The Chemistry of d-block element (Transition Element)

The d-orbitals are partially filled, they are called transition element

Why are they called d-block? because theyve outer orbital in the d-orbital

Introduction:

~~The followin~~ Course Outline

① Position of d-block in periodic table, electronic
(ii) Configuration
(ii) Trends in properties of these elements wrt to size of atoms and ions reactivity, catalytic activity, Oxidation state, colour, complex formation ability, magnetic properties, ~~non stoichiometry~~
(iii) Non stoichiometry, melting and boiling point

Introduction

In the periodic table, the d- block consists of the element of group 3-12.

The d- orbital ~~of~~ of the d- block element in 4th periods are filled. The three Series (Triad) of the transition metals are; the 3d series from Scadium to Zinc, 4d Series from ~~[illegible] Yttrium~~ to Cadium, the 5d Series from La - Hg
(Yttrium)
Lanthanum

The 4th 6d series, begins ~~from begins from~~ Actinium and incomplete till now.

Position of d-block in periodic Table

The element ~~pos~~ with incompletely d-orbitals or subshells in their ground state or most stable oxidation state are called ~~the~~ d- block element.

They are additionally named as transition element. The Partially filled subshells incoporate the (n-1)d orbitals

All the d-block element have a simillar number of electron in the farthest shell. Consequently, because they have similar number no. of electron in the farthest shell, the display comparable chemical properties

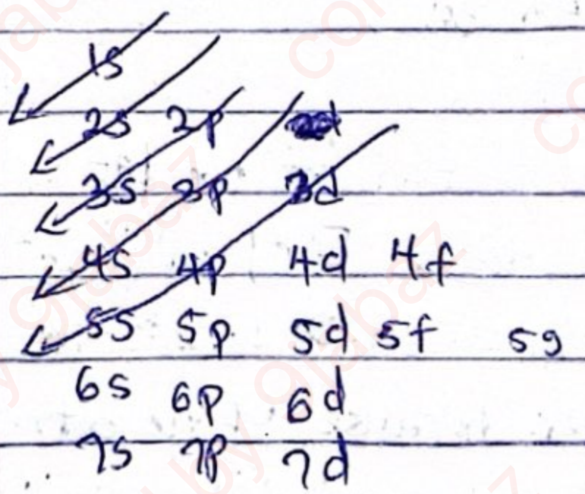
The transition element are set amongst s and p block Shells.

Electronic Configuration

The external electronic configuration remains consistent, so electron is added to the penultimate shell till the d subshell achieves its

There are three series of elements, relying upon the (n-1)d orbitals that is being filled. the orbitals are dipatched altogether of their expanding energy in which case, an orbital of lower energy is filled first (Afbau principle).

Therefore, 4s orbitals with lesser energy is filled first to its full degree, then the 3d orbitals with higher energy is filled.



$4s < 3d$

Triad $1s < 2s < 2p < 3s < 3p < 4s < 3d$

The precisely half filled and totally filled orbital are extraordinary stable ($Cr; 4s^1 3d^5$ and $Cu; 4s^1 3d^{10}$)

$[1s^2 2s^2 2p^6 3s^2 3p^6] = Ar$

$_{21}Sc = [Ar] 4s^2 3d^1$
$_{22}Ti = [Ar] 4s^2 3d^2$
$_{23}V = [Ar] 4s^2 3d^3$
$_{24}Cr = [Ar] 4s^1 3d^5$
$_{25}Mn = [Ar] 4s^2 3d^5$ or $[Ar] 3d^5 4s^2$
$_{26}Fe = [Ar] 4s^2 3d^6$
$_{27}Co = [Ar] 4s^2 3d^7$
$_{28}Ni = [Ar] 4s^2 3d^8$
$_{29}Cu = [Ar] 4s^1 3d^{10}$
$_{30}Zn = [Ar] 4s^2 3d^{10}$

The electronic configuration of the 1st series can be represented as ~~1s~~ $[Ar] 3d^{1-10} 4s^2$ except ~~The electronic configuration of the 1st ser~~ Chromium and copper because of the extra stability due to half filled and completely filled orbital.

$_{25}Mn = [Ar]\,3d^5\,4s^2$

$Mn^{2+} = [Ar]\,3d^5$, $Mn^{3+} = [Ar]\,3d^4$; $Mn^{4+} = [Ar]\,3d^3$

$Mn^{5+} = [Ar]\,3d^2$; $Mn^{6+} = [Ar]\,3d^1$; $Mn^{7+} = [Ar]\,3d^0$

The electronic configuration of the 2nd series, can be represented; $[Kr]\,4d^{1-10}\,5s^2$

$3d = [Ar]\,3d^{1-10}\,4s^2$

$4d = [Kr]\,4d^{1-10}\,4s^2$

$5d = [Xe]\,5d^{1-10}\,6s^2$

The electronic configuration of the 3rd series can be represented as; $[Xe]\,5d^{1-10}\,6s^2$

Oxidation states

All the elements aside from the first and the last individual from d-series, display variable oxidation states. the indicate variable valency in their compound. Some fundamental Oxidation conditions the primary, second, and third transition element are listed below

Atomic Number	Elements	Outer Electronic Configuration	Oxidation state
21	Sc	$[Ar]\ 3d^1 4s^2$	+2, +3
22	Ti	$[Ar]\ 3d^2 4s^2$	+2, +3, +4
23	V	$[Ar]\ 3d^3 4s^2$	+2, +3, +4, +5
24	Cr	$[Ar]\ 3d^5 4s^1$	+2, +3, +4, +5, +
25	Mn	$[Ar]\ 3d^5 4s^2$	+2, +3, +4, +5, +6,
26	Fe	$[Ar]\ 3d^6 4s^2$	+2, +3, +4, +5, +6
27	Co	$[Ar]\ 3d^7 4s^2$	+2, +3, +4, +5
28	Ni	$[Ar]\ 3d^8 4s^2$	+2, +3, +4
29	Cu	$[Ar]\ 3d^{10} 4s^1$	+2, +3
30	Zn	$[Ar]\ 3d^{10} 4s^2$	+2

Size of Atoms and Ions

Generally, the sizes of atoms/ions of the element go on decreasing from left to right across the rows in the transition series. Thus, the extra nuclear charge increases as atomic number increases. The extra electrons are added into the Same d-shell ~~or~~ orbitals, and the d-orbital electrons are having poor shielding effect.

Therefore, the size of atoms and ions goes on increasing from the first transition series element in the group of transition elements.

The atomic and ionic size goes on increasing from top to bottom due to addition of new shell everytime.

The electrons fill into the antipenultimate ~~ff~~ shell of Lanthanide which causes steady decrease in size called Lanthanide contraction: It is only applicable to Scadium group

* What exactly leads to variable oxidation state?

Causes of Variable Oxidation State

The valence electron of the transition elements are (n-1)d and ns orbitals which have a little distinction in energies. Both energy levels are utilized as part of bond development

They demostrate the +2 oxidation state because of the two electrons in ns orbitals, while the electrons in the (n-1)d orbitals remains unaffected

The higher oxidation state from +3 to +7 is because of the utilization of all the ns orbitals and d-electrons in the transition series of the element. In the excited state, the (n-1)d electrons get to be bonding and give the variable state. Subsequently the variable oxidation state is because of the support of both ns and (n-1)d orbitals in bonding

Important Features of Oxidation State of Transition Metals

The most basic oxidation state of transition metals is +2, with the exception of Scadium ~~and Zinc~~ because of the loss of two ns electron

This demostrates d-orbitals are more stable than s orbital after Scadium. The ionic bonds are bi and large framed as +2 and +3 state while the covalent bond are shaped in higher oxidation state.

Covalent bonds are framed by the sharing of d-electrons for instance, the Permaganate particle (MnO_4^-)

All bonds are shaped among Mn and O

~~The variable oxidation state is because of the support of both ns an (n-1)d orbitals in bond~~

The most not worthy oxidation state increment with expanding nuclear number of elements achieves greatest in the center and after that begins diminishing.

1. What are complex

For instance, Fe demostrates the normal oxidation state condition of +2 and +3, however, Ruthenium and Osmium in a similar group shape compounds in the +4, +6 and +8 oxidation state

The element at the beginning of the series displaces less oxidation number because of having less number of electron to lose or contribute

The elements in the midst of the series, demostrate the best number of oxidation

For instance Mn demostrate all the oxidation state from +2 to +7. The most elevated oxidation state appeared by any transition metal is 8, and this demostrated by Ruthenium and Osmium

4d series under Fe

5d series under Ru

Complex Formation Ability

~~Formation of~~ Formation of Complex Compounds

The cations of transition metals have great tendency to form complexes with several molecules or ions called ligands

The bonds involved in the formation of complexes are coordinate/dative and therefore, the complexes are called coordinate complexes, sometimes coordination compounds.

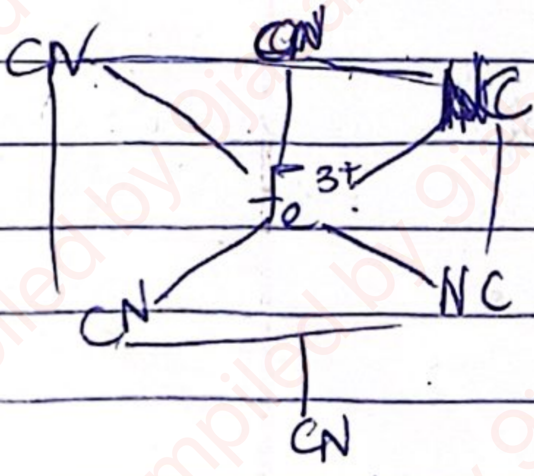
FeC

~~$[Fe(H_2O)_6]^{3-}$~~

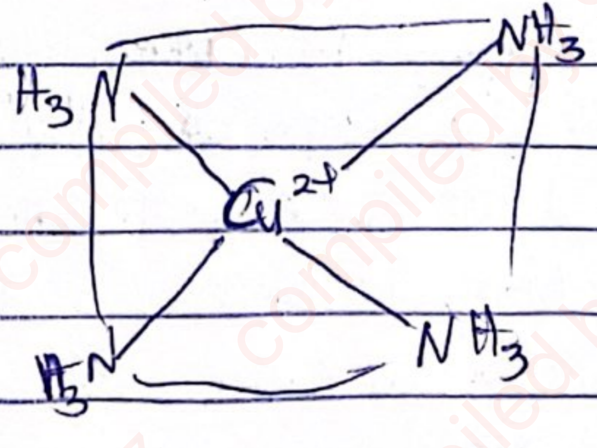
The structure of this complex ion may be linear, square planar, tetrahedral and octahedral depending upon the nature of hybridization of metal ions. The highly electronegative and basic ligand alike fluoride ion, chloride ion can form complexes with transition metals even though there are in higher oxidation state due to the presence of small, highly charged or neutral ligands with lone pairs of electron that can form strong sigma bonds by donating a lone pair of electrons.

In a transition series, the stability of complexes increases with increase in atomic number, hence, the transition metal atom reveals multiple oxidation state. So, the higher valant ion, forms more stable complexes

$[Fe(CN)_6]^{3-}$



Octahedral

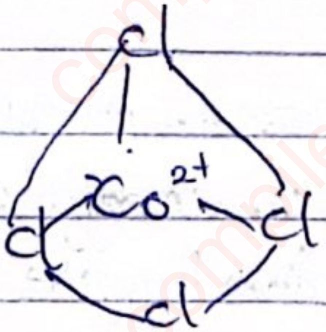


~~tetrahedral~~

d^5 and d^{10} are more willing

* discuss complex formation in transition metals

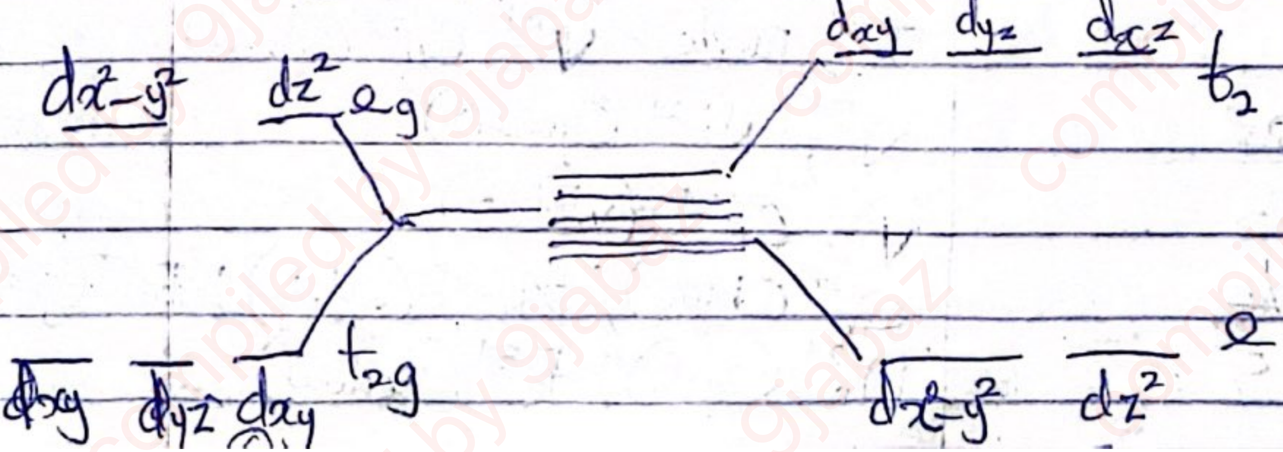
$[Ag(NH_3)_2]^+$
↓
linear



They are found to form complexes due to the following factors;
(i) Small size and high charge of metal ions
(ii) Availability of vacant low d-orbitals to accept lone pairs of electrons donated by other group of ligand
(iii) Availability of variable oxidation state and ability to form pi bonds, i.e multiple bond

Colour Formation

Most d-metal compounds are coloured in their solid or liquid states. In the case of transition metal ions under the influence of ligands, the degeneracy of the 5d orbital is lost and they seperate into two distinct energy levels.



In the transition metal compounds, the electrons can be advanced from one energy level to another energy level in a similar d- subshe
This is referred to as d-d transition. By this property, transition elements display colour

Now, when white light is incident on a transition metal ion the electron in the lower energy d-orbital set absorbs certain radiations and gets promoted to a d-orbital set of higher energy.

The transmitted radiations devoid of the absorbed radiation is the complementary colour of the absorbed light. This complementar colour is the colour of the substance

The Oxidation states of Metals and Their Colour

Number of unpaired electron	Oxidation states/ colour of the compound
0	Sc^{3+}, Ti^{4+} V^{5+} Cu^{+}, Zn^{2+} (Colourless)
1	Ti^{3+}, Purple; V^{4+}, Cu^{2+} (blue)
2	V^{3+}, Ni^{2+} (green)
3	V^{2+}, Cr^{3+} (violet)
4	Cr^{2+} (blue); Mn^{3+} (violet); Fe^{2+} (green)
5	Mn^{2+} (pink); Fe^{3+} (yellow)

Magnetic Properties

The magnetic properties of transition elements, or d-block elements are dictated by the number of unpaired electrons.

** There are however some compounds that are diamagnetic, in that they are repelled by the magnetic line of force; when there are no unpaired electron. **

When we have unpaired eletrons, it is paramagnetic.

There are two fundamental sources of substances

① paramagnetic substances: The paramagnetic character imagines in view of the nearness of unpaired electrons. Substances that are paramagnetic are pulled in by the magnetic field

② Diamagnetic Substances: Emerges as a result of the non appearance of unpaired electron. In other words, electrons are paired. These substance are repelled by the magnetic field either completely filled d-orbitals or d^0 are all diamagnetic

A large portions of the transition elements and their compounds are paramagnetic and are pulled in by the magnetic field. The More prominent, the number of electron in the substances, the more noteworthy is the paramagnetic character and the magnetic character of the substance is expressed as magnetic moment

Notwithstanding paramagnetic and diamagnetic substances, there are a couple of substance. For example, fe, Co and Ni is exceedingly magnetic in contrast with other metals. These substances are known as ferro magnetic substances

Density

The nuclear volume of transition element is much lower than those of S and p block element. This is a result of the filling of the (n-1)d orbitals that cause an expansion in the atomic charge and pulls the electron internally. This clearly leads to decrease in nuclear volume with the decline in nuclear volume, the nuclear thickness of these elements increases.

Osmium consist of the highest density. In a given transition series, the thickness increment in moving over the period achieve the greatest value at group 18. The thickness increases as we move down the group. The nuclear size of elements of the second and third transition series are approximately the same. Yet, their nuclear weights increment to almost double and the density of elements of third transition series are by and large twice corresponding second transition series.

Other factors that affect variable colour

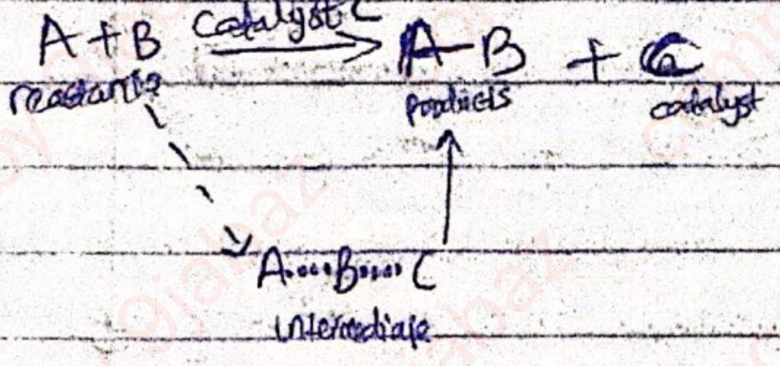
① Intraligand charge transfer e.g $n-\pi^*$, $\pi-\pi^*$

② Ligand to metal charge transfer (LMCT)

③ Metal to ligand charge transfer (MLCT).

Catalytic Analysis

The rate of the chemical reaction increases by decrease in energy of activation of the reactant. This decrease is caused by the catalyst by altering the pathway of reaction. For instance;



Intermediate is of lower energy transition state

Bonds are formed between reactant molecules and atoms on the surface of the catalyst (The first row transition metals uses 3d and 4s electron for bonding), 4d and 5s (second row), 5d and 6s (3rd row)

The results in the formation of reaction intermediate which providing the activation energy and therefore, increases the rate of the reaction.

The reaction intermediate decompose to form the product and regenerate catalyst. Many transition metals are used as catalyst for a number of reaction. For example, Iron in Haber process, Vanadium in contact process of sulphuric acid and Nickel in hydrogen atom.

The catalytic activity of these transition elements are due to their variable oxidation states. The transition metals can absorb and re-emit quite range of energies. Thus, providing necessary energy of activation

Consider a reaction between Iodide and Thiosulphate

$$I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + SO_4^{2-}$$

The above reaction occurs in two stages;

$$2I^- + Fe^{3+} \longrightarrow Fe^{2+} + I_2 \;\text{.......}\; (i)$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2} \;\text{.....}\; (ii)$$

Many transition elements display catalytic activity eg metalloenzymes are biological catalysts that require metal ions of their activity

Nitrogenase enzyme contains Iron and Molybdenium (Mo)

Haemoglobin contains Fe^{2+}

Ribo nucleotide reductase consits of cobalt

Stabilization of Oxidation State

Stability is relative term The Stability of an individual oxidation State for d-block metals depends on the following factors;

① Enthalpy of hydration or Solvation: The higher the hydration energy/enthalpy, the higher the Stability

② Electronic Configuration; Half/fully filled electronic configurations leads to higher stability

③ Ligand filled environment and Crystal filled splitting energy: The higher the Crystal field spliting energy, the higher the stability

④ Size of d-orbitals; Larger size d-orbitals leads to higher metal ligand interaction, thereby leading to higher crystal field splitting energy and consequently higher stability

⑤ Metal-ligand bond energy and effect of π-back bonding; The higher the bond energy, the higher the stability.

