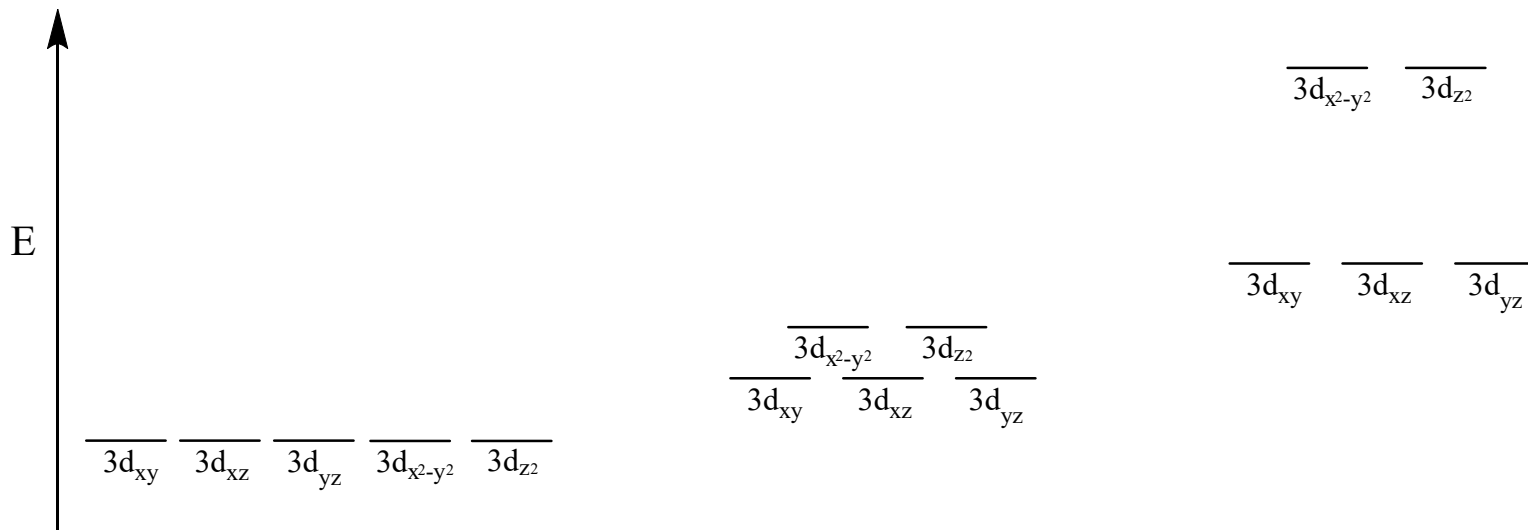
# Electronic Structure and Colour

- Strong field ligands bind tightly to the metal, so there is a strong interaction between the ligand and the  $d$  electrons of the metal, leading to a large  $\Delta_o$ .
- Weak field ligands have weaker interaction with the  $d$  electrons of the metal, leading to a small  $\Delta_o$ .



# Electronic Structure and Colour

- When  $\Delta_o$  is small (because we are using **weak field ligands**), a **high spin** distribution of electrons is observed. This maximizes the alignment of spin of the  $d$  electrons.
- When  $\Delta_o$  is large (because we are using **strong field ligands**), a **low spin** distribution of electrons is observed. This means that the lowest energy  $d$  orbitals are completely filled before any electrons are added to the higher energy orbitals in the  $d$  subshell.



