Lecture 7 - Crystal Field Theory for Octahedral Complexes

- What should a bonding theory explain – color, magnetism, coordination number and reactivity.

- Electrons in d-Orbitals, shapes of d-Orbitals

- Splitting of the d-Orbitals in an Octahedral Field

- Consequences of d-Orbital Splitting: Magnetism

- Consequences of d-Orbital Splitting: Color

Boats and propellers: If you have a single engine, inboard installation, the stern will pull to port (left) when you go into reverse, if you have a right–handed propeller. A left-handed propeller will pull the stern to starboard (right) when in reverse. (Note: You can tell whether your propeller is right (delta) or left-handed (lambda) by the way your boat handles in reverse.)

So a propeller is chiral but left and right handed propellers just push the water in different directions.

http://powerboat.about.com/od/seamanship/a/Boathandli_tips.htm

The Electron Configuration of Transition-Metal Ions

- The relationship between the electron configurations of transition-metal elements and their ions is complex.

  Example: Let's consider the chemistry of cobalt which forms complexes that contain either Co^{2+} or Co^{3+} ions.

  The electron configuration of a neutral cobalt atom is written as follows.

  Co: [Ar] $4s^2$ $3d^7$
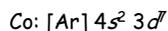
- The discussion of the relative energies of the atomic orbitals suggests that the $4s$ orbital has a lower energy than the $3d$ orbitals. Thus, we might expect cobalt to lose electrons from the higher energy $3d$ orbitals, **but this is not** what is observed. The Co^{2+} and Co^{3+} ions have the following electron configurations.

 Co^{2+}: [Ar] $3d^7$

  Co^{3+}: [Ar] $3d^6$

- In general, **electrons are removed from the valence-shell s orbitals before they are removed from valence d orbitals** when transition metals are ionized.

  A fast way of working out the d-electronic configuration of a TM ion is to subract the oxidation number of the ion away from its group number.
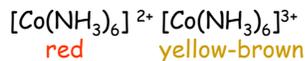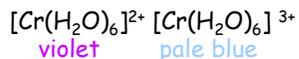
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1. What Should a Bonding Theory Explain?

i. **Colours of Transition Metal Complexes**

- Why are most transition metal complexes brightly colored, but some aren't?
- Why do the colors change as the ligand changes? As a typical example, consider three complexes of the nickel(II) ion:

$$[Ni(H_2O)_6]^{2+} \qquad [Ni(NH_3)_6]^{2+} \qquad [Ni(CN)_4]^{2-}$$
$$\text{green} \qquad\qquad \text{deep blue} \qquad \text{yellow}$$
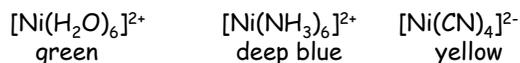
- Why do the colors change as the oxidation state of the metal changes, even for complexes of the same ligand? Here are some examples of this phenomenon:

$$[Cr(H_2O)_6]^{2+} \quad [Cr(H_2O)_6]^{3+}$$
$$\text{violet} \qquad\quad \text{pale blue}$$

$$[Co(NH_3)_6]^{2+} \quad [Co(NH_3)_6]^{3+}$$
$$\text{red} \qquad\qquad \text{yellow-brown}$$

H_2O and NH_3 are both colorless, but when they form a coordinate compound they change color.

$$[NiF_6]^{3-} \qquad [NiF_6]^{2-}$$
$$\text{violet} \qquad\quad \text{red}$$

ii. The Magnetic Moment of a Complex and the Number of Unpaired Electrons

Before we can pose our questions, we need to know:
(i) how the number of unpaired electrons can be determined, and
(ii) how it is related to the magnetic moment of a complex.

A **Gouy balance** can used to measure the mass of a sample first in the absence of a magnetic field, and then when the magnetic field is switched on. The difference in mass can be used to calculate the **magnetic susceptibility** of the sample, and from the magnetic susceptibility the **magnetic moment** can be obtained.