⑥ π-Acid Ligands eg CO, bipyridine, nitrogen monoxide and Cyanide stabilize lower oxidation states by withdrawing electron density from the metal.

⑦ Highly electromagnetic element (oxygen and fluorine) can stabilize the higher oxidation states between oxygen and fluorine, oxygen can form multiple bonds with metal cations and stabilize the higher oxidation state better than fluorine

Generally, the d-block elements have greater tendency to form coloured complexes. The colour of these complexes may arise due to two reasons:

(i) The d-d transition

(ii) The Charge transfer transition

In the presence of ligand field. The d- orbitals of the metals get splitted according to crystal field theory. The extent of the splitting Δ or 10dq depends upon the nature of ligand and the metals, and as well as the coordination number of the metals.

Transition between these two orbitals is called "d-d transition"

The following are the transition....

Coordination number 6 : $t_{2g} \longrightarrow e_g$ Octahedral

" " 4 : $e \longrightarrow t_2$ tetrahedral

" " 4 square planar : $d_{xz} = d_{yz} \longrightarrow d_{z^2}$

$d_{xz} = d_{yz} \rightarrow d_{xy}$

$d_{xz} = d_{yz} \rightarrow d_{x^2-y^2}$

↓

d-d transition

Charge Transfer Transition

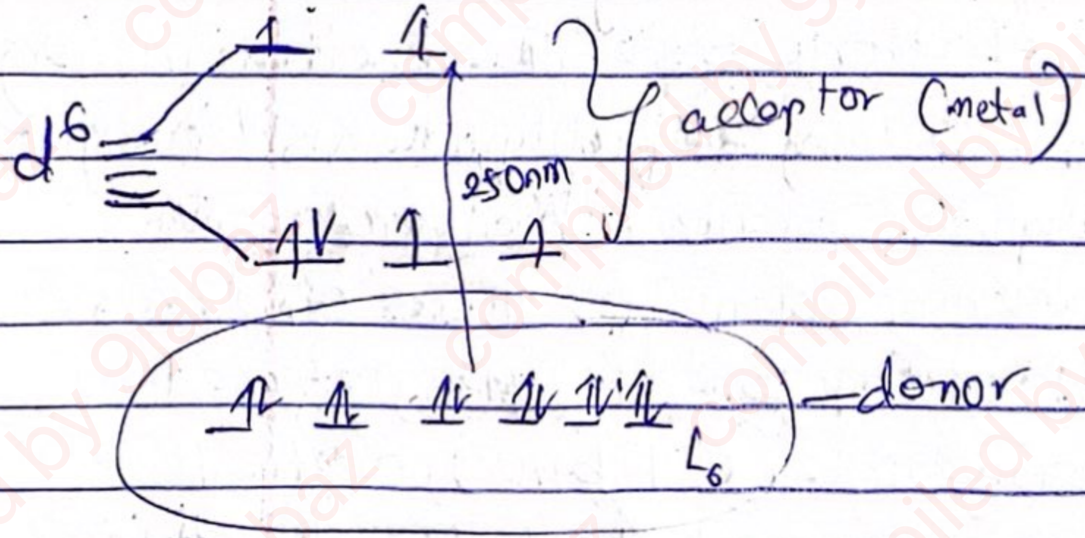
A charge transfer complex (CT complex) or electron donor acceptor complex is an association of two or more molecules, or of different parts of one large molecule in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. the source from which the charge is transferred is called the electron donor and the recieving specie is called the electron acceptor.

Many such complexes can undergo an electronic transition into an excited electronic state. The excitation energy of this transition occurs very frequently in the visible region of the electromagnetic spectrum which produces the characteristic intense colour for these complexes. This optical absorption band are often reffered to as charge transfer band (CT band). Optical spectroscopy is a powerful tool for characterising charge transfer band.

Charge transfer occurs often in inorganic ligand chemistry involving metals. Depending on the direction of charge transfer, they are classified as either ligand-metal (LMCT) or metal-ligand (MLCT) charge transfer.

Ligand- Metal Charge Transfer (LMCT)

Ligand-Metal charge complexes (LMCT) arise from transfer of electrons from molecular orbitals with ligand like character to those with metal-like character. This type of transfer is predominant if complexes have ligands with relatively high energy lone pairs (example, sulphur or selenium) or if the metal has low-lying empty orbital, many such complexes have metals in high oxidation state, even D_0. These conditions implies that the acceptor level is available and low in energy



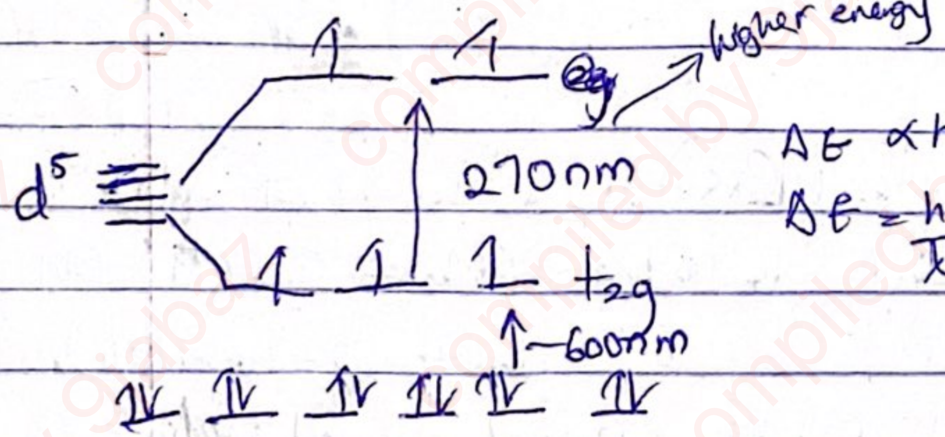
Consider a d-series ~~of~~ octahedral complex such as $[CoBr_6]^{3-}$ (hexabromocobaltate (III) ion) whose t_{2g} orbital as fixed.

$_{27}Co = [Ar]\ 3d^7\ 4s^2$

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

As a conseequence, and intense absorption is observed around 250nm corresponding to a transition from ligand sigma molecular orbital to the empty eg molecular orbital

However, in hexabromocobaltate (III) ion $[CoBr_6]^{2-}$ that is a d^5 complex, two absorption, one near 600nm and another near 270nm are observed. ~~and another near 27~~ This is because two transitions are possible, one to t_{2g} that can now accomodate 1, 1 electron, and another to eg. The 600nm band corresponds to transition to the t_{2g} transition band and the 270nm to the eg molecular orbital of the cobalt.



$\Delta E \propto h\nu$

$\Delta E = \frac{hc}{\lambda}$

Charge transfer band may also arrive from transfer of electrons from non bonding orbital from the ligand to the eg molecular orbitals. The energy of transitions correlates with the order of the electrochemical series. The metal ions that are most easily reduced corresponds to the lowest energy transition. For instance,

+7 $MnO_4^- < TcO_4^- < ReO_4^-$

+6 $CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$

+5 $VO_4^{3-} < NbO_4^{3-} < TaO_4^{3-}$

The energy

Example includes ① permanganate ion having tetrahedral geometry is intensely purple due to strong absorption involving charge transfer from molecular orbital derived primarily from fill oxygen p orbital to empty molecular orbital derived from Mn (VII)

(ii) Cadium Sulphide (CdS): The colour of active pigment, Cadium yellow is due to transition of Cd (II) ion 5s orbital to sulphide ion, π - orbital (p-orbital)

(iii) Mecury Sulphide is red 6s orbital to sulphide ion π -transition.

(iv) Iron (III) oxide red or yellow, due to transition from 3d to oxide π -orbital

Metal-Ligand Charge Transfer Complexes

This arise from transfer of electrons from molecular orbitals with metal-like character with those with ligand like character.

This is most commonly observed in complexes with Ligands having low line π^* orbital especially aromatic ligands. The transitions occur at Low energy if the metal ion has a low oxidation number. For its d-orbitals will be relatively high in energy. Examples of such ligands taking part in metal-ligand charge transfer include; CO, CN^-, bipyridine, phenanthroline.

Question

Comment on the Magnetic Property & Colour

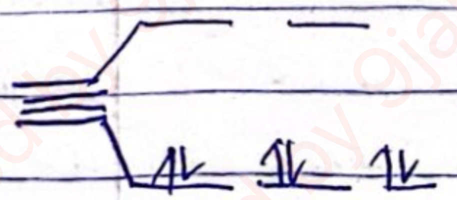
$[Co(CN)_6]^{3-}$ hexacyanate cobalt (III)

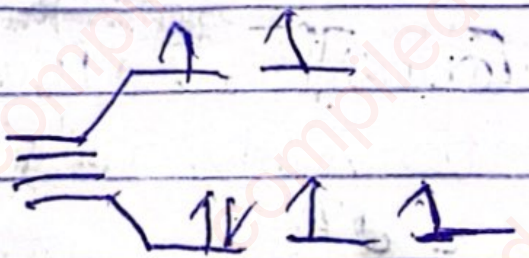
$[Co(Cl)_6]^{3-}$

(find the oxidation number of the metal

$Co = [Ar]\,3d^7 4s^2$

$Co^{3+} = d^6$





Paramagnetic

$[Co(CN)_6]^{3-}$

Diamagnetic

no magnetic moment

$[Co(Cl)_6]^{3-}$

⇅ ⇅ ⇅ ⇅ ⇅ ⇅

For $[Co(Cl)_6]^{3-}$, magnetic moment is

$\mu = \sqrt{n(n+2)}$ n = number of unpaired electrons

$\mu = \sqrt{4(4+2)}$

$\mu = \sqrt{24} = 4.96 BM$

Steps:

① Work out the oxidation number of the metal

② Deduce the number of electron in the d orbital

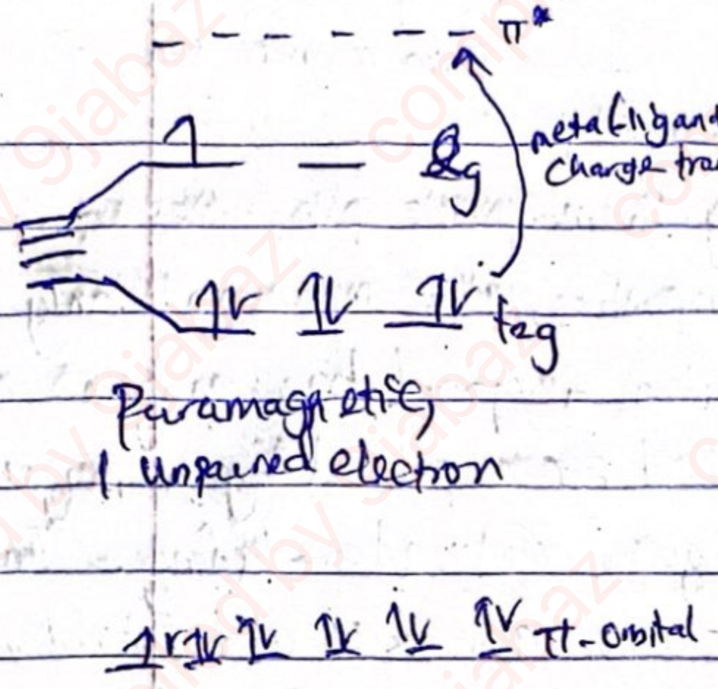
③ Determine whether the ligand is strong or weak. If it is a strong ligand, it forces the the electron to pair, if it is a weak ligand, it simply obey Hund's rule, by singly filling before pairing.

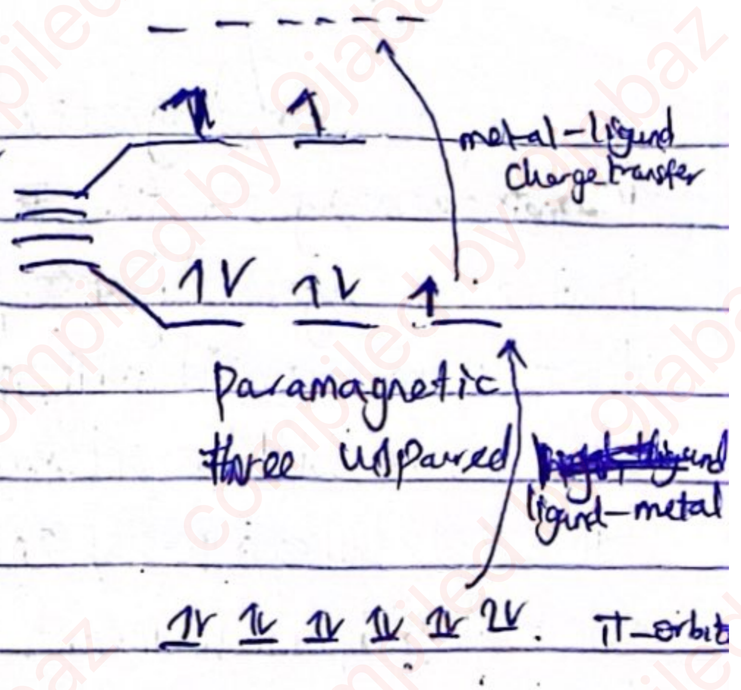
④ Draw the Crystal field splitting diagram, thereafter fill the diagram with electrons according to the strength

$[Co(CN)_6]^{4-}$ & $[Co(Cl)_6]^{4-}$

oxidation number is +7

$Co^{2+} = d7$





Assignment

$[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$

comment on the magnetic property. colour.

State the similarities and differences of 3d and higher d-block elements

13/11/25

* If it attracted, para
* if it repels, di
* can form magnetic bar, ferro

Magnotochemistry

Magnetochemistry is the study of magnetic properties of materials, by magnetic properties, we mean not only that a material will make a good bar magnet but whether it will be attracted or repelled by a magnet. This includes synthesis, analysis, and understading. This short description is meant to give a basic understanding before going into more complex treatment.

Magnetism arises from moving charges such as an electric current in a coil of wire. In a material which does not have any current present, there are still magnetic intera
Atoms are made of charged particles (proton and electro which are moving constantly. The processes which creates magnetic ~~properties are~~ fields in an atom are;

① Nuclear spin: Some nuclear such as a hydrogen atom have a net spin which creates a magnetic field

② Electron spin: An electron has two intrinsic spin states (similar to a top spining) which we call up and down

③ Electron orbital motion: This is a magnetic field due to the electron moving around the nucleus. Each of this magnetic fields interacts with one another and with external magnetic fields. However, some of these interactions are strong and others are negligible

Measurement of interactions with nuclear spin are used to analyze compounds in nuclear magnetic resonance (NMR) and ~~e~~ electron spin resonance (ESR) spectroscop

In most other situations, interactions with nuclear spin is a very minor effect. Interactions between the intrinsic spin of one electron and the intrinsic spin of another ~~spin~~ electron are strongest for very heavy elements such as the Actinite this is called spin-spin coupling

For these elements, the coupling can shift the electron orbital energy level.

The interaction between an electron intrinsic spin and its orbital motion is called spin orbit coupling

Spin orbit coupling has a significan effect on the energy levels of the orbital in many inorganic compounds.

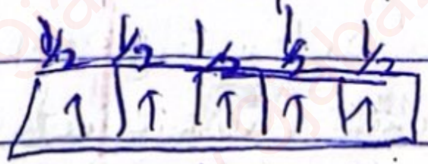
Macroscopic effects such as the attraction of a piece of iron to a bar magnet are primarily due to the number of unpaired electron in the compounds and their arrangemen

The various possible cases are called magnetic states of matter

~~Magnetic Sta~~

Magnetic States of Matter

① Diamagnetic: A diamagnetic compound has all of electron spin paired, given a net spin of zero



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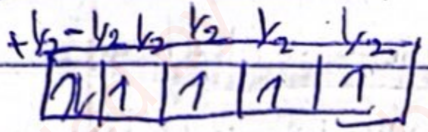

= net = $4/2 = 2$

Diamagnetic compounds are weakly repelled by a magnet

② Paramagnetic: A paramagnetic compound will have some electrons with unpaired spins. Paramagnetic compound a attracted by a magnet

③ Ferromagnetic: There are unpaired electron spin whi are held in alignment by a process known as ferromagn coupling. Ferromagnetic compounds such as Fe, Co, Ni are strongly attracted to magnets.

④ Ferrimagnet: Have unpaired electron spins which are held in a pattern with some up and some down, this is known as ferrimagnetic coupling

In a ferrimagnetic compounds, there are more spins held in one direction, and so the compound is attracted to a magnet,

⑤ Antiferromagnetic: The unpaired electrons are held in an alignment with an equal number of spins in each direction, the substance in strongly repelled by a magnet. This is referred to as antiferromagnet.

⑥ Superconductor: Superconductors are repelled by a magnetic field because the magnetic field is excluded from passing through them. This property of superconducto Called the meissner effect is used to test the presence of a super conducting state.

The underlying theory of how superconductivity arising is still a matter of serious research.

Interaction With External Magnetic Field

A magnetic field H ~~Which~~ is a vector quantity, since it has both direction and magnitude, it means it is in one direction, that make H and many other quantities will be defined scalars. This gives us result for ~~avelance of a~~ a homogenous magnetic field and is a very good approximation for the way that most magnetic measurement are performed. The magnitude of the magnetic field is usually given in unit of Gauss (G) or Tesla (T) where 1T = 10,000G.

When a material is placed in a magnetic field, the magnetic field inside the material will be the sum of the external magnetic field and the magnetic field generated by the material itself. The magnitude of the magnetic field in a material is called magnetic induction and is given the symbol B

$$B = H + 4\pi M \quad — ①$$

where B = magnetic induction

H = external magnetic field

$\pi \approx \frac{22}{7}$ or 3.142

M = magnetization

For mathematical and experimental convenience, this equation is often written as;

$$\frac{B}{H} = 1 + \frac{4\pi M}{H} \text{ ——— ⑤}$$

$$\frac{M}{H} = X_v \qquad X_v = \text{volume magnetic susceptibility}$$

$$\therefore \frac{B}{H} = 1 + 4\pi X_v$$

X_v is so named because B, H, and M are defined by unit volume. This result in X_v being unitless
It is convenient to use volume magnetic susceptibility instead of magnetization because the magnetic susceptibility is independent on the magnitude of the external magnetic field H for diamagnetic and paramagnetic materials
Many studies are done using X_g (magnetic susceptibility per gram), which is $\frac{X_v}{\rho}$ (ρ = density)

$$\rho = \frac{m}{v} \Rightarrow X_v \times \frac{g}{\cancel{v}} = X_{(g)}$$

This gives unit $cm^3 g^{-1}$
Another useful for is X_m (molar magnetic susceptibility) whi
is X_g multiplied by molecular mass. this gives unit of $cm^3 mol^{-1}$

Another measure of magnetic interaction that is often used is an effective magnetic moment M.

Where $M = 2.828 (X_m T)^{1/2}$

M = effective magnetic moment

X_m = molar magnetic susceptibility

T = temperature (usually in absolute value).

The numeric factor puts M in unit of Bohr magnetons (BM) Where $1BM = 9.274 \times 10^{-24} J T^{-1}$.

The effective magnetic moment is a convenient measure of the materials magnetic property because it is independent of temperature as well as external field strength for diamagnetic and paramagnetic material.