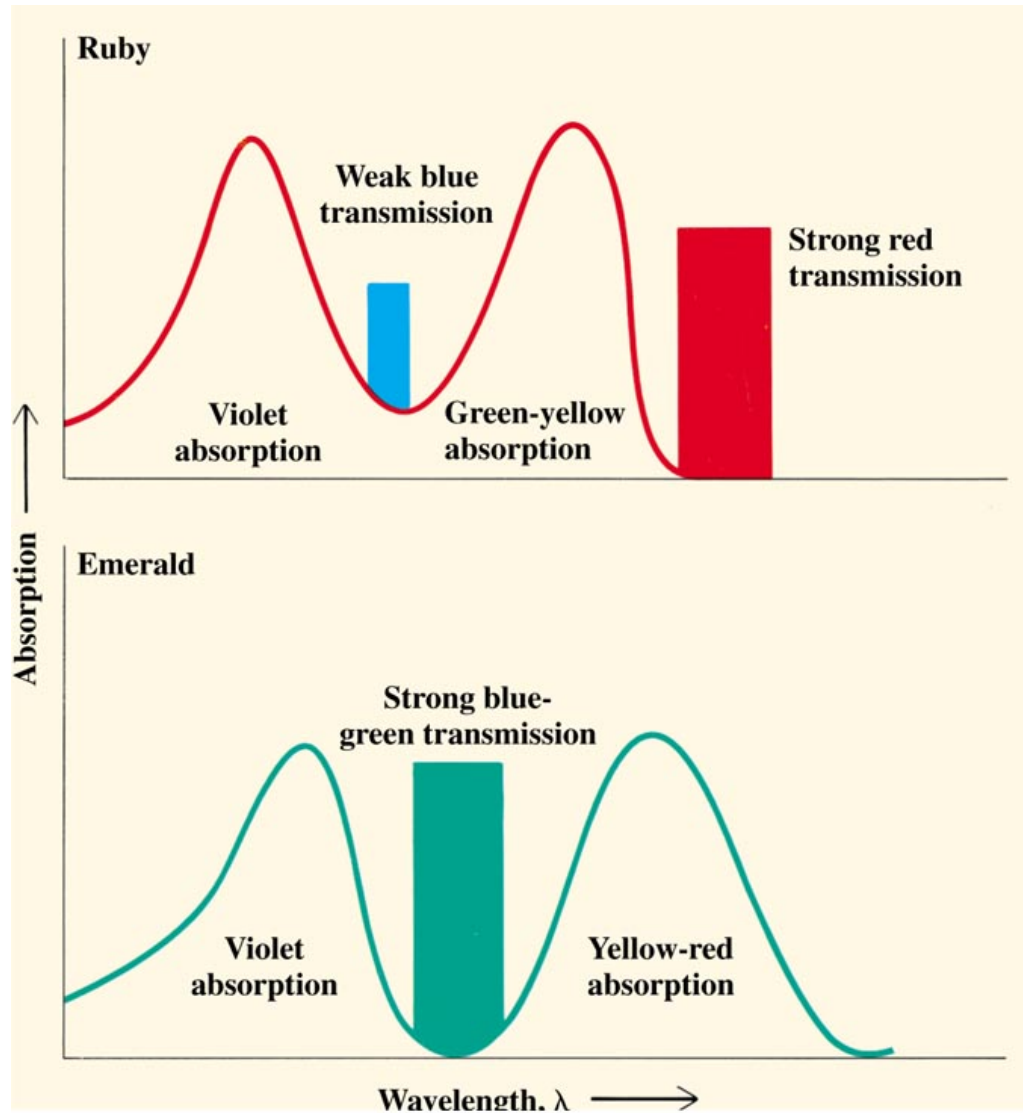


# Electronic Structure and Colour

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- How does this make for coloured solutions?
  - Recall that photons are emitted when electrons drop from a higher energy orbital to a lower energy orbital. (*see Atomic Line Spectra*) Similarly, the electrons get to the higher energy orbital by absorbing photons of light.
  - Electrons in the lower energy  $d$  orbitals can absorb photons and be excited into the higher energy  $d$  orbitals. Since  $\Delta_o$  corresponds to the energy of light in the visible region (and there is more than one way to absorb a photon), some wavelengths of visible light are absorbed. The **wavelengths** that are **not absorbed** give the **colour of solution**.
  - To see how this works, watch this cute (if very old fashioned) video: [Eureka 30 - Radiation Spectrum.mov - YouTube](#)

# Electronic Structure and Colour





# Electronic Structure and Colour

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- To absorb coloured light, the transition metal needs to have electrons in at least one of the low-energy  $d$  orbitals and an empty space in at least one of the high-energy  $d$  orbitals.
- Which of these two requirements does  $Zn^{2+}$  lack (making it colourless)?



# Electronic Structure and Colour

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- Different ligands provide different amounts of crystal field splitting.  $[Fe(OH_2)_6]^{3+}$  and  $[Fe(C_2O_4)_3]^{3-}$  are both complexes of  $Fe^{3+}$  but  $[Fe(OH_2)_6]^{3+}$  is extremely pale purple\* (frequently appearing colourless) while  $[Fe(C_2O_4)_3]^{3-}$  is green.
  - What colour of light is each compound most likely absorbing?
  - Which of these two ligands is splitting the  $d$  orbitals of  $Fe^{3+}$  more? (i.e. which complex has a larger  $\Delta_o$ )

\* The orange colour you're used to seeing for aqueous solutions of  $Fe^{3+}$  salts is due to  $[Fe(OH_2)_5OH]^{2+}$ , the conjugate base of  $[Fe(OH_2)_6]^{3+}$ . We've seen previously that complexes like  $[Fe(OH_2)_6]^{3+}$  are acidic.

# Isomers

- Even a very small change in the structure of a complex ion can change its colour drastically.
  - Draw two **different** structures for  $[CoCl_2(NH_3)_4]^+$ .
  
- One of these compounds is purple while one is green! The purple one is referred to as *cis*- $[CoCl_2(NH_3)_4]^+$  while the green one is *trans*- $[CoCl_2(NH_3)_4]^+$
- These compounds are **isomers**. They have the same molecular formula but are not the same substance. No matter how much you rotate either, you cannot superimpose them.







# Isomers

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- Draw two isomers of  $[PtCl_2(NH_3)_2]$ , a square planar complex.

The *cis* isomer is an anti-cancer drug while the *trans* isomer is toxic!



# Isomers

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- Draw two isomers of  $[CoCl_3(NH_3)_3]$ , an octahedral complex.