The **magnetic susceptibility** and thus the **magnetic moment** are due to **moving charges**. In an atom, the moving charge is an electron:
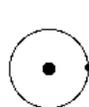
electron spinning on its axis ↑ or ↓
gives the spin magnetic moment

electron moving in its orbital creates
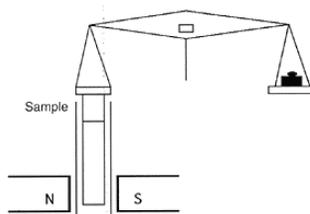an additional magnetic field, leading
to the orbital magnetic moment

$$\mu = 2.84 \sqrt{\chi_{M} T}$$

μ = magnetic moment in Bohr magnetons (B.M.)
χ_{M} = magnetic susceptibility
T = absolute temperature

The Gouy balance

Sample

N   S

- The Gouy method makes use of the interaction between unpaired electrons and a magnetic field; a diamagnetic material is repelled by a magnetic field, whereas a paramagnetic material is attracted into it.
- The compound for study is placed in a glass tube, suspended from a balance on which the weight of the sample is recorded.
- The tube is placed so that one end of the sample lies at the point of maximum magnetic flux in an electromagnetic field while the other end is at a point of low flux.
- Initially the magnet is switched off, but on applying a magnetic field, paramagnetic compounds are drawn into it by an amount that depends on their number of unpaired electrons.
- The change in weight caused by the movement of the sample into the field is recorded, and from the associated force it is possible to calculate the magnetic susceptibility of the compound.
- The effective magnetic moment can then be derived.
- Nowadays for research, we use a **SQUID** (superconducting quantum interference device) for measuring magnetic susceptibilities. It is extremely sensitive.

For the 3d transition metals, the orbital moment is not very important, and the **measured magnetic moment can be directly related to the number of unpaired electrons in the ion**. This value is called the **spin-only magnetic moment**, and its units are **Bohr Magnetons (B.M.).**

$$\text{spin-only magnetic moment } \mu_s = \sqrt{n(n+2)}$$

Number of unpaired electrons	Spin-only magnetic moment, B.M.
1	1.7
2	2.8
3	3.9
4	4.9
5	5.9

- Why do different complexes of the same metal ion in the same oxidation state have different numbers of unpaired electrons? Some examples follow for Fe^{3+}, Co^{3+}, and Ni^{2+}:

$FeCl_3.6H_2O$ μ = 5.9 B.M.; 5 unpaired electrons	$K_3[Fe(CN)_6]$ μ = 1.7 B.M.; 1 unpaired electron
$K_3[CoF_6]$ μ = 4.9 B.M.; 4 unpaired electrons	$[Co(NH_3)_6]Cl_3$ μ = 0; no unpaired electrons
$[Ni(NH_3)_6]Cl_2$ μ = 2.8 B.M.; 2 unpaired electrons	$K_2[Ni(CN)_4]$ μ = 0; no unpaired electrons

Co   [Ar] $3d^7 4s^2$
Co^{3+} [Ar] $3d^6$ ⥮ ↑ ↑ ↑ ↑

4 unshared pairs of electrons
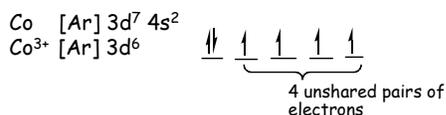
- Why are there only certain values of the number of unpaired electrons for a given metal ion? For example, complexes of Fe(II) and Co(III) can only have zero or 4 unpaired electrons, never two. Complexes of Fe(III) can only have 5 unpaired electrons or 1 unpaired electron.
- Why is it that for Ni^{2+} complexes, all octahedral complexes have 2 unpaired electrons (paramagnetic), but square planar complexes are diamagnetic (no unpaired electrons)?

### iii. Coordination Numbers and Geometries

- Why do some transition metal ions seem to have a fixed coordination number and geometry, but other metal ions are quite variable?

Examples:

Cr^{3+} practically always 6-coordinate, octahedral	
Co^{3+} practically always 6-coordinate, octahedral	Co^{2+} 6-coordinate octahedral and 4-coordinate tetrahedral complexes known
Ni^{2+} octahedral and square planar complexes common; some tetrahedral complexes known	Ni^{4+} only octahedral complexes known
Pt^{2+} practically always square planar	Pt^{4+} always octahedral

iv. Reactivity

- Why do some metal complexes undergo ligand-exchange reactions very rapidly and other similar complexes react very slowly, even when reaction is thermodynamically favorable?