Paramagnetism

The structural feature most prominent in determining paramagnetic behaviour is the number of unpaired electron in the compound. A spin only formular for the magnetic moment of a aramagnetic compound is given

$$M_{eff} = g(S(S+1))^{1/2}$$

M_{eff} = effective magnetic moment

g = 2.0023, gyromagnetic ratio

$S = 1/2$ for one unpaired electron
1 for two " "
$3/2$ for three " "
2 for 4

This equation is sometimes written with $g = 2$ because it does not introduce a significant since this simple spin only treatment is a decent approximation, but is often not accurate even to 2.s.f. An equation that takes into account both spin and orbital motion of the electron is

$$\mu = \{4S(S+1) + L(L+1)\}^{1/2}$$

where μ = effective magnetic momen
$S = 1/2$ for one unpaired electron, 1 for two ... etc.
L = total orbital angular momentum.

This equation is derived for atoms, it is applicable only to molecul with very high symmetry where the energies of the orbitals containing unpaired electrons are degenerate. L is found

In summary, the effective magnetic moment for spin only value is

- $\mu_{eff} = \sqrt{n(n+2)} = (n(n+2))^{1/2}$

where n = number of unpaired electron and the unit is BM.

~~Calculate the~~

Calculate the effective magnetic moment for the following compounds

ⓐ $[Fe(H_2O)_6]^{3+}$ ⓑ $[Fe(CN)_6]^{3-}$ ⓒ $[FeCl_6]^{2-}$

ⓐ $Fe = [Ar]\,3d^6\,4s^2$

$Fe^{3+} = [Ar]\,3d^5$

↑	↑	↑	↑	↑

$\mu_{eff} = \sqrt{n(n+2)}$

$= \sqrt{5(5+2)} = \sqrt{5(7)} = \sqrt{35}$

$\mu_{eff} = 5.916 BM$

ⓑ $Fe^{3+} = [Ar]\,3d^5$

CN is a strong ligand, therefore it forces the electrons to pair, therefore we have one unpaired electron

$\mu_{eff} = \sqrt{1(1+2)} = \sqrt{1(3)} = \sqrt{3}$

ⓒ $Fe\; x + (-6) = -2$

$x = +4$

$Fe^{4+} = [Ar]\,3d^4$

4 unpaired electron since it is a weak ligand field

Ferromagnetism, Antiferromagnetism and Ferrimagnetism

The advantage of using N_{eff} for describing paramagnetic behaviour is that it is a measure of the material's magnetic behaviour which is not dependent upon either the temperature or the magnitude of the external field. It is not possible to setup such a convention of ferromagnetic, anti-ferromagnetic and ferrimagnetic.

All the three class of these materials are considered a special of paramagnetic behaviour. The description of Paramagnetic behaviour is based on the assumption that every molecule behaves independently. The materials discussed here results from a situation in which the direction of the magnetic field produced by 1 molecule is accepted by the direction of the magnetic field produced by an adjacent molecule. In other words, their behaviour is coupled. If this occurs in a way in which the magnetic field or tend to align in the same direction, a ferromagnetic material dissolves and the Phenomenon is called ferromagnetic coupling.

Antiferromagnetic coupling gives an equal number of magnetic field in opposite direction. Ferrimagnetic coupling gives magnetic fields in two opposite orientation with more in one direction than in the other.

With a few exception, the magnetic moment are not aligned throughout the entire material.

Typically regions called domains will form with different orientation. The existence of domain of coupled molecule gives rise to a number of types of behaviour known as ~~Ferromagneti~~ ferro, antiferro and ferrimagnetism.

Question 19/11/25

Predict the magnetic property of the following and hence calculate the spin only magnetic moment

ⓐ $[Fe(CN)_6]^{4-}$

ⓑ $[Mn(H_2O)_6]^{2+}$

ⓒ $[Fe(F)_6]^{4-}$

(d) $[Ni(CN)_4]^{2-}$

ⓔ $[Ni(NH_3)_6]^{2+}$

Solution

ⓐ $[Fe(CN)_6]^{4-}$

~~Fe~~ $x + (-6) = -4$

$x = +2$

$Fe = [Ar]\,3d^6\,4s^2$

$Fe^{+2} = [Ar]\,3d^6$

Please

Similarities of 3d and 4d, 5d-block elements

* Variable Oxidation state
2 Catalytic activity
3 Formation of Complexes
4 Colour
5 Magnetic properties

Differences

① Oxidation state : ~~Before than~~ The 4d and 5d elements exist in higher oxidati on state than the 3d elemts. Because they have low ionization energy. The higher oxidation state in this elements are generally more stable.

② Magnetic properties. ~~The 4d and 5d elements~~ According to crystal field theory, the d-oribatal split into t_{2g} and eg sublevel (octahedral) The magnitude of splitting for any given ligand is greater for 4d and 5d members than 3d elements. These metals form predominantly spin pair complexes. Even in weaker ligands, the complexes are diamagnetic in nature.

The 3d elements form spin free paramagnetic complexes with weak ligands

(CO, CN, bipyridine and phenanthrolene) – Strong ligand

③ Metal – Metal Bonding: The 4d and 5d have a greater tendency ~~have~~ to form metal-metal bonds compared to 3d elements. This results in formation of large number of polynuclear and cluster compounds. Eg $[Re_2Cl_8]^{2+}$, $[Mo_2Cl_9]^{3-}$, $[Rh_4(CO)_{12}]$, $[Ir_4(CO)_{12}]$

④ Coordination number of complexes: For the 3d series, metal complexes with coordination number 6 and those commonly used Whereas, the 4d and 5d elements are larger in size and can accomodate a large number of ligands around them. Therefore, 4d and 5d elements form complexes with coordination number greater than 6. ~~[illegible]~~ $[Na_3(ZrF_7)]$ and $(Cu_2(ZrF_6))$

⑤ Abundance: The 3d series transition metals are more abundant in the earth crust as compared to the other elements. The first series consist about 6.8% of the earth crust while the second and third, ~~fourth and fifth~~ (4d and 5d) constitute only 0.025% of the earth crust

* Colour depends on the one absorbed by EmR. The one that is not absorbed is the one displayed / transmitted.

* Transition metals have partially filled orbitals 28/4/25

* Inert transition element are f-block metals

The f-block metals referred too as inert transition metals.

They are Lanthanides and Actinides, 4f and 5f respectively

f has overlying orbitals of 5p and 5s orbitals

They are also called rare earth elements. They also also able to form variable oxidation states because of the flexibility of oxidation n

Atomic Number	Lanthanides f- block metals	Symbol	
57	Lanthanum	La	$[Xe]\,4f^0\,5d^1\,6s^2$
58	Cerium	Ce	$[Xe]\,4f^1\,5d^1\,6s^2$
59	Praseodymium	Pr	$[Xe]\,4f^2\,5d^1\,6s^2$
60	Neodymium	Nd	$[Xe]\,4f^3\,5d^1\,6s^2$
61	Promethium	Pm	$[Xe]\,4f^4\,5d^1\,6s^2$
62	Samarium	Sm	$[Xe]\,4f^5\,5d^1\,6s^2$
63	Europium	Eu	$[Xe]\,4f^6\,5d^1\,6s^2$
64	Gadolinium	Gd	$[Xe]\,4f^7\,5d^1\,6s^2$
65	Terbium	T	$[Xe]\,4f^8\,5d^1\,6s^2$
66	Dysprosium	Dy	$[Xe]\,4f^9\,5d^1\,6s^2$
67	Holimium	Ho	$[Xe]\,4f^{10}\,5d^1\,6s^2$
68	Erbium	Er	$[Xe]\,4f^{11}\,5d^1\,6s^2$
69	Thulium	Tm	$[Xe]\,4f^{13}\,5d^1\,6s^2$
70	Ytterbium	Yb	$[Xe]\,4f^{13}\,5d^1\,6s^2$
71	Lutetium	Lu	$[Xe]\,4f^{14}\,5d^1\,6s^2$

Lanthanides are between the s and p block element at period 6
They are highly electropositive metals and Lanthanides they are characterized by the filling of the anti-penultimate 4f energy level which are largely screened from the surrounding by the over lying shell of electrons, i.e 5s and 5p electrons.

~~short form~~ → azimuthal

$n+l$ value ; 4f, $n=4$, $l=3 \Rightarrow 4+3=7$

5s, $n=5$ $l=2 \Rightarrow 5+2=7$

↓ Principal

↓ energy content

Other factors also come in like kinetics, stability, etc in the determining of the energy are inner obitals of orbital

The 4f orbital is hardly ~~surrounded~~ reachable to bond with. They have similar physical and chemical properties. ~~They chemistry of the~~ This makes their seperation very difficult because the chemistry of these elements are homologous. Though can be seperated by chemical methods ~~using~~ ion exchange chromatography is the best ~~done~~ due to differents ionic sizes and they are all similar in size because the characterized inner orbital are similar.

* The size of an atom is the distance between the nucleus and the outermost shell. Because electrons go into the inner shell, their states are almost the same.

Abundance, Sources, and Seperation/ Extraction

Name: Inner transition element, rare earth elements

Abundance

Lanthanites are not very rare except promethium, which is radioactive, i.e not stable

Cerium is as abundant as copper. All the other elements are more abundant than Iodine except promethium which does not occur in nature. ~~They are n~~

They are never found as free metals in the earth crust. They are found in low concentration widely distributed throughout the earth crust. They are found on the moon and in the sun. They naturally occur together because they have similar chemical properties

Odd number elements are less abundance than those with even numbers

~~So~~

Sources

① Monazite sand which contains Lathanites phosphates which are cerium

It contains 78% of

(ii) Bastnaesite: It is a mixed fluoro carbonates, $M^{III}CO_3F$ where M^{III} is the Lanthanites
It provides 22% of total supply of lanthanites. It Only found in USA and Madagascar

(iii) Xenotime: It is the principal source of the heavier elements

(iv) Samarskite: It is the source of Samarium

Extraction

(i) From Monazite: Monazite is hot conc. H_2SO_4, the Lanthanites dissolves as sulphates and they are seperated from insoluble material. Thorium is precipitated from the ~~The (soluble~~ soln mixture as ~~thorium oxide~~ thorium(IV) oxide by partial neutralization of NH_4OH (ammonium hydroxide), giving Lanthanide Ln^{3+} suphate solution which can be removed by solvent extraction with n-butyl phosphate. We use ion-exchange chromatography to obtain individual lanthanide element in the mixture.

The metal is finally obtained by electrolysis of the fused Lanthanide chloride ($LnCl_3$) and Calcium chloride or NaCl is added to lower the melting point and then the metal is finally obtained

Cerium and Europium are usually the first to be removed

Cerium by oxidation to cerium (IV) and removal by precipitation of the iodate which is insoluble in 6M HNO_3 or by solvent extraction

Europium is removed by induction to Europium^{2+} and precipitation ~~as~~ insoluble $EuSO_4$

* Why are Cerium and Europium the easiest to isolate?

Lanthanide have variable oxidation state. Cerium is $4f^1 5d^1 6s^2$ which is the most stable oxidation state, it can exist as +3 and +4, and Europium as +2 or +3. So, they can exist in other oxidation state apart from the general +3 oxidation state. Therefore when the Lanthanide mixture is oxidized, Cerium is precipitated, ~~then it~~ while Eu is passed through reduction process and Europium is gotten

~~The ion exchange process depends primarily on the hydrated ionic size, therefore, Lanthanum will be high while Lutetium will be the least, i.e La would be tightly bound to the~~

subsequent electron goes in and also reduces the [illegible]

The ion exchange process depends primarily on the hydrated ionic size. Therefore, Lanthanium will be the highest and Lotetium will be the least.
Lanthanium will be tightly bound to the while Letetium is least bound because of the size is greater than Lanthanium

Seperation of the Lanthanite Elements

While it is very difficult because of the similarities in the physical and Chemical properties (this is also because of the similar sizes) and they have similar trivalent states.

Due to these reason, only classical methods are used. The classical methods are used to exploit slight difference in their basic properties such as stability, solubility and then using ion exchange, valency change

Methods : Process of Seperation

(i) precipitation method
(ii) Thermal reaction
(iii) fractional crystallization
(iv) Complex formation
(v) Valency change
(vi) Ion exchange chromatography
(vii) solvent extraction

① Precipitation: The precipitating agent is OH^-. The substance with the lowest solubility is most rapidly precipitated first and it is completely precipitated. The weakest base is Lutetium hydroxide, and it is precipitated first. OH^- is added again, then Ytterbium hydroxide is precipitated, and so on

② Thermal reaction: The mixture is heated and a temp. is reached where a less basic nitrate decomposes to give the oxide. The mixture is now   with water. The nitrate is dissolved again and filtered off and we have the insoluble oxide. The process is repeated.

③ Fractional Crystallization

It is used to seperate Lanthanite salt. The solubility decreases from Lanthanum to Lutetium. Lutetium salt crystallize out first and seperated. The nitrate salt, sulphate salt, amides, oxalates, perchlorate, bromates, Salt of lanthanite have been used because they crystallize out well

Complex formation: The mixture of the lanthanite ion is treated with complex e.g EDTA.

All lanthanite ions forms complexes with EDTA ions such as Lu^{3+} form the strongest complexes, because of the small size, and it can seperated

The oxalate of the lanthanite ions are insoluble. Therefore, the addition oxalate ions to solutions containing lanthanite and EDTA does not give a precipitate because all the Lanthanide ions have already complexed with EDTA

If acid is added, the least stable EDTA will be ~~seperated~~/dissociated, therefore the Lanthanide ion will be available to be complex oxalate.

Valency change

The ability of Cerium and Europium to exist in different state other than the +3 state enables further seperation of the lanthanite. Why? Because the properties of Lanthanum in the +4 state and +2 state are quite different from the properties of Lanthanide in the +2 state and therefore can be easily seperated. For example, cerium can be easily seperated from Lanthanide mixture as it is the only Lanthanide that has Ln^{4+} ions stable in aqueous solution

The Seperation is by oxidizing the mixture, the only that will be oxidized is the Lanthanide ion. The Lanthanid ion and the Ce^{4+} ~~when~~ has a high charge, therefore it is smaller and $\overset{Ce^{4+}}{}$ it is less basic than Ce^{3+} or other Ln^{3+}. The cerium is seperated by carefully controlled precipi of CeO_2 (cerium(iv) oxide) or $Ce(IO_4)_2$ (cerium iodat Finally, the CeO_2 can be readily extracted. Similarly Eu^{2+} has different properties from the Ln^{3+} ions. $EuSO_4$ is insoluble while Ln^{3+} Sulphate is soluble. A mixture of Ln^{3+} ion reduced electrolytically using mercury cathode and zinc amalgam, Eu^{2+} will be produced and with the presence of H_2SO_4, $EuSO$ will be precipitated and then filtered off.

Samarium has ~~at~~ +2, Sm^{2+} can also be precipitated The valency change method is still a very useful method for purifying Ce and Eu

(vi) Ion Exchange Chromatography

The ion exchange chromatography method is the most importa the most rapid and the most effective general method of seperation of the Lanthanide. It is also the best

* principle of column chromatography

The less stable complex will be last to come out

method for the purification of Lanthanides

The basis or the principle is the ability to form complex ion

Procedure

The solution of Lanthanide ion is introduced at the top of a cation exchange column (it is the Dowex - 50, which is a sulfonated polysterene). The Ln^{3+} ions adsorbed unto the resin displacing the H-atoms on the resin

$$Ln^{3+}_{(aq)} + 3H_{(resin)} \rightleftharpoons Ln^{3+}_{(resin)} + 3H^{+}_{(aq)}$$

The Ln^{3+} ions are then eluted in a selective manner using an anionic complexing agent such as citrate, lactate, ~~Slowly~~ which are passed through the column slowly to have interaction between the element and the ions

The anionic chelating ligand form complexes with Ln^{3+} and they are displaced from the ion exchange material onto the solution.

$$Ln^{3+}_{(resin)} + 3H^{+}_{(aq)} + Citrate \longrightarrow Ln(citrate)_3 + 3H_{(resin)}$$

The elusion order follows the order of the hydrated Lanthanide ion such as Lutetium is first eluted and Lanthanum last.

(vi) Solvent Extration: The heavier Lanthanide ions are more soluble tri-n-butyl phosphate because it is an organic solvent, but in water, the solubility is reversed-

Physical and chemical properties

Physical Properties

① They are silvery white metal that tarnish when exposed to air because they are highly electropositive forming the oxides

② They are relative soft metals

③ Highly dense metals

④ They have have melting point and high boiling point

⑤ They form alloys with other metals especially the ions

Chemical properties

① ~~with~~ The element reacts with water slowly in cold and quickly when heated and this due to their electropositive nature

③ Order of basicity L

with Lutethium as the least, i.e basicity decreases as the atomi number increases and this basicity differences are indicated in the solubility of the salt and in the formation of the complex species, all this are linked to why the lutetium is aluted first

③ With air and oxygen: They are rapidily oxidized in moist air, reaction with oxygen is slow at room temperature but they can ignite at about 150° - 200° C

③ Reaction with acid: They dissolve rapidly in acid because they are metals

④ They combine with halogens upon heating, they also combine with sulphur, hydrogen, carbon and Nitrogen

⑤ They are highly reducing agent. The reducing properties are similar to that of alkaline earth metals (group 2A) such as Mg.

Oxidation state

(i) When we have half table configuration

(ii) When we have full filled

(iii) While we have thermodynamically or kinetic stable structure (either in aqueou (non aqueous take

Common oxidation state is +3, which is ionic and most stable for all except those

Higher oxidation state can occur for the fluorides

Low " " can occurr for the Iodide

The +2 and +4 state when;

① A noble gas configuration is obtained e.g Ce^{+4} which is (f^0)

② When there is a half filled orbital e.g Eu^{2+} or Tb^{4+} which is (f^7)

③ When there is a completely filled f-level e.g Yb^{2+}

electronic factors

The Ln^{3+} is the most stable i.e Ln^{2+} and Ln^{4+} are less stable

E.g Ce^{4+} is ~~highly reducing~~ strongly oxidizing, which means it is easily reduced.

Due to electronic factors

Due to kinetic and thermodynamic factors; Sm and Tm

+2 states are well establishing for Tb, Sm and Eu

+4 state; Ce

8/12/25

Q1: If oxalate ions are added to solution containing Ln ions of EDTA. What happens? Why

The ~~EDTA~~ Ln ions would have complexed with EDTA, and because EDTA is a stronger complexing agent, the oxalate cannot displace EDTA and then nothing happens.

Q2: What happens when dil. HCl is added?

When dil HCl is added, dissociation of Ln complex mixture happens. The first one that will disintegrate is the least stable complex which is the one with the largest size (Lutetium)

ronic

ors

Spectral properties of Lanthanide

The lanthanides are coloured,

* Laporte selection rule says you cannot have transitions unless you have ΔL ($\Delta L \neq 0$)

The colours of the Lanthanide complexes originates almost entirely from charge-transfer interactions between the metal and the ligand.

f→f transitions are symmetric forbidden or Laporte forbidden, just as for transition metals. However

The metals are a able to use Vibrony coupling to break this rule. Also most importantly, the buried nature of ~~The valence orbital~~ the f-orbitals coupling with the fact that the molecular vibrations are weak. The Spectral of Ln ions are very weak and the adsorption bands are very narrow.

The f→f transitions are very weak and very narrow than the d→d transitions: Because, the bands are weaker, the colours are very faint. Where the f-f transitions are not possible the ions are colourless in aqueous solution.

$$\left.\begin{array}{lll} Pr^{3+} & 4f^{2} & \text{green} \\ Tm^{3+} & 4f^{12} & \text{green} \end{array}\right\} 14-n$$

$$\left.\begin{array}{lll} Nd^{3+} & 4f^{3} & \text{pink} \\ Er & 4f^{11} & \text{pink} \end{array}\right\} 14-n$$

Magnetic Properties

The magnetic properties are quite different from the d-block elements, mainly because the 4f electron is possible for the Ln ions are very effectively shielded from the influence of external orbit by the overlying $6s^2$ and $5p^6$ of the shell / orbital. The Ln ions have ~~The Ln ion general~~ groundstate with a single well-defined volume of total angular momentum

Ln^{3+}, Ce^{4+}, La^{3+} $\}$ f^0 No unpaired electron and therefore diamagnetic

All other f state are paramagnetic due to the presence of f-electrons

Compounds

Compounds of Ln exists in +2, +3, +4 oxidation states. Ln(III) compounds are mostly ionic salt, Ln^{2+} compounds the most common divalent of Ln^{3+} is Eu^{2+} which have.

All Ln have divalent halides. The divalent halides are either conventional ~~source~~ salt or they are Ln(III) electride-like salt. Eg YbI_2, EuI_2, SmI_2

Halides

The halides of Ln form tetrahalides, trihalides and dihalides. The only tetrahalides are the tetrafluorides of ~~Cerium, praseodymium~~ Ce, Pm, Tb, Nd, and Dy

Neodymium and Dysprosium tetrafluorides are only known under matrix isolation techniques

For trihalides, ~~All~~ Ln form trihalides with, F, Cl, Br and I and they are high metting compounds and ionic in nature

The fluorides are only slightly soluble in water and not sensitive to air.

The trihalides are very important because the pure metals can be prepared from trihalides

- We have stable dihalides with Eu, Yb and

Oxides of Lanthanides

The ~~Ln~~ reacts with oxygen ~~to~~ to form oxides. The reaction at room temp. can be slow but can be aided by heat. All the Ln form sesquioxides, Ln_2O_3, the lighter or larger Ln adopts a hexagonal seven coordinate structure while the heavier or smaller ones adopt a cubic six cordinate structure.

All the oxides are basic, absorbs water and CO_2 from air to form CO_3^{2-}, OH^- and hydroxy carbonates

The oxides dissolves in acid to form salts

Cerium form stoichiometric dioxide (CeO_2) because of the stable oxidation of +4. CeO_2 is also basic and dissolves typically in acids to form Ce^{4+} solution from which Ce^{4+} salt can be isolated

Eu and Yb forms Salt like monoxide EuO and YbO which have a rock salt structure. EuO is ferromagnetic at low temperatures

Hydroxides

All the Ln form hydroxides of the formular $Ln(OH)_3$, since the ionic since decreases from Ln^{3+} to Lu^{3+} the basicity of the OH decrease; i.e $Ln(OH)_3$ is the strongest and $Lu(OH)_3$ is the weakest base. The hydroxide can be ppt from the soln of Ln and can be formed by the rxn of Ln oxide with water. Although the reaction btw oxide & water is thermodynamically favourable but kinetically slow for the heavier element

Hydrides

The Ln metals combine endothermically with hydrogen to form Ln dihydrides and with the exception of Eu and Yb which resemble Ba and Ca hydrides, i.e non conducting, transparent salt

like compounds. All the others form black conducting compounds. Conducting because it is a dihydride and in +3 oxidation state, a mobile electron
conducting

Complexes

The Ln have little tendency to form complexes because of the fact that the available inner orbital is inaccessible. They are f-block orbital, the 4f is deeply buried and covered by 6s. 5p & [illegible]
Also, another reason is that they are not small.

They have almost the same size because the inner orbital filled is shielded. The effect of increasing electron leading to strong nuclear attraction is been nullified by the shielding effect.

Small tendency to form complexes because;

(i) They have high charge and this high charge is the reason they form complexes
(ii) Large sizes, large radii
(iii) Vacant orbitals: Unavailability of the 4f orbitals deeply buried inside the atom.

They have little tendency to form complex because of the unavailability of 4f orbital which are burried inside the atom

The complexes are not very stable

$M(H_2O)_n]^{3+} + H_2O \rightarrow M(OH)(H_2O)_{n-1}]^{2+} + H_2O^+$

The tendency for this hydrolysis increases with increasing atomic number

(2.) Halogeno Complexes

$MF^{2+}_{(aq)}$: they are formed aqueous solution and they are weak complexes

(3.) Complexes with Oxygen Ligands

This complexes are the most stable and most common Lanthanide complexes because they form chelates e.g with EDTA complexes are the most stable, also other hydroxo acid such as tartaric acid or citric acid to form water soluble complexes

(4) Complexes with monodentate ligands are less stable than most of the chelate and tends to dissociate in aqueous solution

(5) Nitrogen Ligands: Addition of amines to form Complexes but complexes with amines are not

formed in aqueous solution, because H_2O is a stronger ligand than ammonia so ammonia cannot displace water. However the amine complexes can be obtained in non aqueous solvent and few nitrogen complexes are know. We can also prepare this amine complexes N-based ligand under anhydrous conditions containing CH_3CN giving rise to polyamine complexes such as trisethylenediamine (Men_3Cl_3) Ln compound. They form very few stable complexes with CO, CN, and other organometallic compounds.

Lanthanide Contraction

The steady decrease in the size of Lanthanide atoms and ions with increasing atomic number from Lanthanum^{57} to Lutetium^{71}. The addition of electrons into an inner shell 4f leads to screening or shelding effect; i.e the nucleus reduces its attraction on the valence electrons due to the presence of these electrons in the innershell.

Therefore there is poor shielding of the 5s and the 5p electrons by the 4f electrons.

Other thing that contributes to the imperfect poor shielding is the shape of the f-orbitals

With the poor shielding the positively charged nucleus has a greater attraction to the electrons therefore decreasing the atomic size as the atomic number increases.

The subsequent electrons goes to the inner 4f orbital leads to poor shielding of 5f and 5p. increase atomic size = greater attraction = decrease size

Consequences of Lanthanide Contraction

① They have similar atomic size

② Identical properties of the Ln elements

③ Difficulty in the separation of Lanthanides

④ Effect ~~on~~ the basic strength of hydroxides

$Lu(OH)_3$
Lutetium hydroxide less basic than $Ln(OH)_3$ and more covalent

⑤ Ability of complex formation decrease

⑥ Increase in ionization energy

⑦ Increase in electronegativity

Application of Lanthanides

The Ln elements and their compound have many uses but the quantity consumed is very small in comparison to other elements

① They are used as catalytic converters, that consumes about 45% of their uses.

② They are used as petroleum refining catalyst, 25% used

③ 12% are used as Permanent magnet

④ Used as glass polishing and ceramics, CeO_2 is used to polish glass

⑤ Used as Coating for Self cleaning ovens

⑥ Used for metalleurgical process, i.e formation of alloys

⑦ Used as ~~phosphorus~~ Phosphors in TV screen e.g EuO is used as red phosphorus in TV and computer terminal display

⑧ $CeSO_2$ is used as an oxidizing agent in volumetric analysis.

⑨ Lanthanides have been widely used as alloys to impact strength and hardness to metals. The main Ln used for the purpose is Ce is mixed with Small amount of La, Nd, Pr. Specifically we have Ln 40% ; Ce 50%, Fe (7% and other metals 3%. This mixture is added to steel for more effective quality to impact strength and workability of steel

⑩ Ln are used in the petroleum industry to refine crude oil into gasoline product

(11) They are used as superconductor, magnets, ceramics

⑫ In medicine, current research shows than Ln elements can be used as anticancer agent and the main role of Ln is no inhibit multiplication poliferation of the cell. Ce and Ln has been study as anti cancer agent

⑬ Ln element used as biological tracer for drugs (because they have sharp absorption spectra) in animals and human beign, because Ln elements are easy be follow spectromically because their peaks are narrow, sharp and characterized

⑭ They are used for the caliberation of intrument due to their sharp absorption band

⑮ They ~~can~~ be used for nuclear purposes e.g the hydrides can be used as hydrogen moderator carriers. The oxide too can be used as diloluent in nuclear fields and the Eu can be used as radiation sources.

ACTINIDES

Actinides are 5f elements and they are also typical metals. They have the properties of both the d-block & f-block element; They are radioactive in nature and release a lot of energy in radioactive decay. Uranium and Thorium are the most abundant naturally occurring actinide

Actinium	Ac	$6d^1 7s^1$	3
Thorium	Th	$6d^2 7s^2$	4 (3, 2)
Protactinium	Pa	$5f^2 6^2$	5 (3, 4)
Uranium	U	$5f^3 6d^1 7s^2$	6 (3, 4, 5
Neptunium	Np	$5f^5 7s^2$	5 (3, 4, 6, 7)
Plutonium	Pu	$5s^6 7s^2$	4 (3, 5, 6, 7)
Americium	Am	$5f^7 7s^2$	3 (2, 4, 5, 6)
Curium	Cm	$5f^7 6d^1 7s^2$	3 (4)
Berkelium	Bk	$5f^9 7s^2$	3 (4)
Californium	Cf	$5f^{10} 7s^2$	3, (2)
Einsteinium	Es	$5f^{11} 7s^2$	3, (2)
Fermium		$5f^{12} 7s^2$	3, (2)
Mendelevium		$5f^{13} 7s^2$	3 (2)
Nobelium		$5f^{14} 7s^2$	2 (3)
Lawrencium		$5f^{14} 6d^1 7s^2$	3

General properties

They are also referred to as. rare earth metals characterized by the filling antipenultimate 5f orbitals. They are typical metal and have the property of both d and f - block metal. They are also radioactive. They have high diversity in oxidation state. They have similar chemical properties

Actinides are more electropositive than Lanthanides because they have lower ionization energy, they are more reactive and more basic than lanthanides.

They require special handling because some of them are radioactive and unstable. The most common and know element of the Actinide is Uranium which is used as nuclear fuel and can be converted to plutonium through nuclear reaction.

The occure

Occurence

The element of Ac — Th occur in nature but they however undergo radioactive decay.

Th and U are nevertheless rare, they occur in earth crust Th — 8.1 ppm and U — 2.3 ppm. The elements after U have shorter half life hence they undergo decay which takes about few minutes. This makes it impossible to perform anything on them except quick tracer experiment

Th is found in monazite sand which is the combination of

~~The~~ [illegible] and $LnThPO_4$ 10% of Th is gotten from it

Th is found in ~~Thoride~~ ($ThSi(O_4)$) Thoride silicate

U is mined as a ore in pitchblende – UO_2, very small quantities actinide ~~[illegible]~~ Pa, Np, Pu can also be found in nature but very unstable

Pu is formed in large amount of Uranium fuel in nuclear reactors

The elements higher than U are called trace uranium elements

Before 1940, the only actinides known are Th, Pa and U

They were then wrongly thought to be part of the d-series

(i) ~~Be~~ Because of chemical similarity with group of transition metals, i.e titanium, Zirconium group

(ii) Increase in the number of oxidation state

(iii) Increase in the stability of higher oxidation state

Preparation

The first few members of the actinides are usually formed by neutron-Gamma reactions followed by beta emission.

They were first made in 1940 by the bombardment of uranium in a ~~[illegible]~~ cyclotron at Berkley

They are now obtained in spent uranium fuel rod

The uranium fuel road are radiated with slow neutrons and the main reaction is the fission of $^{235}_{92}U$ into smaller nuclei

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{236}_{92}U + ^{1}_{0}n \rightarrow ^{237}_{92}U \xrightarrow{\beta} ^{237}_{93}Np$$

The half life of   is 6.7 days

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + ^{1}_{0}n \xrightarrow{\beta} | \xrightarrow{\beta} ^{239}_{94}Po$$

½ life 24 mins   t½ 2.3 days

$$^{239}_{94}Po + ^{4}_{2}He \longrightarrow ^{243}_{96}Cm \quad \begin{bmatrix} \alpha - ^{4}_{2}He \\ \beta - ^{0}_{-1}\beta \end{bmatrix}$$

α patch

ratio of neutron to proton becomes so much increased, becomes unstable

Reaction of Actinides

(1) Reactions with air: The tarnish in air because of the electropositivity forming the oxide coating. In case of ThO, the oxide coating is protected

(2) The also react with hot water

(3) They react readily with acid HCl, but slowly in other acids.

Oxidation state

The most stable O.S of the lower element is +3. The most stable O.S is the highes O.S of each element

The +2 state of Am is $5f^7$ which is stable configuration.

The +2 state of Am is the most stable

The Am^{2+} only exist in the solid state as the fluoride. In constrast to this, Cf^{2+}, Es^{2+}, Fm^{2+}, Md^{2+} exists as ion in solution and their properties are close to the properties of group 2 especially Ba^{2+}

For the elements, the lower O.S tends to be ionic and the higher O.S tends to be covalent

They all exist in +3 state, however it is not always the most stable state like in the lanthanide.

O.S > 3: Th, Pa, U, Np have O.S greater than <3 by using all the outer electron

Complex Formation

Actinides are better complexing agents than lanthanides from the general properties that favours complex formation
It is often impossible to say which orbitals are utilized in bonding due the similarities of the energy of the 5f, 6d, , 7p and 7s levels. Most the complexes are in aqueous solution. The coordination number of the complexes is between 6 and 12

Spectral properties

The colour of the actinides is due to the electronic transition within the 5f levels. Electronic transitions of actinide are about 10 times more intense than those of Lanthanides. The difference is due to the difference in the 4f and 5s electrons.
The f-orbital are deep inside and overlap deeply with ligand metals due to the complexity of the structure
The spectral are very complex and difficult to interpret, U, Np, Pd, Cm have very sharp light in their absorption spectral and this is characteristics of f-f spectra

Magnetic Properties

The magnetic properties of actinide ions arise from the spin and orbital angular momentum of 5f electrons. The 5f electrons are also ~~not~~ not so well localized as the 4f electrons and they have energies comparable to those of the 6d and 7s electrons.

This lead to greater variety in the properties of the actinides. Therefore ligand effect are expected since 5f orbital can participate to some extent in covalent bonding because the 5S electrons are not well localized

	f	Compound	Magnetic moment	Corresponding lanthanide
Th^{4+}	0	$Th(C_5H_5)_4$	Diamagnetic	~~3.59~~
U^{4+}	2	$U(C_5H_5)_4$	2.78	3.59
Np^{4+}	3	$N(C_5H_5)_4$	2.43	3.62
Pu^{3+}	5	$Pu(C_5H_5)_3$	1.12	1.54
Am	6	$Am(C_5H_5)_3$	1.72	3.84

Lower value of Actinide are due to the ligand effect and spin ~~orbit~~ orbit coupling.

Compounds of Actinides

Halides of Actinides: Majority of the actinide form halides with halogens at specific temperatures

They combine with halogen with the formular MX_3 and MX_4

The actinides halides are water soluble but the fluorides are insoluble. The halides are very important binary compound

The trihalides are the most well known halides

$$Ac(OH)_3 + 3HF \xrightarrow{700^\circ C} AcF_3 + 3H_2O$$

$$Th + 2F_2 \longrightarrow ThI_4$$

Uranium usually give colourless hexafluoride which sublimates at a temperature of 56.5°C because of its volatility

The actinides hexa fluoride have properties close to anhydride, very sensitive to moisture and they hydrolyze forming the oxyfluorides AnO_2F_2

Oxides of Actinides

All actinides form oxides with different oxidation state and the most common oxides are AC_2O_3

For $M_2O_3 \rightarrow AC, Pu — Es$

$MO_2 \longrightarrow Th, U$

$M_2O_5 \longrightarrow$ Pa, Np

$MO_3 \longrightarrow$ U, (Np) query

the actinium, An_2O_3 are amphoteric, An_2O_2, AnO_2 and AnO_3 are basic and easily combin with water to form bases

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The hydroxides are obtained from action of water on the oxide

$$An_2O_3 + 3H_2O \longrightarrow 2An(OH)_3$$

The $Pn(OH)_5$ is weak

Important uses of Actinides

The actinides are valuable because they are radioactive. They are mostly used in nuclear weapons are used as a fuel in nuclear reactor. The most useful actinides are U, Th, Pu. The salts of actinides are used in the glass industry for impacting green colour. They are also used in the ceramic industry, textile and medicine

Th is used in the atomic reactors and in the treatment of of cancer

U is used in the nuclear fuel machines

Pu also used in nuclear fuel and also used for making Atomic bombs

Americium is used in daily life application such as detecting smoke

Curium is used in gas mantle

Actinium is used in scientific medical reasearch, as neutron source, indicator and gamma source

Chemistry of Thorium and Uranium

Thorium and Uranium are naturally occuring and the most abundant actinide in nature. Uranium mostly occurs in nature/earth crust as a mixture of its oxides and in minerals such as

Uranimide	U_3O_2
Carnotite	$KUO_2NO_3 \cdot 3H_2O$
Autrite	$Ca(UO_2)_2PO_4 \cdot nH_2O$

Naturally occuring Uranium contain three is isotopes of Uranium $^{233}U - 99.3\%$, $^{235}U - 0.7\%$, traces of ^{234}U.

Monazite is the main ~~source~~ one of Thorium ($ThLnPO_4$)
Thorium is also found in Uranothorite which is mixed silicate of Th and U.

Th and U are the easiest to isolate. Th is extracted mainly from monazite. The monazite is treated with NaOH, the soluble hydroxide is filtered of and disolved in HCl. The pH is adjusted to 6 when hydroxide of Th(IV), U(IV) and Ce(IV) are precipitated. This Seperates them from the trivalent lanthanide.

The hydroxide precipitate is dissolved in 6M HCl and extracted with tributyl phosphate and kerosene. This leads to the precipitate of the oxide. The metal can then be obtained by reducing the oxide, ThO_2 with Calcium

Other Properties of Thorium

(i) Th metal is silvery white and bright, because of the absence of f electrons/orbitals.

(ii) Th is soft and melts at 1750°C

(iii) It tarnishes in air to give a dull black colour.

(iv) It exihibits +4 oxidation state, the +4 state. is known both in the solid state or aqueous solution

(v) The +2 and +3 oxidation states are only known to iodides e.g ThI_2

(vi) It form complexes easily due to its high charge.

(vii) The complexes have high coordination number and uncommon structure especially with oxygen donor ligand.

Chemistry of Uranium

(i) U has a silvery appearance when pure, when attacked by air → yellow colour initially and black coating develops

(ii) Exists in oxidation state of +3 to +6

(iii) Many of the compounds in +4 and +6 are non stoichiometry (variable composition).

(iv) Oxide system is very complicated

(v) form hexahalides

Dr. George 11/12/25

H_2O - aquo

They are certain elements that have ~~odd~~ electronic configuration due to stability

** Naming of coordination compounds

$CoCl_2 \rightarrow$ ionic bond

$[CoCl_4]^{2-}$

$\downarrow$ coordinate covalent bond.

Rules for Naming Coordination compounds

(i) Name cation before the anion

$\underset{\text{cation}}{K_4}\underset{\text{anion}}{[Fe(CN)_6]}$, $Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]Cl_3$, $[Co(H_2O)_2(en)_2]^{2+}$

(ii) Within the complex, name the ligands first in alphabetical order

H_2O — aquo

en — ethylenediamine

di - bis, ~~tetra~~ tri - tris, tetra - tetrakis

(iii) Calculate oxidation number, written in roman figure and capital letter. If it is an anionic complex, the name of the metal will end with "ate"

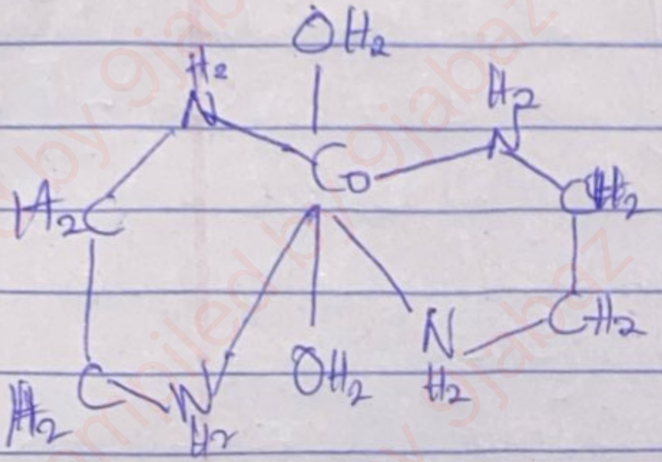
$K_4[Fe(CN)_6]$ - Potassium hexacyanoferrate (II)

$[Fe(CN)_6]^{3-}$ - hexacyanoferrate (III) ion

$[Co(NH_3)_6]Cl_3$ - hexaammine cobalt (III) Chloride

Element that donates lone pair in a coordination compound,

N, O, P, S, F^-, Cl^-, Br^-, I



The coordination number gives us idea of the shape ~~dat~~ will adopt

C.n of 6 – octahedra or trigonal prism

C.n of 4 – Square planar or tetrahedral.