- As an example, consider the reaction between hexaamminecobalt(III) ion and hydronium ion:

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \dashrightarrow [Co(H_2O)_6]^{3+} + 6NH_4^+$$
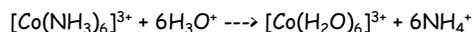
The equilibrium constant for this reaction is approximately 1×10^{25}, and yet an acidic solution of the hexamminecobalt(III) ion requires **several days before noticeable change occurs.**

- In contrast however, the corresponding copper(II) complex:

$$[Cu(NH_3)_6]^{2+} + 6H_3O+ \dashrightarrow [Cu(H_2O)_6]^{2+} + 6NH_4^+$$
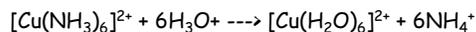
In this case, acidification of the hexamminecopper(II) complex results in practically **instantaneous reaction.**

We will find the answers to these questions as we study the simplest bonding theory for transition metal complexes, called **Crystal Field Theory.**

2. Electrons in d-Orbitals

- All d-orbitals have the **same energy** (in spite of their different shapes and/or orientations) on a **bare metal ion**. However, some d-orbitals have **different energies** from the others in a **metal complex**. This is called **d-orbital splitting**.

Consider the 5 d-orbitals in an xyz coordinate system. We will not try to give perspective drawings, rather we will rotate the coordinate system so that it is easy to draw the orbitals.
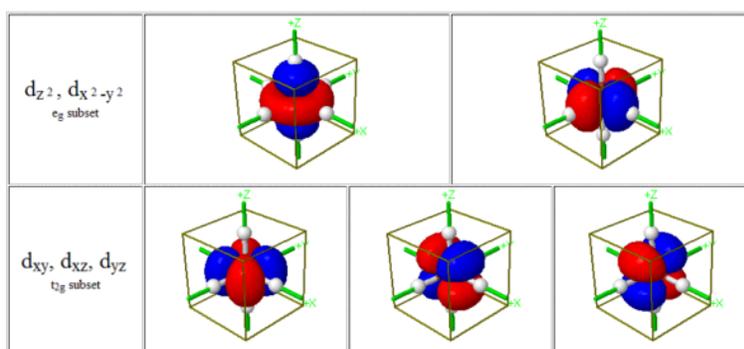

d_{xy}
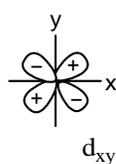
**The black and white lobes refer to the alternating sign of the wavefunction**
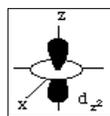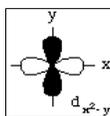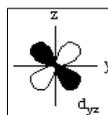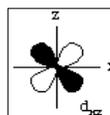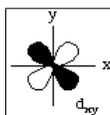
**You will need to be able to draw the d-Orbitals for the exam.**

The five d-Orbitals

$d_{z^2}, d_{x^2-y^2}$
e_g subset

d_{xy}, d_{xz}, d_{yz}
t_{2g} subset

The odd-shaped d_{z^2} orbital results because there are six solutions to the **Schroedinger equation** for the angular momentum quantum number **l** (the d-orbitals), but only **5 solutions are independent**. The combination of two orbitals produces the unique d_{z^2} orbital:
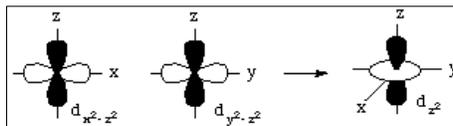
3. Splitting of the d–Orbitals in an Octahedral Field
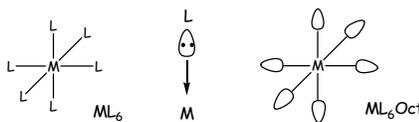
Coulomb's Law – Energy of interaction between two charges q_1 q_2 is proportional to the product of charges divided by the distance between there centres.


E is proportional to q_1q_2/r
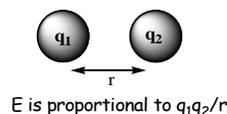
Crystal Field Theory - Assumptions

- Focuses on the d-orbitals of the metal.
- Assumes ionic bonding between the metal and the ligand instead of covalent bonding
- i.e ionic bonding due to electrostatic interactions
- Electrostatic interactions in a complex between +ve metal ion and –ve charges of ligand - treats ligands as point (negative) charges. If the ligand is negatively charged: ion-ion interaction. If the ligand is neutral : ion-dipole interaction.
- Provides stability and holds complex together.
- Repulsion between the lone pair of electrons on the ligand and the electrons in the d-orbital of the metal ion
- This influences the d-orbital energies