MODULE ONE

REFRESHER

- **Unit One –** Odd Electronic configuration
- **Unit Two –** Naming coordination compounds and molecular structure
- **Unit Three –** Bonding in transition metal complexes and oxidation state
- **Unit Four –** Hard and soft acids and bases in transition metal complexes

UNIT ONE - Odd Electronic Configuration

The electronic configurations of transition element from Scandium to Zinc (Sc, Ti, V, Cr, Mn, Co, Fe, Ni, Cu, Zn) follow the usual rules ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^x 4s^2$ $where\ x = 1 - 10$ note that the 4s is filled before the 3d). However in this first row of transition metal Cr and Cu do not follow the rules; according to the rules chromium would be $Cr_{24} = 1s^2 2s^2 2p^6 3s^2 3p^6 \boldsymbol{3d^4 4s^2}$ but the correct electronic configuration $\boldsymbol{Cr_{24}} = 1s^2 2s^2 2p^6 3s^2 3p^6 \boldsymbol{3d^5 4s^1}$**.** Similarly instead of $Cu_{29} = 1s^2 2s^2 2p^6 3s^2 3p^6 \boldsymbol{3d^9 4s^2}$ its electronic configuration is $Cu_{29} = 1s^2 2s^2 2p^6 3s^2 3p^6 \boldsymbol{3d^{10} 4s^1}$ is the correct one. This is because a half filled or completely filled orbital are stable and hence the preferred configuration.

The second row of transition metals (from Yttrium-cadium) follows the principle of filling of electrons but again except for Nb, Mo, Ru, Rh, Pd,

Element	Correct	Following rules
Niobium (Nb)	$4p^6 4d^4 5s^1$	$4p^6 4d^3 5s^2$
Molybdenum	$4p^6 4d^5 5s^1$	$4p^6 4d^4 5s^2$
Ruthenium (Ru)	$4p^6 4d^7 5s^1$	$4p^6 4d^6 5s^2$
Rhodium (Rh)	$4p^6 4d^8 5s^1$	$4p^6 4d^7 5s^2$
Palladium (Pd)	$4p^6 4d^{10} 5s^0$	$4p^6 4d^8 5s^2$
Silver	$4p^6 4d^{10} 5s^1$	$4p^6 4d^9 5s^2$

Similarly, the third row of transition metal (from lanthanum to mercury) the same kind of odd electronic configuration is observed. For platinum instead of $\boldsymbol{5d^8 6s^2}$ the correct one is $\boldsymbol{5d^9 6s^1}$ and then for gold it is $\boldsymbol{5d^{10} 6s^1}$ but following the rules it would have been $\boldsymbol{5d^9 5s^2}$.

UNIT TWO - Naming Coordination Compounds

Coordination complexes are compounds which consist of a central metal atom or ions surrounded by a definite number of electron donating molecules or ions. These molecules or ions surrounding the metals are referred to as ligands. A coordination complex maybe a neutral molecule or an ion. The number of ligands surrounding the central metal is called the **coordination number** of the complex and this is different from oxidation number of the complex.

$[Fe(CN)_6]^{4-}$

-4 is the oxidation number of the complex ion

6 is the coordination number.

Oxidation number is referred to as the Primary/Principle Valence while coordination number is referred to as Secondary/Auxiliary valence. Primary valences are non-directional while secondary valences are directional.

The rules for naming coordination compounds are as following:

1. The cation is named before the anion. This rule holds whether the complex ion is negatively charged or positively charge. For example, in $K_4[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$; K^+ and $[Co(NH_3)_4Cl_2]^+$ are the cations and are named first.

2. Within a complex ion the ligands are named first, in alphabetical order, and the metal ion is named last.

Ligand	Abbreviation	Name of ligand in coordination compound
Bromide Br^-		Bromo
Chloride Cl^-		Chloro
Cyanide CN^-		Cyano
Hydroxide OH^-		Hydroxo
Oxide O^{2-}		Oxo
Carbonate CO_2^{3-}		Carbonate
Nitrite NO_2^-		Nitro
Oxalate $C_2O_4^{2-}$	$[ox]^{2-}$	Oxalato
Ammonia NH_3		Ammine
Carbon monoxide CO		Carbonyl

Water H_2O		Aquo or aqua
Ethylenediamine $H_2NCH_2CH_2NH_2$	en	Ethylenediamine
Acetylacetonate $CH_3COCH_2COCH_3$	$[acac]^-$	Acetoacetate
Ethylenediaminetetraacetate $(^-O_2C)_2NCH_2CH_2N(CO_2^-)_2$	$[EDTA]^{4-}$	Ethylenediaminetetraacetate

3. The names of the anionic ligand end with the letter o, whereas a neutral ligand is usually called by the name of the molecule except for H_2O, CO, and NH_3.

4. When there are more than one ligands present, we use the Greek prefixes di-(2), tri-(3), tetra-(4), penta-(5), and hexa- (6) to name. For example $[Co(H_2O)_6]^{3+}$ will be *hexaaquocobalt*.

5. When there are different ligands the ligands are names in alphabetical order. Thus the ligands in the cation $[Co(NH_3)_4Cl_2]^+$ are "*tetraamminedichloro*".
6. If the name of the ligand contains a Greek prefix, we use the prefixes *bis*-(2), tris-(3), and tetrakis-(4) to indicate the number of ligands present. For example, the ligand *ethylenediammine* already contain the word '*di*' which is a Greek word therefore if two of such ligands are present, the name will be *bis(ethylenediammine).*

7. The oxidation number of the metal in Roman numerals following the name of the metal. For example the Roman numerals III is used to indicate the +3 oxidation state of Co in $[Co(NH_3)_4Cl_2]^+$ which is called *tetraaminedichlorocobalt(III) ion*.

8. If the complex is an anion, its name ends in –ate. For example, in $K_4[Fe(CN)_6]$, the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the Roman numeral II indicates the oxidation state of iron.

Metal	**Names of metal in anionic complex**
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate

Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

Coordination Number and Molecular Structure

With the coordination number it is possible to predict the shape/structure of a complex. However further experimental data will be required to confirm the structure.

Coordination number	Shape	Examples
2	Linear	$[CuCl_2]^-$, $[Ag(NH_3)_2]^{2+}]$.
3	Trigonal planar	$[Cu(CN)_3]^{2-}$, $[HgI_3]^-$
4	Tetrahedral	$[CoCl_4]^{2-}$, $[MnCl_4]^{2-}$
4	Square planar	$[PdCl_4]^{2-}$, $[AuCl_4]^-$, $[PtCl_4]^{2-}$
5	Trigonal bipyramid	$[CdCl_5]^{3-}$, $[CuCl_5]^{3-}$
5	Square base pyramid	$[WCl_4O]^-$, $[TcCl_4N]^-$
6	Octahedral	$[Ti(OH_2)_6]^{3+}$, $[Co(OH_2)_6]^{2+}$
6	Trigonal prism	$[Zr(CH_3)_6]^{2-}$

UNIT THREE - Bonding in Transition Metal Complexes

There are 3 theories of metals to ligand bonding in complexes

1. VALENCE BOND THEORY (VBT): In this theory the complex ion has its ligands forming coordinate bonds to the metal. Hence the ligands must have a lone pair of electrons and the metals must have an empty orbital of suitable energy. The ligands would donate electrons to the metals which they now share. With this theory the shape of the complex can be predicted.

2. CRYSTAL FIELD THEORY (CFT): According to this theory the interaction between metals and ligands is purely electrostatic it could be **(a)** ion-ion interaction e.g. +ve ion Co^{3+} and –ve ion Cl^-. **(b)** ion-dipole interaction and this is between a neutral molecule e.g. NH_3 and CO and the metal ion. For example, $[Co(NH_3)]^{2+}$, NH_3 has a dipole moment with the δ- charge on the N and the δ+ on the H, and the δ- pointing towards cobalt. This theory is able to explain the electronic spectra and the magnetic properties of transition metal complexes.

3. LIGAND FIELD THEORY (LFT): This theory explains the bonding of metal to ligand in terms overlapping of orbitals using molecular orbital theory. Because of molecular orbital theory in LFT both covalent bonds and ionic contribution are allowed. It also entails using group theory.

Oxidation State: Oxidation entails the loss of an electron(s). In transition metal the removal or loss of electrons starts from the **ns** orbital instead of the **(n-1)d** even though the **ns** is filled before the **(n-1)d**. A good question is why? The reason why the **ns** is filled before the **(n-1)d** is because the **ns** orbitals are more penetrating (less shielded) than the **(n-1)d** orbitals]. But as electrons begin to fill the **(n-1)d** orbitals the energy of the **(n-1)d**-orbitals decreases greatly, that is why when it comes to removal of electrons it is lost from the s-orbitals rather than the d-orbitals.

The most common and stable oxidation state is the +2 and +3. The +3 oxidation states are more stable towards the beginning of the series (the left of the periodic table) whereas the +2 oxidation states are more stable towards the right of the periodic table. Very high oxidation states are found towards the center e.g. +7, in addition these high oxidation state are found in compounds with electronegative elements such as oxygen and fluorine e.g. V_2O_5, CrO_3, Mn_2O_7.

UNIT FOUR - Hard and Soft Acids and Bases in Transition Metal Complexes

The interaction between the metal atom and the ligands and are considered to be Lewis acid – base reactions. A Lewis base is an electron pair donor while Lewis acids are electron pair acceptor. So ligands are Lewis bases and the central metals are Lewis acids.

Acids

- Hard (Class a) acids are metal ions are either small and/or but highly charged (i.e. have high charge density) and therefore are not easily polarized. e.g. Mn^{2+}, Zn^{2+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Y^{3+}, Ti^{4+}, etc. Any atom/ion that is easily polarized (i.e. polarizable) means that it is easy to distort its electron clouds.
- Soft (Class b) acids on the other hand are easily polarized because they are large (having low charge density) e.g. Tl^{+}, Cu^{+}, Ag^{+}, Au^{+}, Cd^{2+}, Pd^{+}, $Fe^{2+,}$ Co^{2+}, Cu^{2+}.

Bases

- Hard (Class a) bases are ligands which are small in size and highly charged hence not easily polarized e.g. F^{-}, Cl^{-}, NH_3, OH^{-}, ox^{2-} etc.
- Soft (Class b) bases are large and highly polarizable e.g. I^{-}, CN^{-}, CO, SCN^{-} etc.

There is also the intermediate class e.g. Br^{-}, NO_2^{-}, pyridine.

Hard acids tend to bind to hard bases and soft acids to soft bases. Therefore, the interaction between hard acid-base is predominately electrostatic i.e. ionic or dipole-dipole interactions. Soft acid-bases being more polarizable have their interaction predominantly covalent in character.

MODULE TWO

VALENCE BOND THEORY (VBT)

- **Unit One –** VBT vs VSEPR
- **Unit Two –** Hybridization in Transition metal complexes
- **UNIT Three -** Limitations to VBT

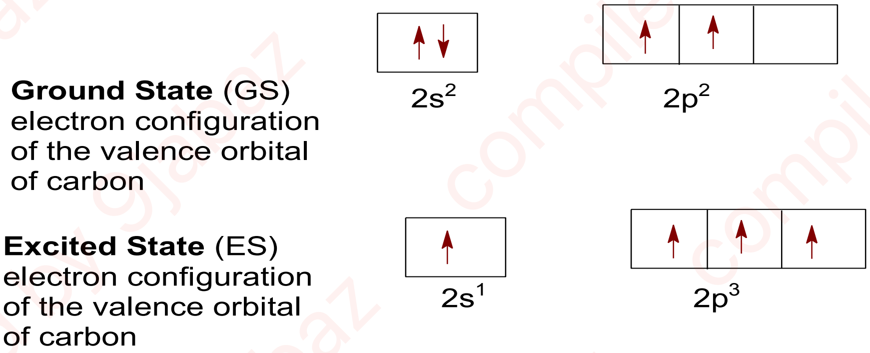
UNIT ONE – VBT vs VSEPR

According to this theory, bonding is as a result of the use of unoccupied hybridized bonding orbitals of the metal for the formation of coordinate covalent bonds with the donor electrons pairs of the ligands.

This theory is based on quantum mechanics and it assumes that bonds are formed by the overlapping of atomic orbitals. Only valence orbitals are involved in bonding, while the inner electrons remain unaffected by the bonding. The greater the orbital overlap, the stronger (more stable) the bond.

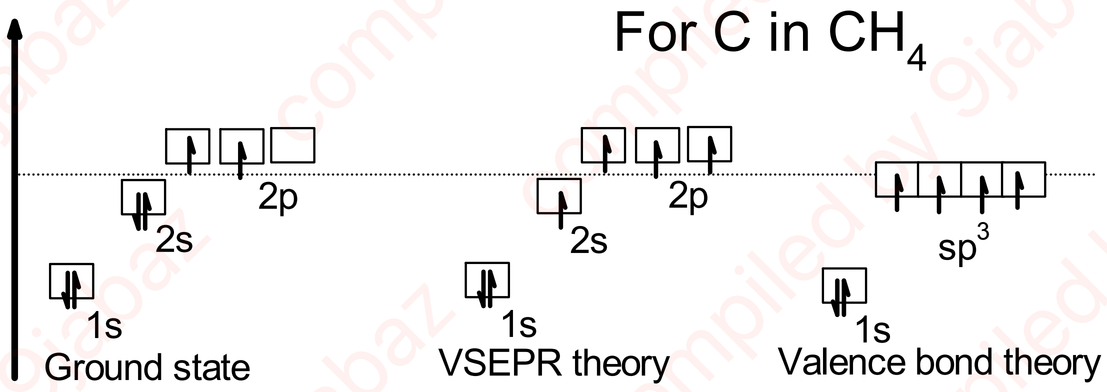
VSEPR theory	VB theory
Based on Lewis structures	Based on quantum mechanics
Covalent bond are formed by sharing electrons	Covalent bonds are formed by overlapping of atomic orbitals
All atomic orbitals in the molecule are pure orbitals	The valence atomic orbitals in a molecule are hybrid orbitals
Cannot explain differences in bond length and bond energy between in different molecules.	Can explain differences in bond length and bond energy can be explained.
It does not distinguish between sigma bonds and pi bonds	Can distinguish between sigma bonds and pi bonds.

Hybridization is the mixing of dissimilar atomic orbitals to generate a set of hybrid orbitals that have of the properties of the parent orbitals that would be used in covalent bonding. The hybridized orbitals are directional and their orientation in space gives a definite geometry to the complex ion.



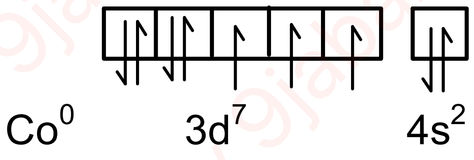
According to VSEPR theory for CH_4 to be formed, one of the 2s electron of carbon will be promoted to its empty 2p orbital. There would four unpaired electrons for bonding with hydrogen. However, this does not solve the problem as the 3-2p orbitals would be 90° to each other (p-orbitals are 90° to each other) but bond angles in CH_4 a tetrahedral molecule are 109.5°.

VBT is able to explain this phenomena using hybrid orbitals. In the case of CH_4 in order to for carbon to bond with 4-H atoms to form the stable compound, the 2s and 3-2p orbitals of carbon would mix to form a hybrid called sp^{3}orbitals. (Note the 2s and 2p of carbon are the valence orbitals i.e. orbitals in the outermost shell). They are four in number (1-s + 3-p = 4-sp^3). It has a regular tetrahedral shape (no lone pair) as described in VSEPR model.

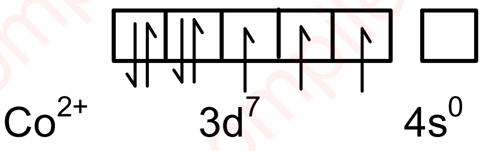


UNIT TWO – Hybridization in Transition Metal Complexes

$[Co(H_2O)_6]^{2+}$ This complex has a coordination number of 6 because Co has six water molecules bonding to it. Valence electronic configuration of cobalt in the +2 oxidation is $3d^7, 4s^0$



Co in its free state



Co in its bonded state

Each water molecule is coming with a lone pair of electrons (2 electrons each). In the +2 oxidation state the only empty orbital is the 4s, which can only accommodate one of the ligands. VBT is able to explain Co can coordinate with 6 molecules accommodating 12 electrons. With this theory one can predict the shape of the transition metal complex and its magnetic properties.

Application of VBT

1. Determine the oxidation number of the transition metal in the complex bearing in mind that the ligands may be charged or neutral **$[ML_n]^z$**.

(Oxidation state of metal 'x') + (charge on ligand 'y') = total oxidation state of complex 'z')

$$\mathbf{x + ny = z}$$
$$\mathbf{x = z - ny}$$

Neutral ligands		**Charge**	**Charged ligands**		**Charge**
aquo/aqua	H_2O	0	Chloro iodo	Cl^- I^-	-1 -1
ammine	NH_3	0	Fluoro bromo	F^- Br^-	-1 -1
carbonyl	CO	0	cyano	CN^-	-1
Ethylenediamine (en)	$H_3NCH_2CH_2NH_3$	0	hydroxo	OH^-	-1
nitrosyl	NO	0	Oxalate (ox)	$^{-}_{2}OC - CO_2^-$	-2

2. The number of ligands would give you an idea of how many orbitals would be used in hybridization. For example, 4 ligands could be an sp^3 hybridization, 6 ligands could be a d^2sp^3 hybridization.

3. We know that electrons would rather exist singly rather pair up. However, if the ligand involved is a "strong field ligand" then it will force the electrons to pair. This forced pairing occurs in 3d orbitals. The 4d and 5d orbitals are bigger and therefore they overlap more strongly with the orbitals of the ligands as compared to the 3d orbitals. In addition, because of the 4d and 5d orbitals are large it takes less energy to put the two electrons together into the same orbital therefore even when the ligand is a "weak field ligand" the electrons in 4d and 5d orbitals will be paired.

4. When all the electrons are paired it is diamagnetic complex and any unpaired electrons makes it paramagnetic.

5. The table below shows the relationship between the coordination number, type of hybridization and the shape the complex would have. This serves as a guide towards predicting the hybridization and shape of a complex.

Coordination number	Types of hybridization	Shape/Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[FeBr_4]^{2-}$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$
5*	sp^3d	Trigonal bipyramid	$[Cu(Cl_5)]^{3-}$
5*	dsp^3	Square pyramidal	$[Ni(CN)_5]^{3-}$
6	sp^3d^2 or d^2sp^3	Octahedral	$[Co(NH_3)_6]^{3+}$
6*	spd^4	Trigonal prismatic	$[Zr(Me)_6]^{2-}$

6. Experimental studies are always needed to confirm predictions such as the magnetic susceptibility and x-ray crystallography studies.

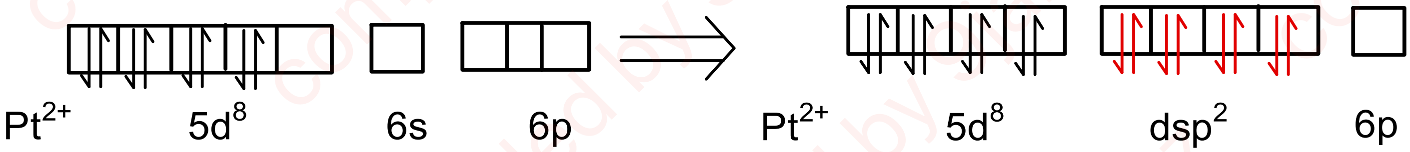
Worked examples

1. $[Pt(NH_3)_4]^{2+}$

Since NH_3 is a neutral molecule (having no charge) the oxidation number of Pt in the complex will be

$$x + (4 \times 0) = +2$$
$$x + 0 = +2$$
$$x = +2$$

Each ammonia molecule is donating a lone pair of electrons. Therefore, for Pt to accommodate these 8 electrons (from 4 NH_3) it would need to form 4 hybrid orbitals. The 5d orbital are large, they would bond strongly and it would rather pair the electrons. This would make the one of its 5d orbital vacant and then it would use the vacant 5d, 6s and 2 of its 6p orbitals generating a dsp^2 hybridization which is square planar in shape. The complex is diamagnetic – having no unpaired electrons.



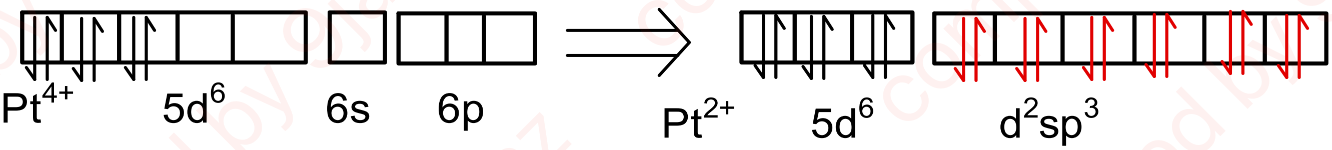
5d^8 and 6p are unhybridized and the red arrows in the dsp^2 orbital represents the electrons donated by the 4 NH_3 molecules.

$[PtCl_6]^{2-}$

Cl is charged species (-1) the oxidation number of Pt in the complex will be

$$x + (6 \times -1) = -2$$
$$x - 6 = -2$$
$$x = -2 + 6$$
$$x = +4$$

Each chloride atom is donating a lone pair of electrons therefore for Pt to accommodate these 12 electrons (from 6 Cl^-) a hybrid that is made up of 6 orbitals. With the 5d orbitals being large, they would bond strongly and can accommodate paired electrons. It would therefore make use of its vacant 2 of the vacant 5d, 6s and 3 of its 6p orbitals generating a d^2sp^3 hybridization which is octahedral in shape. This complex is also diamagnetic.



$5d^6$ is unhybridized and the red arrows in the d^2sp^3 orbitals represents the electrons donated by the 6 Cl^- ions.

$[Cu(CN)_4]^{3-}$

CN is charged species (-1) the oxidation number of Cu in the complex is +1.

Cu^0 $3d^{10}$ $4s^1$ **Cu^+** $3d^{10}$ $4s^0$

In this case the 3d orbital is completely filled hence each cyano molecule is donating a lone pair of electrons making a total of 8 electrons (2 electrons from each of the CN^-). Therefore, a hybrid that is made up of 4 orbitals would be required. It would therefore make use of its vacant 4s and three of its 4p orbitals generating a sp^3 hybridization which is tetrahedral in shape. This complex is also diamagnetic.

$[Cu(NH_3)_4]^{2+}$

NH_3 is a neutral molecule the oxidation number of Cu in the complex is +2.

Cu^0 $3d^{10}$ $4s^1$ **Cu^{2+}** $3d^9$ $4s^0$

Each ammonia molecule is donating a lone pair of electrons therefore for Cu to accommodate these 8 electrons (from 4 NH_3). This means that Cut would need to form a 4-hybrid orbital system. It would therefore make use of its vacant 4s and three of its 4p orbitals generating a sp^3 hybridization which is tetrahedral in shape. This complex is also paramagnetic because of the unpair electron.

Experimental studies revealed that the complex is not tetrahedral but square planar. This would mean that its hybridization is dsp^2. This is achieved by the promotion of the single unpaired electron from the 3d orbital one of the 4p orbital. Cu would then use the vacant 3d, 4s and the remaining 2- 4p orbitals to form dsp^2 hybridization.

$[Ni(CN)_4]^{2-}$ and $[Ni(Cl)_4]^{2-}$

In this case the oxidation number of Ni in both complexes is +2.

Ni^0 $3d^8\ 4s^2$ **Ni^{2+}** $3d^8\ 4s^0$

The cyano complex is square planar in shape and diamagnetic while the chloride complex is tetrahedral and paramagnetic. This is because the CN^- group can force pairing and are called strong field ligands while chloride cannot do this because it's a weak field ligand. Hence the hybridization of the cyano complex is **dsp^2** while the chloride is **sp^3.**

$[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ are both diamagnetic while **$[Fe(NH_3)_6]^{2+}$ and $[CoF_6]^{3-}$** are paramagnetic.

In both cases the oxidation number of Fe is +2 and that of Co is +3.

Fe^0 $3d^6\ 4s^2$ Fe^{2+} $3d^6\ 4s^0$

Co^0 $3d^7\ 4s^2$ **Co^{3+}** $3d^6\ 4s^0$

The presence of the cyano ligands force pairing so that the electrons in the 3d orbital occupy only 3 or these, leaving 2 vacant orbitals for which a **d^2sp^3** hybridization is formed.

Ammonia and fluoride ligands are weak field ligands and do not force pairing hence the unpaired electronic configuration is retained. To accommodate the six ligands instead of using the 3d orbitals they use their 4d orbitals generating a hybridization of **sp^3d^2** which is also octahedral.

Unlike the case of $[Cu(NH_3)_4]^{2+}$ which promoted its single unpaired electrons to the unhybridized 4p orbital $[Fe(NH_3)_6]^{2+}$ and $[Co(F)_6]^{3-}$ cannot do so it would require more energy to promote the three unpaired electrons from the 3d to the 4d orbitals.

UNIT THREE - Limitation to VBT

1. It cannot explain the spin state of complexes
2. Without experimental data it cannot predict accurately if a 4 coordinated complex is square planar or tetrahedral.
3. It cannot explain why transition metal complexes have varying colours.
4. It cannot also explain the electronic spectra of complexes.

MODULE THREE

CRYSTAL FIELD THEORY (CFT)

- Unit One – The theory
- Unit Two – Spectrochemical series and magnetic properties
- Unit Three – Jahn-Teller Distortion and Square Planar complexes
- UNIT Four – Crystal Field Stabilization Energy (CFSE)

UNIT ONE – The Theory

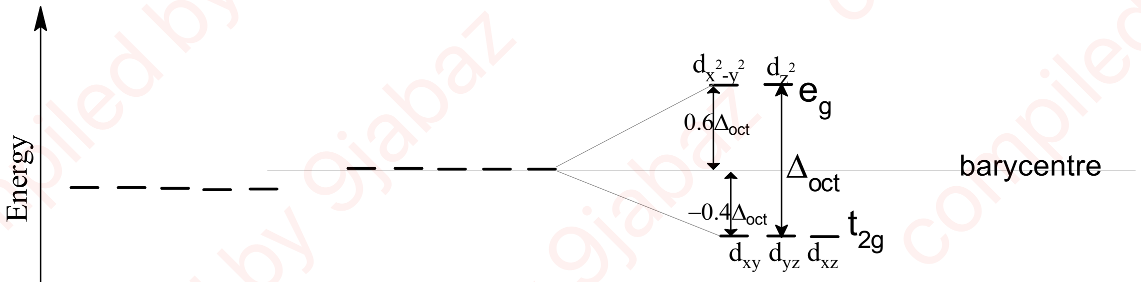
This theory explains the bonding between metals and ligands to be electrostatic where the metal is positively charged and the ligands are negative spherical point charge. Before the ligands approach the metal the d-orbitals are degenerate (i.e. equal in energy). Although the electrons of the ligands are attracted to the metal ion because it is positively charged but as the ligands approach closer to the metal ion there is also repulsion between the electrons in d-orbitals and ligands. This effect raises the energy of the d-orbital and consequently split them. The direction of approach of the ligand to the d-orbitals affect the type of splitting that occurs.

Considering the d-orbitals on the x-, y-, z- axis; the $d_{x^2-y^2}$ is pointing along the x- and y-axis and the d_{z^2} points along the z-axis. While the d_{xy} lies between the x- and y-axis; d_{yz} lies between the y- and z-axis and d_{xz} lies between the x- and z-axis.

- If the ligands are approaching directly along the x, y, z axis, then they affect the $d_{x^2-y^2}$ and d_{z^2} and then raise their energy while the d_{xy}, d_{yz} and d_{xz} are lowered in energy.
- If the ligands are approaching in between the x, y, z axis, then they affect the d_{xy}, d_{yz} and d_{xz} directly raising their energy while that of the $d_{x^2-y^2}$ and d_{z^2} are lowered.

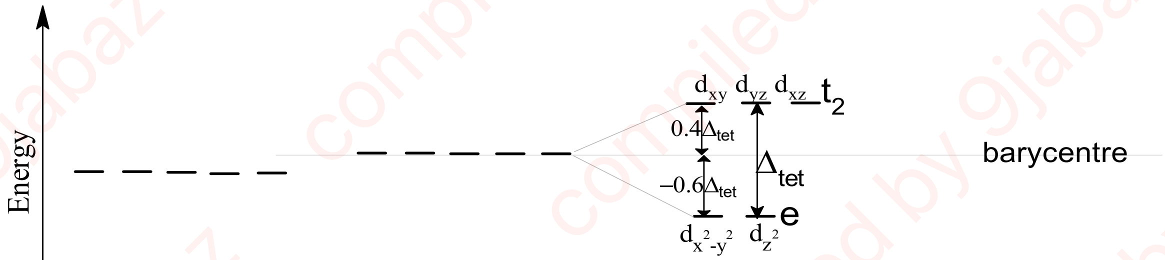
Crystal field is the field created by the electrostatic interaction as the point charges are arranged in an orderly manner (like crystal structure). The difference in energy between the higher and lower energy level of the crystal field splitting is given by Δ.

In an octahedral environment the d-orbital are split as illustrated in the diagram below. The d_{xy}, d_{yz} and d_{xz} are lowered in energy hence are stabilized and possess a t$_{2g}$ symmetry while the $d_{x^2-y^2}$ and d_{z^2} are higher in energy are destabilized and possess e$_g$ symmetry. Therefore the energy difference between the t$_{2g}$ – orbitals and the e$_g$ – orbitals is labelled as Δ_{oct} which is the crystal field splitting parameter in an octahedral field. The orbital in the e$_g$ set are raised by $0.6\Delta_{oct}$($\frac{3}{5}\Delta_{\text{oct}}$) with respect to the barycentre while those of the t$_{2g}$ set are lowered by $-0.4\Delta_{oct}$ (-$\frac{2}{5}$ Δ_{oct}).



Splitting pattern in an octahedral field

In a tetrahedral environment the ligands approach the d_{xy}, d_{yz} and d_{xz} directly and this result in a splitting which is the inverted form of the octahedral complex. So the d_{xy}, d_{yz} and d_{xz} are raised and the $d_{x^2-y^2}$ and d_{z^2} lowered. Because this is a tetrahedral complex, the $d_{x^2-y^2}$ and d_{z^2} are now labelled **e** and the d_{xy}, d_{yz} and d_{xz} are labelled **t$_2$**. The t$_2$ orbitals are raised by $0.4\Delta_{tet}$ ($\frac{2}{5}\Delta_{\text{tet}}$) and e orbitals are lowered by $-0.6\Delta_{oct}$ (-$\frac{3}{5}\Delta_{\text{tet}}$) with respect to the barycentre. However the Δ_{tet} is less than Δ_{oct} i.e. $\boldsymbol{\Delta_{\text{tet}} = \frac{4}{9}\Delta_{\text{oct}}}$.



Splitting pattern in an tetrahedral field

UNIT TWO – Spectrochemical series and magnetic properties

The magnitude (size) of Δ depends on the strength of the ligands. Ligands that result in large values of Δ are referred to as strong field ligands and those that result in small values of Δ are called weak field ligands. The arrangement of ligands according to their field strength is called the spectrochemical series. Strong field ligands force the electrons in the d-orbitals to pair up. Electrons fill in singly first before paring, however due to the wide crystal field splitting caused by strong field ligands, the electrons cannot enter the raised d- orbitals and would rather pair up in the lowered d-orbitals.

These will force pairing

$$I^- < Br^- < Cl^- < OH^- < RCO_2^- < F^- < H_2O < NCS < \overbrace{NH_3 < en < NO_2 < Phen < CN \cong CO}$$

$$\xrightarrow{\hspace{30em}}$$

Order of increasing field strength

Note that in some case NH_3 can force pairing.

Another factor that affects the crystal field energy is the oxidation state of the metals ions:

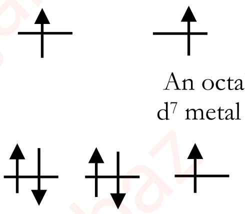
Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV)

$$\xrightarrow{\hspace{30em}}$$

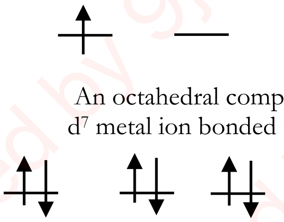
Increasing field strength

(i) Increase in oxidation number: the higher the oxidation number the smaller the size of the ion but the greater the charge density (charge/volume). As result shorter metal-ligand distance hence stronger interactions and this increases the crystal field strength.

(ii) Going down a group shows that the large size of the 4d and 5d orbitals has a greater impact than the 3d hence stronger interaction and this leads to larger splitting of these d-orbitals hence large Δ.



An octahedral complex made up of d^7 metal ion bonded to a weak field ligand

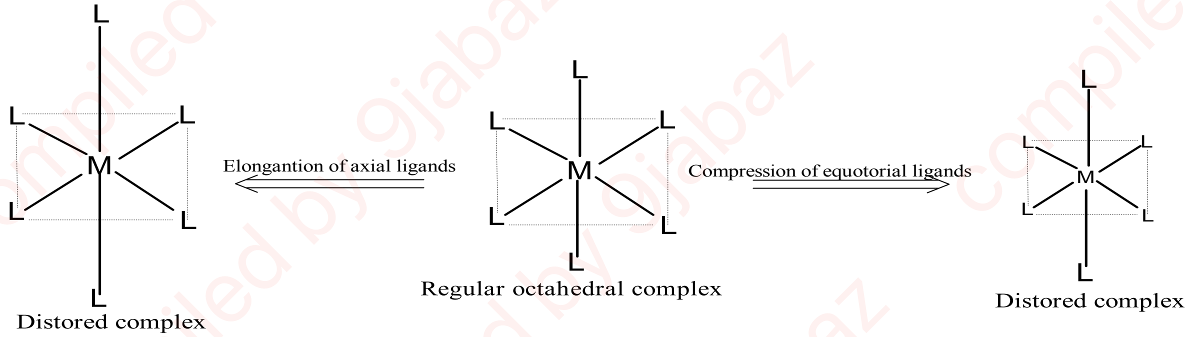


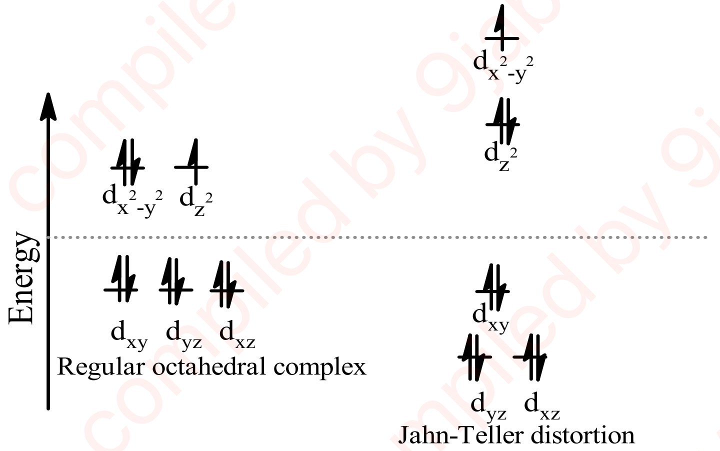
An octahedral complex made up of d^7 metal ion bonded to a strong field ligand

When electrons are forced to pair the complex is referred to as being **low spin** and in the absence of forced pairing it is described as **high spin.** Low spin is a state where there are few paired electrons while high spin state has a higher number of unpaired electrons. These occur in in d^4 to d^8.

UNIT THREE - Jahn-Teller Distortion and Square Planar Complexes

An octahedral complex undergoes distortion in its shape. This distortion can take place either by the elongation of the axial ligands or the compression of equatorial ligands. This effect occurs when the ground state electronic configuration is asymmetrically filled making the geometry unstable and in order to bring about stability the distortion occurs. A common example is d^9 complexes of Cu(II). It can also occur with high spin d^4 and low spin d^7. This distortion is called **Jahn-Teller Distortion** (or tetragonal distortion).



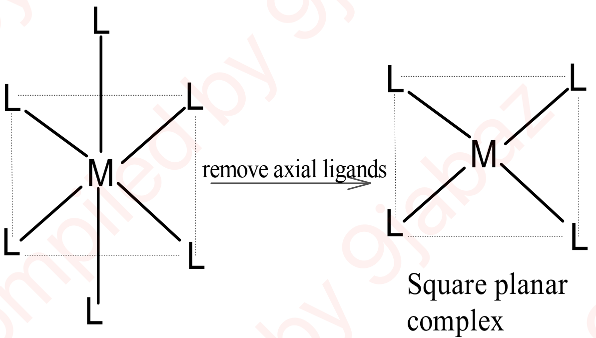


The asymetrical filling of the e_g orbital caused the distortion

There are no ligands approaching the metal along the z-axis and this greatly stabilize (lowers) the d_{z^2} orbital as well as lower the energy of the d_{xz} and d_{yz}while the $d_{x^2-y^2}$ and d_{xy} will be raised.

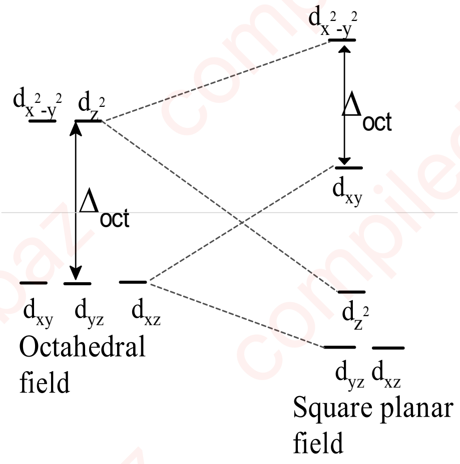
A square planar shape can be derived from the octahedral geometry by removing the two axial ligands (ligands along the z-axis). This would greatly stabilize the d_{z^2} orbital as well as lower the energy of the d_{xz} and d_{yz}while the $d_{x^2-y^2}$ and d_{xy} will be raised.

For example, some Cu^{2+} complexes are square planar instead of the expected octahedral. This is due to Jahn-Teller distortion, bonding at the equatorial position readily occurs as the bonds are short. However, the weak interactions at the elongated axial position result in the ease to lose these ligands, yielding a square planar complex rather than octahedral.