Octahedral Complex

1) Ligands approach metal ion along X, Y, Z axes

2) e⁻'s in d-orbitals are repulsed by - charges of ligands and experience increases in potential energy. Degree of electrostatic repulsion experienced depends on orientation of the d-orbitals. d-orbitals with lobes directed at the ligands experience more repulsion.
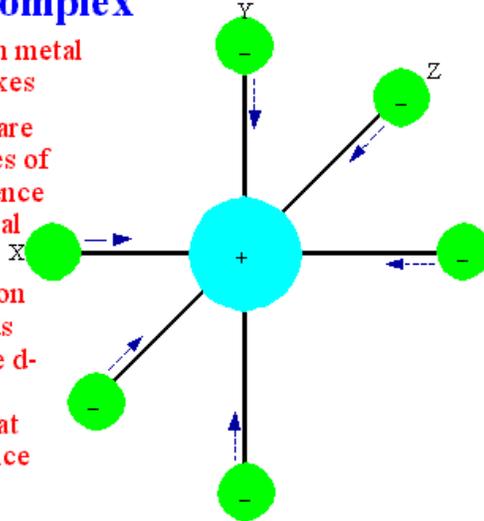

Lets look in more detail to see what happens to the energies of electrons in the d-orbitals as six ligands approach the bare metal ion:

ligand lone pair of electrons
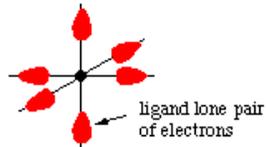
If we compare the d_{xy} and the d_{x2-y2}, we can see that there is a significant difference in the repulsion energy as ligand lone pairs approach d-orbitals containing electrons.
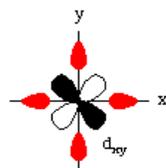

Electrons in the d_{xy} orbital are concentrated in the space between the incoming ligands.
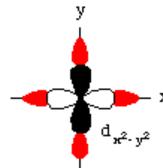
Electrons in the d_{x2-y2} orbital point straight at the incoming ligands.

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- Now, d_{xz} and d_{yz} behave the same as d_{xy} in an octahedral field, and d_{z2} behaves the same as d_{x2-y2}. This means that the d-orbitals **divide into two groups**, **one lower energy than the other**, as shown in the following diagram.

d-orbital energies in an octahedral complex
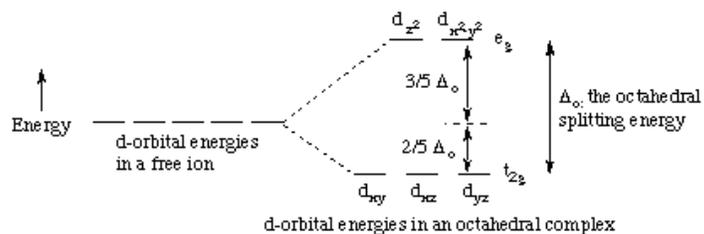
The d_{xy}, d_{xz}, and d_{yz} orbitals are collectively called the t_{2g} orbitals, whereas the d_{z2} and d_{x2-y2} orbitals are called the e_g orbitals. The octahedral splitting energy is the energy difference between the t_{2g} and e_g orbitals. In an octahedral field, the t_{2g} orbitals are stabilized by 2/5 Δ_o, and the e_g orbitals are destabilized by 3/5 Δ_o.

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4. Consequences of d-Orbital Splitting: Magnetism

- Let's consider the complexes $[Fe(H_2O)_6]Cl_3$ (mu = 5.9 B.M.; 5 unpaired electrons) and $K_3[Fe(CN)_6]$ (μ = 1.7 B.M.; 1 unpaired electron).
- The free Fe^{3+} ion is a d^5 ion. The two complexes are 6-coordinate and octahedral. First let's look at the d-orbital diagram for $[Fe(H_2O)_6]^{3+}$:
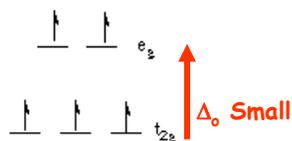
d-orbital diagram for $[Fe(H_2O)_6]^{3+}$
HIGH SPIN

The first three electrons go into t_{2g} orbitals unpaired. The 4th and 5th electrons must choose whether to pair up with electrons already in t_{2g} (which costs energy) or to go into higher energy e_g orbitals (which also costs energy). In this case, the splitting energy is less than the pairing energy so the 4th and 5th electrons go into the e_g orbitals.