Octahedral complex

Square planar complex



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UNIT FOUR - Crystal field stabilization energy (CFSE)

CFSE is defined as the energy of the electronic configuration in the ligand field (LF) (splitting of d orbitals) minus the energy of the electronic configuration in the isotropic field (IF) (before splitting). This is the decrease in energy resulting from the crystal field splitting.

$$\mathbf{CFSE = E_{LF} - E_{IF}}$$

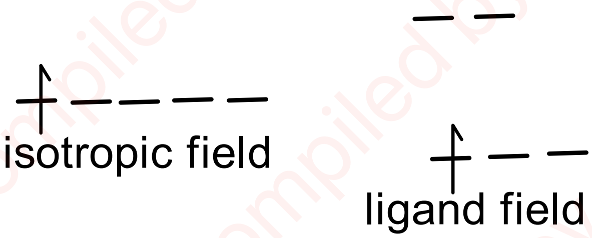
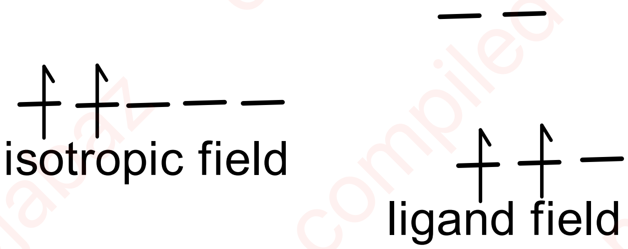
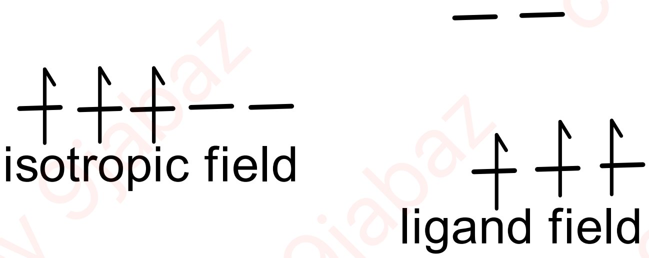
$$\text{Energy} = (\text{number of electrons n}) \times (\text{corresponding splitting parameter}\Delta) + (\text{number of paired electrons m}) \times (\text{spin pair energy P})$$

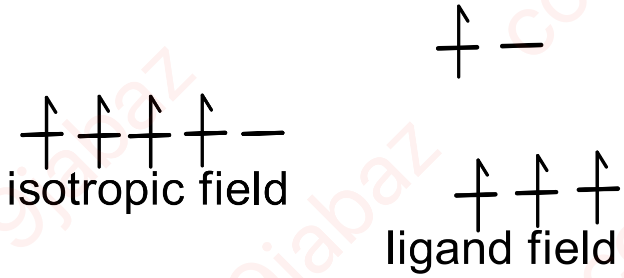
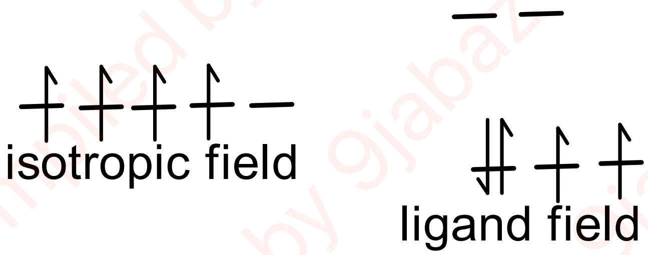
$$E_{LF} = (n\Delta + mP)$$

In an isotropic field both $\mathbf{\Delta_{oct}}$ **and** $\mathbf{\Delta_{tet} = 0}$ because there is no splitting

$$E_{IF} = (mP)$$

In an octahedral environment the CFSE d-orbital are as illustrated.

	For a d¹ (t_{2g}^{1}) $E_{LF} = 1 \times (-0.4\Delta_{oct}) = -0.4\Delta_{oct}$ $E_{IF} = 0$ $\mathrm{CFSE = E_{LF} - E_{IF}} = \mathbf{-0.4\Delta_{oct}}$
	For a d² (t_{2g}^{2}) $E_{LF} = 2 \times (-0.4\Delta_{oct}) = -0.8\Delta_{oct}$ $E_{IF} = 0$ $\mathrm{CFSE = E_{LF} - E_{IF}} = \mathbf{-0.8\Delta_{oct}}$
	For a d³ (t_{2g}^{3}) $E_{LF} = 3 \times (-0.4\Delta_{oct}) = -1.2\Delta_{oct}$ $E_{IF} = 0$ $\mathrm{CFSE = E_{LF} - E_{IF}} = \mathbf{-1.2\Delta_{oct}}$

	For a d^4, there are two situations (i) No pairing (t_{2g}^3, e_g^1) $E_{LF} = 3 \times (-0.4\Delta_{oct}) + (1 \times 0.6\Delta_{oct})$ $-06\Delta_{oct}$ $E_{IF} = 0$ $\mathrm{CFSE} = \mathrm{E_{LF}} - \mathrm{E_{IF}} = \mathbf{-0.6\Delta_{oct}}$
	(ii) Pairing (t_{2g}^4, e_g^0) $E_{LF} = 4 \times (-0.4\Delta_{oct}) + 1p =$ $-1.6\Delta_{oct} + P$ $E_{IF} = 0$ $\mathrm{CFSE} = \mathrm{E_{LF}} - \mathrm{E_{IF}} = \mathbf{-1.6\Delta_{oct} + \mathit{P}}$

In a case like this the preferred configuration is the one with lower energy. Pairing is often avoided, however when it does occur the pairing electrons experience strong repulsion called the pairing energy P. When there are no forced pairing electrons will fill in singly before pairing (high spin d^4 – d^8).

If $\Delta_{oct} < P$, then electrons will not pair. This is a weak field.

If $\Delta_{oct} > P$, then electrons will pair. This is a strong field.

Class work

Calculate the crystal field stabilization energy of (i) high spin d^7 (ii) low spin d^7.

For a high spin d^7 (t_{2g}^5, e_g^2)

$E_{LF} = 5 \times (-0.4\Delta_{oct}) + 2P + (2 \times 0.6\Delta_{oct})$

$(-2.0\Delta_{oct}) + 2P + (1.2\Delta_{oct})$

$(-0.8\Delta_{oct}) + 2P$

$E_{IF} = 2 \times P = 2P$

$\mathrm{CFSE} = \mathrm{E_{LF}} - \mathrm{E_{IF}} = [(-0.8\Delta_{oct}) + 2P] - 2P$

$CFSE = -0.8\Delta_{oct}$

For a low spin d^7($\boldsymbol{t_{2g}^6, e_g^1}$)

$E_{LF} = 6 \times (-0.4\Delta_{oct}) + 3P + \ (1 \times 0.6\Delta_{oct})$

$(-2.4\Delta_{oct}) + 3P + \ (0.6\Delta_{oct}) = -1.8\Delta_{oct}$

$(-1.8\Delta_{oct}) + 3P$

$E_{IF} = 2 \times P = 2P$

$\mathrm{CFSE} = \mathrm{E_{LF}} - \mathrm{E_{IF}} = [(-1.8\Delta_{oct}) + 3P] - 2P$

$CFSE = -1.8\Delta_{oct} + P$

The same is applicable in a tetrahedral environment only this time instead of Δ_{oct}; Δ_{tet} would be used. (Remember to reverse the orbitals)

ASSIGNMENT #1

CHM401

MODULE ONE AND TWO

1. What is the expected and true valance electronic configuration of copper, silver and gold? What do you think is the reason for their anomaly?

2. What is the IUPAC name of the compounds below?

   i. $Ca[Ni(Br)_4]$
   ii. $[Ni(en)_2(Br)_2]Br_2$
   iii. $[Ni(CO)_4]Br_2$

   Predict the hybridization, shape and magnetic property of the complexes (i) and (iii)

3. Take a look at the table below and classify each item as hard acid, hard base, soft acid or soft base.

V^{3+}	Ti^{4+}	Fe^{2+}	CO	OH^-
F^-	CN^-	V^{2+}	Fe^{3+}	NO_2^-

4. The electronic configuration of osmium is $[\boldsymbol{Xe}], \mathbf{4}\boldsymbol{f}^{\mathbf{14}}, \mathbf{5}\boldsymbol{d}^{\mathbf{6}}, \mathbf{6}\boldsymbol{s}^{\mathbf{2}}$ and that of iron is $[\boldsymbol{Ar}], \mathbf{3}\boldsymbol{d}^{\mathbf{6}}, \mathbf{4}\boldsymbol{s}^{\mathbf{2}}$**.** What type of hybridization and magnetic property would $[\boldsymbol{OsCl_6}]^{\mathbf{4-}}$ and $[\boldsymbol{FeCl_6}]^{\mathbf{4-}}$ have since both are octahedral complexes?

5. (a) In not more than 10 line discuss valence bond theory (b) mention its limitations.

Marking Guide to Assignment One

Assigmment 1

1.

	Expected E.C	True E.C
Cu	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9\,4s^2$	$1s^2.2s^2\,2p^6\,3s^2\,3p^6\,3d^{10},4s^1$
Ag	[Kr] $4d^9\,5s^2$	[Kr] $4d^{10},\,5s^1$
Au	[Xe] $5d^9\,6s^2$	[Xe] $5d^{10}\,6s^1$

10

$[Kr] = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6$

$[Xe] = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6$

The reason for this anomanly

1. Generally stability is attained with an orbital is half or completely filled.
2. In addition to this 5s & 6s orbital ~~requre~~ more energy to retain paired electrons, hence they would rather not. [For Ag & Au]

②

Find oxidation state of Ni in each complex, let it be x

~~Ca~~ $[NiBr_4] = 0$

$+2 + x + 4(-1) = 0$

$x + 2 - 4 = 0$

$x = +2$

$[Ni(en)_2Br_2]Br_2 = 0$

$[Ni(en)_2Br_2] + 2(-1) + 2(-1) = 0$

$x + 2(0) + 2(-1) + 2(-1) = 0$

$x + 0 - 2 - 2 = 0$

$x = +4$

$[Ni(CO)_4]Br_2 = 0$

$x + 4(0) - 2 = 0$

$x - 2 = 0$

$x = +2$

①

$Ca[NiBr_4]$

Calcium tetrabromonickelate(II)

06

$[Ni(en)_2Br_2]Br_2$

Dibromobis(ethylenediamine)nickel(IV) bromide

$[Ni(CO)_4]Br_2$

Tetracarbonylnickel(II) Bromide

Oxidation state of Nickel in $Ca[Ni(Br_4)]$ ~~Ca~~ $= +2$

Valence electronic configuration of Ni

$Ni^0\ 3d^8\,4s^2$

$\underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}\quad \underset{4s^2}{\uparrow\downarrow}$

$Ni^{2+}\ 3d^8\,4s^0$

$\underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}\quad \underset{4s^0}{\_}$

In order to accommodate the 4 pairs of electron (ie 8 e's) from ~~the~~ 4 Br^-, nickel will need an ~~that will~~ ~~accommodate~~ that has 4 hybrid hybridization orbitals only. This could be sp^3 or dsp^2. Br^- is a weak field ligand and will not force pairing. Therefore nickel will use it vacant 4S and 4p orbitals to form sp^3 hybrid orbitals

10

$\underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}\quad \underset{4s}{\_}\quad \underset{4p}{\_\ \_\ \_} \Longrightarrow \underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}\quad \underset{sp^3}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}$

The hybridization of the $Ca[NiBr_4] = sp^3$

Shape = Tetrahedral

Magnetic property = paramagnetic

②

$[Ni(en)_2Br_2]Br_2$, oxidation state of Ni = +4

valence electronic configuration of Ni

Ni^0 $3d^8$ $4s^2$

$\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}\ \underbrace{\uparrow\downarrow}_{4s}$ ✓

Ni^{4+} $3d^6$ $4s^0$

$\underbrace{\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{3d^6}\ \underbrace{\ \ }_{4s^0}$ ✓

Ethylenediammine is a bidentate ligand, and because there are 2 of them. They coordinate to nickel in 4 place plus the 2 Br^- ion. Thin make a coordination number of 6. In order to accommodate the 6 pairs of electron (ie $12e^-$) nickel will need a hybridization that has 6 hybrid orbitals only. This could be sp^3d^2 or d^2sp^3, Ethylene-diammine is a strong field ligand ~~and~~ will force pair, over the 2 weak field Br^- ligand.

15

Ni^{4+} $\underbrace{\uparrow\downarrow\ \uparrow\ \_\ \uparrow\ \uparrow\ \uparrow}_{3d^6}\ \underbrace{\_}_{4s}\ \underbrace{\_\ \_\ \_}_{4p}$ $\xrightarrow[\text{pairing}]{\text{force}}$ Ni^{4+} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \_\ \_}_{3d^6}\ \underbrace{\_}_{4s}\ \underbrace{\_\ \_\ \_}_{4p}$

It would therefore make use of ~~its~~ 2 vacant 3d orbital, the 4s and the 4p orbitals to form d^2sp^3 hybridization

Ni^{4+} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \_\ \_}_{3d}\ \underbrace{\_}_{4s}\ \underbrace{\_\ \_\ \_}_{4p}$ $\xrightarrow{\text{hybridization}}$ Ni^{4+} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{3d^6}\ \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{d^2sp^3}$

The hybridization of $[Ni(en)_2Br_2]Br_2$ ⇒ d^2sp^3

Shape ⇒ Octahedral

magnetic properties ⇒ diamagnetic

③

$[Ni(CO)_4]Br_2$. oxidation State = +2

Valence electronic configuration of Ni

Ni^0 $3d^8$ $4s^2$

$\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}\ \underbrace{\uparrow\downarrow}_{4s}$ ✓

Ni^{2+} $3d^8$ $4s^0$

$\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}\ \underbrace{\_}_{4s^0}$

In order to accommodate the 4 pairs of e^- from CO, nickel will need to form a hybridization that has 4 hybrid orbitals. This could be sp^3 or dsp^2. Since CO is a strong field ligand ~~it~~ would force pairing

13

Ni^{2+} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}\ \_\ \underbrace{\_}_{4s^0}$ $\xrightarrow[\text{pairing}]{\text{force}}$ $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \_}_{3d^8}\ \underbrace{\_}_{4s^0}$

It would therefore make use of the single vacant 3d orbital, the 4s and 2 of the 4p orbitals to form dsp^2 hybridization

Ni^{2+} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \_}_{3d^8}\ \underbrace{\_}_{4s}\ \underbrace{\_\ \_\ \_}_{4p}$ $\xrightarrow{\text{hybridization}}$ Ni^{2+} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{3d^8}\ \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{dsp^2}\ \underbrace{\_}_{4p}$

The hybridization of $[Ni(CO)_4]Br_2$ = dsp^2

Shape ⇒ Square planar

magnetic property ⇒ diamagnetic

④

Acid		Base	
Hard	Soft	Hard	Soft
V^{3+} ✓	V^{2+} ✓	F^- ✓	CO ✓
Fe^{3+} ✓	Fe^{2+} ✓	OH^- ✓	CN^- ✓
Tl^{4+} ✓			NO_2^- (intermediate) ✓

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Osmium = [Xe] $4f^{14}$, $5d^6$, $6s^2$

Iron = [Ar] $3d^6$, $4s^2$

Oxidation state of osmium in $[OsCl_6]^{4-}$, = x

$$x + 6(-1) = -4$$
$$x - 6 = -4$$
$$x = \cancel{-}4 + 6 = \underline{+2}.$$ ✓

Oxidation state of Iron in $[FeCl_6]^{4-}$ = x

$$x + 6(-1) = -4$$
$$x - 6 = -4$$
$$x = \underline{\underline{+2}}$$ ✓

⑤

Valence electronic configuration of Os

Os^0 $5d^6$ $6s^2$

$\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}_{5d}$ $\underline{\uparrow\downarrow}_{6s}$ ✓

Os^{2+} $5d^6$ $6s^0$

$\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}_{5d^6}$ $\underline{\ \ }_{6s^0}$ ✓

Cl^- is a weak field ligand. ✓

Os 5d orbitals are large and so will accommodate paired electrons, hence force pairing will occur. ✓

Os^{2+} $\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}_{5d^6}$ $\underline{\ \ }_{6s^0}$ $\xrightarrow[\text{forced pair}]{}$ $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}_{5d^6}\ \underline{\ \ }\ \underline{\ \ }$ $\underline{\ \ }_{6s}$ ✓

In order to accommodate the ~~6~~ pair electrons coming from ~~each of~~ 6 ~~Cl~~ Cl^- group (i.e. 12 e^-) Os will be ~~to~~ form a hybridization with 6 hybrid orbitals. Because of the forced pair due to the large 5d orbital. It would make use of it 2 vacant 5d orbital, it 6s and 3 of it 6p to form d^2sp^3 hybridization. ✓

Os^{2+} $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}_{5d}\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }_{6p}$ $\xrightarrow[\text{hybridizatio}]{}$ $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}_{5d^6}$ $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}_{d^2sp^3}$ ✓

The hybridization is d^2sp^3 ✓

Magnetic property = diamagnetic ✓

⑥

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valence electronic configuration of Fe.

Fe^0 $3d^6$ $4s^2$

↑↓ ↑ ↑ ↑ ↑ ($3d^6$) ↑↓ ($4s$)

Fe^{2+} $3d^6$ $4s^2$

↑↓ ↑ ↑ ↑ ↑ ($3d^6$) __ ($4s^0$)

Cl^- is a weak field ligand and therefor cannot force pair. the 3d orbital is small and will require a strong field ligand to force pair. In order to accommodate the 6 pair of electrons from 6 Cl^- groups; (ie 12 e^-). Fe needs to form a hybridization that will have only 6 hybrid orbitals. To do this it will make use of its 4s, 4p and 2 of its 4d orbitals to form sp^3d^2 hybridization

Fe ↑↓ ↑ ↑ ↑ ↑ (3d) __ (4s) __ __ __ (4p) __ __ __ __ __ (4d)

$\xrightarrow{\text{hybridization}}$ ↑↓ ↑ ↑ ↑ ↑ ($3d^6$ unhybridized) ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ (sp^3d^2) __ __ __ (4d unhybridized)

The hybridization is sp^3d^2

Magnetic properties = paramagnetic

7

bioconjugate are

MODULE FOUR

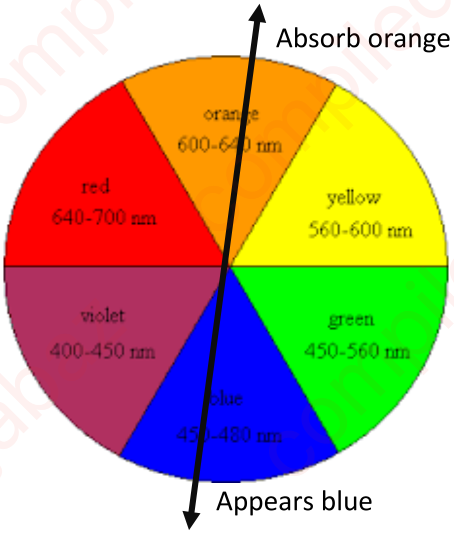
ELECTRONIC SPECTRA (in CFT)

- UNIT ONE – Colours
- UNIT TWO – Electronic Transitions in transition metal complexes
- UNIT THREE – Selection rule
- UNIT FOUR - Charge transfer absorptions

UNIT ONE – Colours

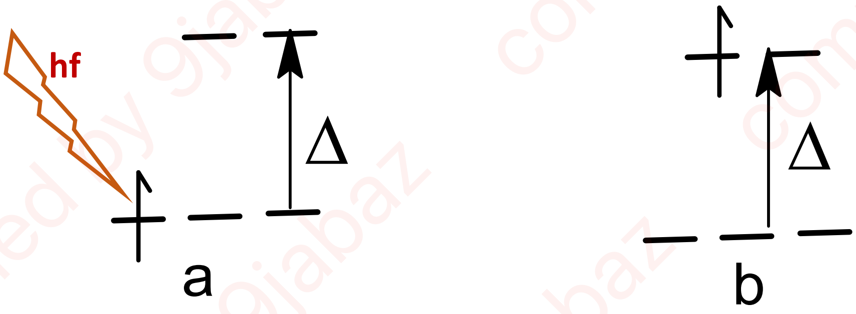
An electronic spectrum is a measure of the amount of light absorbed by molecules. The region of the electromagnetic spectrum that interacts with the electrons of the molecules is the ultraviolet and visible region. The spectra are measure using uv-visible machine.