- Now let's consider the $[Fe(CN)_6]^{3-}$ ion. Again we have five d-electrons. However, there is only one unpaired electron, so the 4th and 5th electrons must pair with electrons already in t_{2g} orbitals.

- This happens because the octahedral splitting energy is much greater in the hexacyanoferrate(III) ion than it is in the hexaaquoiron(III) ion. That is, the **cyanide ligand** causes a much **greater d-orbital splitting than water** does.

— — e_g

Δ_o **large**

↿⇂ ↿⇂ ↿ t_{2g}

$\Delta_o > P$
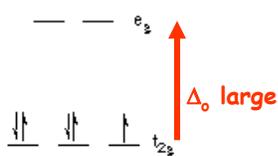
d-orbital diagram
for $[Fe(CN)_6]^{3-}$
LOW SPIN

The first three electrons go into t_{2g} orbitals as before. Now, however, the splitting energy is much greater so it is less energetically costly for electrons to pair up in the t_{2g} orbitals than to go into the e_g orbitals.

- $[Fe(CN)_6]^{3-}$ is called a **low-spin complex** because it has the lowest number of unpaired spins (electrons) possible for an octahedral iron(III) complex.

- $[Fe(H_2O)_6]^{3+}$ is called a **high-spin complex** because it has the highest number of unpaired spins for an octahedral iron(III) complex.

- The terms "high-spin" and "low-spin" do not refer to specific numbers of unpaired electrons, but rather to different electron configurations in d-orbital diagrams that result from the pairing energy being greater than or less than the splitting energy.

5. Consequences of d-Orbital Splitting: Color

■ Color in transition metal complexes is due to an electron being excited from one d-orbital to a higher-energy d-orbital.

■ In the case of octahedral complexes, an electron is moved from a t_{2g} orbital to an e_g orbital.

■ The energy difference for the first transition series generally falls in the visible region. Absorption of one color in the visible spectrum results in the ion having the **complementary color**. The amount of d-orbital splitting depends on the ligands. thus different ligands have different splitting energies, and different colors result.

Δ_o varies with the ligand, thus absorption energy and colour also vary with the ligand
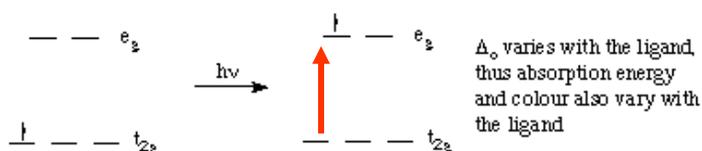

The color wheel

■ This color wheel demonstrates which color a compound will appear if it only has one absorption in the visible spectrum. For example, if the compound absorbs red light, it will appear green.

■ λ __absorbed__ **versus colour** __observed__
400nm Violet absorbed, Green-yellow observed (λ 560nm)
450nm Blue absorbed, Yellow observed (λ 600nm)
490nm Blue-green absorbed, Red observed (λ 620nm)
570nm Yellow-green absorbed, Violet observed (λ 410nm)
580nm Yellow absorbed, Dark blue observed (λ 430nm)
600nm Orange absorbed, Blue observed (λ 450nm)
650nm Red absorbed, Green observed (λ 520nm)

Illustration of Crystal Field Theory

$[Ti(H_2O)_6]^{3+}$ is a d^1 complex and the electron occupies the lowest energy orbital available, i.e. one of the three degenerate **t2g orbitals**. The **purple color** is the result of the absorption of light which results in the promotion of this **t2g** electron into the **eg** level.

t2g1eg0 -> t2g0eg1
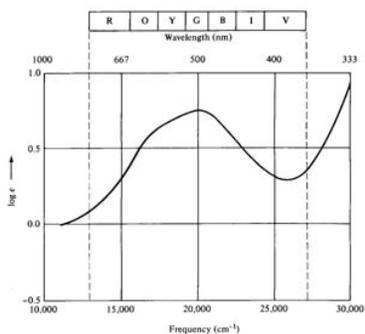
The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm^{-1} which corresponds to Δ_o 243 kJ/mol.

(1000 cm-1 = 11.96 kJ/mol , 2.86 kcal/mol or 0.124 eV.)

Typical Δ_o values are of the same order of magnitude as the energy of a chemical bond.