We can see and distinguish between colours because our eyes respond to visible light. A substance appears black because it absorbs all the visible light. If it absorbs no visible light it will be white or colorless. The visible region of light (400 nm – 700 nm) is made up red, orange, yellow, green, blue and purple. An object appears green if it absorbs all light and reflects the green light. An object also looks green if it reflects all the colors except red which it absorbs, i.e. the complementary colour of green (colour circle). $[Cu(H_2O)]_6SO_4$ is blue in colour (ie what we see) but this means it absorbs orange region (600 – 640 nm).



UNIT TWO – Electronic Transitions in Transition Metal Complexes

Light is made up of particles of called photons and they have quantized energy. For transition metal complexes the energy of the photon is equal to the energy of the crystal field split, which is has a corresponding wavelength

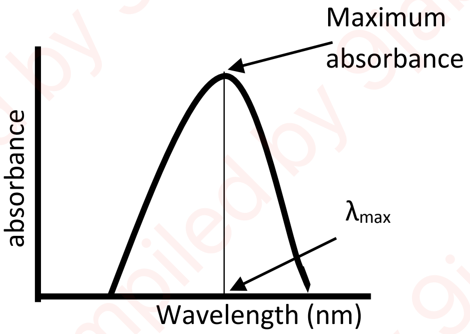


(a) The process of photon absorption
(b) Electrons gaining energy undergo transition from $t_{2g} \rightarrow e_g$

Let us assume that the maximum absorbance of $[Cu(H_2O)_6]SO_4$ occurs at a wavelength of 600 nm then the crystal field splitting energy can be found using the equation,

$$E = hf \quad \left(f = \frac{c}{\lambda}\right)$$

$$\boldsymbol{E = \Delta = h\frac{c}{\lambda}}$$



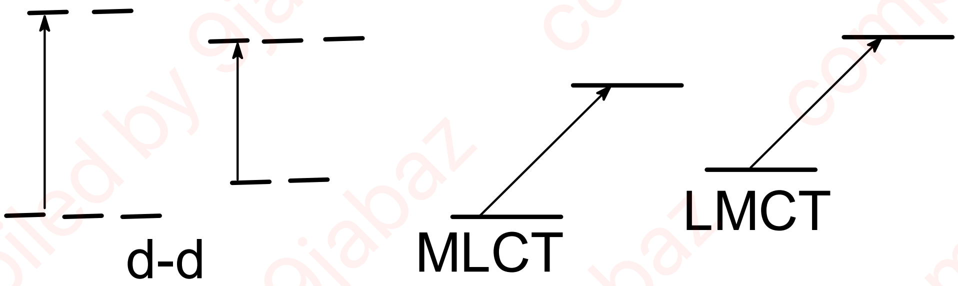
Where h is planks constant (6.63 x 10^{-34}Js) c is speed of light (3.0 x10^8 m/s), and λ wavelength (nm). λ_{max} = wavelength at maximum absorbance.

$$\Delta = \boldsymbol{h}\frac{c}{\lambda} = 6.63 \times 10^{-34}\mathrm{Js} \times \frac{3\times10^8\cancel{\mathrm{m}/\mathrm{s}}}{600\times10^{-9}\cancel{\mathrm{m}}} = \mathbf{3.32 \times 10^{-19}}\boldsymbol{J}.$$

Due to the fact the crystal field stabilization energy of tetrahedral complexes are lower than that of octahedral complexes ($\Delta_{tet} = \frac{4}{9}\Delta_{oct}$), the absorption wavelength of tetrahedral complexes occur in longer wavelengths than the octahedral complexes.

The absorption spectra of coordination complexes arise from the transition of electrons

a. In the d orbitals within the metal (d-d transition)
b. From the metal to the ligand (Metal to Ligand Charge Transfer (MLCT))
c. From the ligand to the metal (Ligand to Metal Charge Transfer (LMCT))



(The reason why transition metals are coloured is simple because the energy of d-d transition occurs with the visible region of the electromagnetic spectrum).

UNIT THREE – Selection Rule

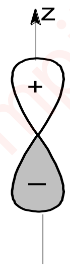
When a compound has a high molar absorptivity it means it would have very intense absorbance (high absorbance) and would be observed to have very deep colours even at very low concentrations. While substances with pale colour, have low absorbance hence would have low molar absorptivity. The value of absorbance is obtained from the electronic spectra.

$$A \propto c \quad \therefore \quad \boldsymbol{A = \varepsilon c l} \quad where\ \varepsilon\ and\ l\ are\ constants$$

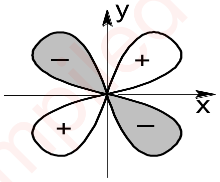
A= absorbance,
ε = molar absorptivity/molar extinction coefficient,
l = path length,
c = concentration

The reason why there is that difference in molar absorptivity can be explained using the **<u>SELECTION RULES</u>**. Not all electronic transitions are allowed but they occur. These are forbidden transitions. It is these forbidden transitions that result in low molar absorptivity.

1. **Laporte selection rule**- There must be a change in parity (sign of wave function **g-gerade u-ungerade**) during an electronic transition.
   A gerade 'g' orbital is one where an inversion operation leads to no change in phase of the orbitals. When there is a change in phase then its ungerade 'u'.



p_x - ungerade



d_{xy} - gerade

   This occurs in centrosymmetrical molecules like octahedral complexes. On the other hand, tetrahedral molecules have no center of symmetry; hence the labels 'g' and 'u' cannot be used.
   Allowed transition g ↔ u i.e. s→p, p→d, d→f
   Forbidden transition g ↔ g, u ↔ u i.e. s→s, p→p, **d→d**, f→f, s→d, p→f etc.

Therefor any orbital that has a center of symmetry its electronic transition would be forbidden for example d-orbitals.

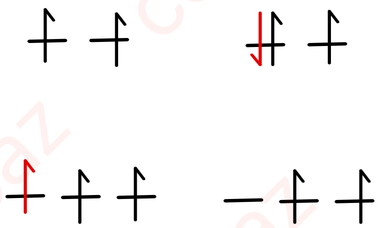
If the complex as a whole as a centre of symmetry, then would also produce weak absorbance. Octahedral complexes are centrosymmetric and the electronic transition should not be observed but as a result of molecular vibration there is a temporary loss of the center of symmetry. This is because during molecular vibrations there is mixing of the d and p orbitals and these vibrations last longer than the electron transition. This is referred to as vibronic coupling. Hence although they are forbidden, they are also observed.
However tetrahedral complexes are more intense in colour than octahedral complexes because they are non-centrosymmetric as in this case the mixing of p and d orbitals occurs to a greater extent.

2. **Spin selection rule**- There must not be a change in spin of the electron (direction of spin) during electronic transition.

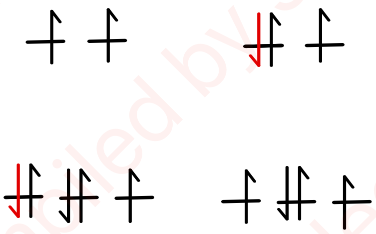
Allow transition	singlet to singlet, or triplet to triplet
Forbidden transition	singlet to triplet or triplet to singlet

Spin forbidden transitions become allowed when spin-orbit coupling occurs resulting in weak spin forbidden bands.

MnCl₂ and CoCl₂ were dissolved in water, they each form high spin complexes [Mn(H₂O)₆]Cl₂ and [Co(H₂O)₆]Cl₂. The solution MnCl₂ was very pale pink while CoCl₂ was red (not pale). Explain why.



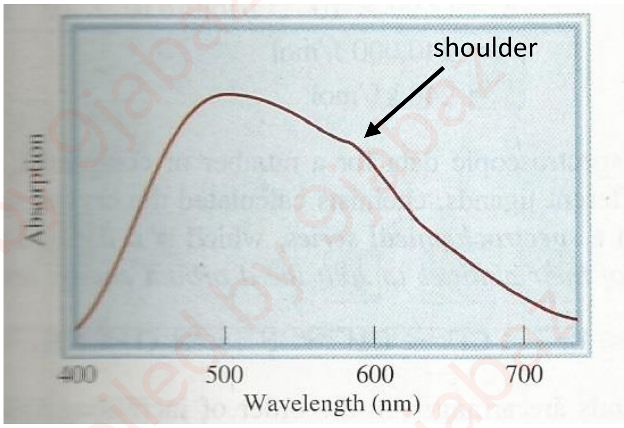
$[Mn(H_2O)_6]^{2+}$
change in spin from clockwise to anticlockwise (red)



$[Co(H_2O)_6]^{2+}$
No change in spin (red)

The Mn and Co complexes have similar colours (pink and red) hence they must be absorbing light between 490 nm and 560 nm. However $[Mn(H_2O)_6]Cl_2$ is pale because its transition is spin forbidden while that of $[Co(H_2O)_6]Cl_2$ is spin allowed. Note that both complexes are Laporte forbidden because they are both octahedral complexes and therefore centrosymmetrical.

The electronic spectra of d^1 should be one broad band because it has just one electron but in this case $[Ti(H_2O)_6]^{3+}$ there in the presence of a shoulder indicating that the absorption is actually two closely spaced bands.



Electronic spectrum of $[Ti(H_2O)_6]^{3+}$

The transition that occurred was a $e_g \leftarrow t_{2g}$. The shoulder is as a result of Jahn-Teller effect taking place in the excited state e_g. This is because the single electron entering the e_g cause it to lose its degeneracy. The energy difference between the orbitals is small. Note the same effect occurs in the ground state t_{2g} but the loss of degeneracy is even smaller, hence ignored. There are two possible transitions from the ground state to the excited. These transitions are closed in energy and the spectrum exhibit two absorption which are of similar wavelength.

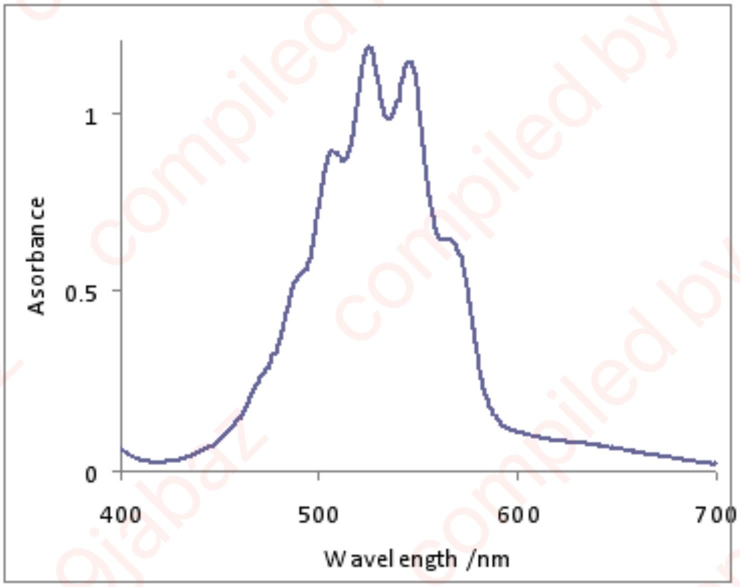
UNIT FOUR - Charge Transfer Absorptions

Ligand-to-Metal Charge Transfer (LMCT): This a transfer of an electron from a ligand which has lone pairs of electron of relatively high energy to the vacant low lying d orbitals of the metal has occurred. These ligands can easily be oxidized (lose an electron) when bonded to a central metal that can easily be reduced (gain electron because they are usually in a higher oxidation state).

Metal-to-Ligand charge transfer (MLTC): On the other hand, this occurs when metal can easily be oxidized and the coordinating ligands can be readily reduced. MLCT occurs when the ligands have vacant low-lying π* orbitals for example CO, py, bpy, phen and other heterocylic aromatic compounds.

Both LMTC and MLTC bands can occur in the uv or the visible region of the electromagnetic spectrum. However, for it to occur in the visible region then the orbitals of the ligand and metals must be very close in energy.

The deep (intense) purple colour of aqueous solution of $KMnO_4$ is as a result of intense LMCT occurring in the visible region of the electromagnetic spectrum. This transition is a result of an electron promoted from the orbital of the oxygen mainly the lone pair to the vacant orbitals of manganese. This transition is both spin as well as symmetry allowed.



Absorption spectra of $KMnO_4$ LMCT, responsible for the deep purple colour

Types of Transition	**ε_{max} ($dm^3mol^{-1}cm^{-1}$)**	**Examples**
Laporte & spin-forbidden	<1	Centrosymmetric complex e.g $[Mn(H_2O)_6]^{2+}$ (d^5)
Laporte - forbidden, spin-allowed	1 – 10	Centrosymmetric complex e.g $[Ti(H_2O)_6]^{3+}$ (d^1)
Laporte - partially allowed, spin-allowed	10 – 1000	Non-centrosymmetric complexes e.g tetrahedral $[NiCl_4]^{2-}$
Laporte - allowed, spin-allowed	1000 - 50 000	Charge transfers e.g. $[MnO_4]^-$

Limitation of CFT

1. The theory is based on the fact the interaction between metal and ligand are purely electrostatic and not considering the covalent nature of their bonds.
2. In this theory the s and p valence orbitals are ignored. It is based only on the d orbitals of the metal
3. It cannot explain why some ligands are weak field ligands and other are strong field ligands.
4. It cannot account for the pi-bonds found in certain complexes as well as back bonding.
5. It does not consider the interaction of the orbitals of the ligand with the metal.
   CFT cannot explain all the electronic spectra observed in transition metal complexes.

MODULE FIVE

LIGAND FIELD THEORY (LFT)

- UNIT ONE – About LFT
- UNIT TWO – For complexes only σ– bonds and (σ & π)– bonds under O_h symmetry
- UNIT THREE – Summary of LFT

UNIT ONE - About LFT

Ligand-field theory is more powerful than either the valence-bond or crystal-field theories. It takes into account all the limitation of VBT and CFT. It is based on molecular orbital theory (MOT) where atomic orbitals (AO) overlap to create molecular orbital (MO) i.e. a linear combination of atomic orbital (LCAO).

Recall that when atomic orbital overlap, they form molecular orbital comprising of a set of bonding MO and a set of antibonding MO. Lateral overlapping of AO yields σ-bonds while vertical overlapping yields π–bond. MOT also takes into account symmetry and of course group theory.

A transition metal ion has nine valence atomic orbitals - consisting of five *n*d, three (*n*+1)p, and one (*n*+1)s orbitals e.g. 3d, 4s and 4p. Considering only the first row transition metals; their valence AO are 3d, 4s, 4p, in an octahedral environment, we shall be taking a look at 2 cases (1) when there are only sigma bonds (2) when there are pi bonds.

The symmetry of each AO is listed below.

Metal orbital	Symmetry	Degeneracy
s	a_{1g}	1
p_x p_y p_x	t_{1u}	3
d_{xy} d_{yz} d_{xz}	t_{2g}	3
$d_{x^2-y^2}$ d_{z^2}	e_g	2

For the 6 ligands in the octahedral complex, 6 symmetry-adapted linear combination (SALC) can be formed. Each ligand L provides one orbitals derived from the ligand group orbitals (LGO) for the O_h. The LGO are a_{1g}, t_{1u} and e_g symmetries.

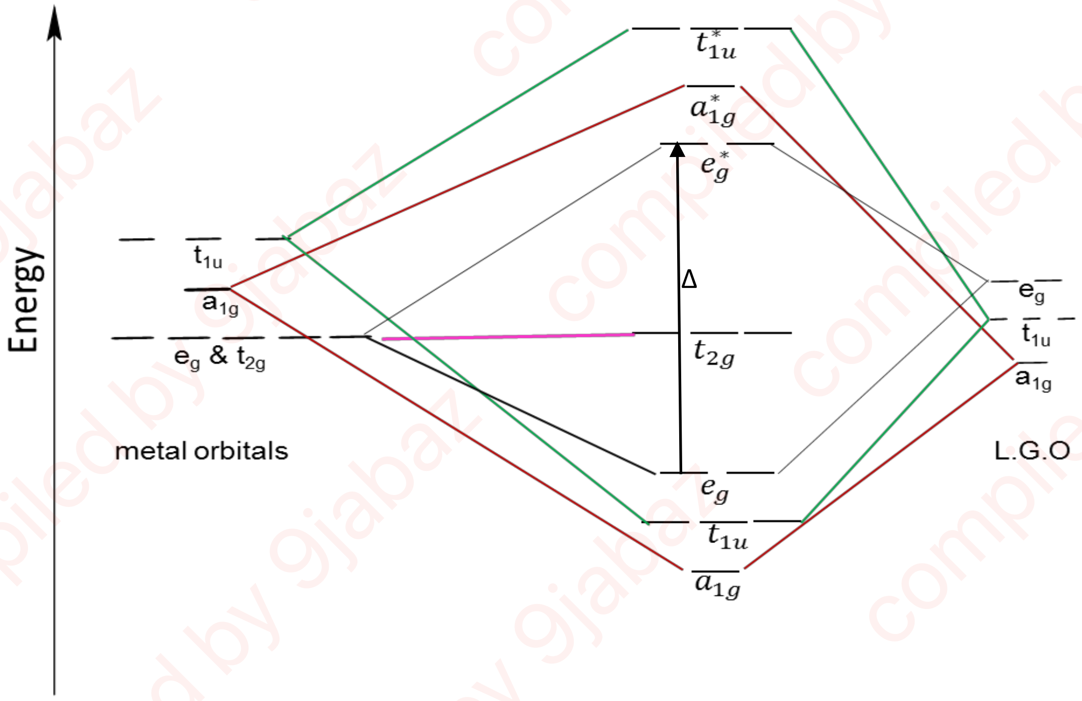
Symmetry of LGO	Degeneracy
a_{1g}	1
t_{1u}	3
e_g	2

Matching symmetries between the metal and the Ligand allow for the formation of MO. The order of energy arrangement of the electrons in the orbitals of the metal is $e_g \approx t_{2g} < a_{1g} < t_{1u}$ and for the LGO = $a_{1g} < t_{1u} < e_g$.

You will notice that the d_{xy} d_{yz} d_{xz} orbitals have a t_{2g} symmetry and since there is no match in symmetry with the ligand, they become non-bonding MOs.
The s and p orbital of both metal and ligand have similar symmetries and so overlap accordingly.
This overlapping brings about stability in the a_{1g} and t_{1u} orbital compared e_g MO's that is why the e_g is higher in energy.
The overlapping orbitals are from the metal (e_g, a_{1g}, t_{1u}) (total of 6), from the ligand (a_{1g}, t_{1u}, e_g) (total of 6) create a total of 12MO, = 6 BMO & 6 Anti-BMO. The order of filling of the molecular orbitals is:

$$\boldsymbol{a_{1g}, t_{1u}, e_g\ , t_{2g}, e_g^{*}, a_{1g}^{*}, t_{1u}^{*}}$$

This is a molecular orbital diagram below is showing the overlapping of the metal orbitals and LGO of a complex with **only sigma bonds** between them. Just like in CFT. The energy difference between the t_{2g} and e_g^{*} orbital corresponds to Δ_{oct} in LFT and is referred to as Ligand Field Stabilization Energy (LSFE).

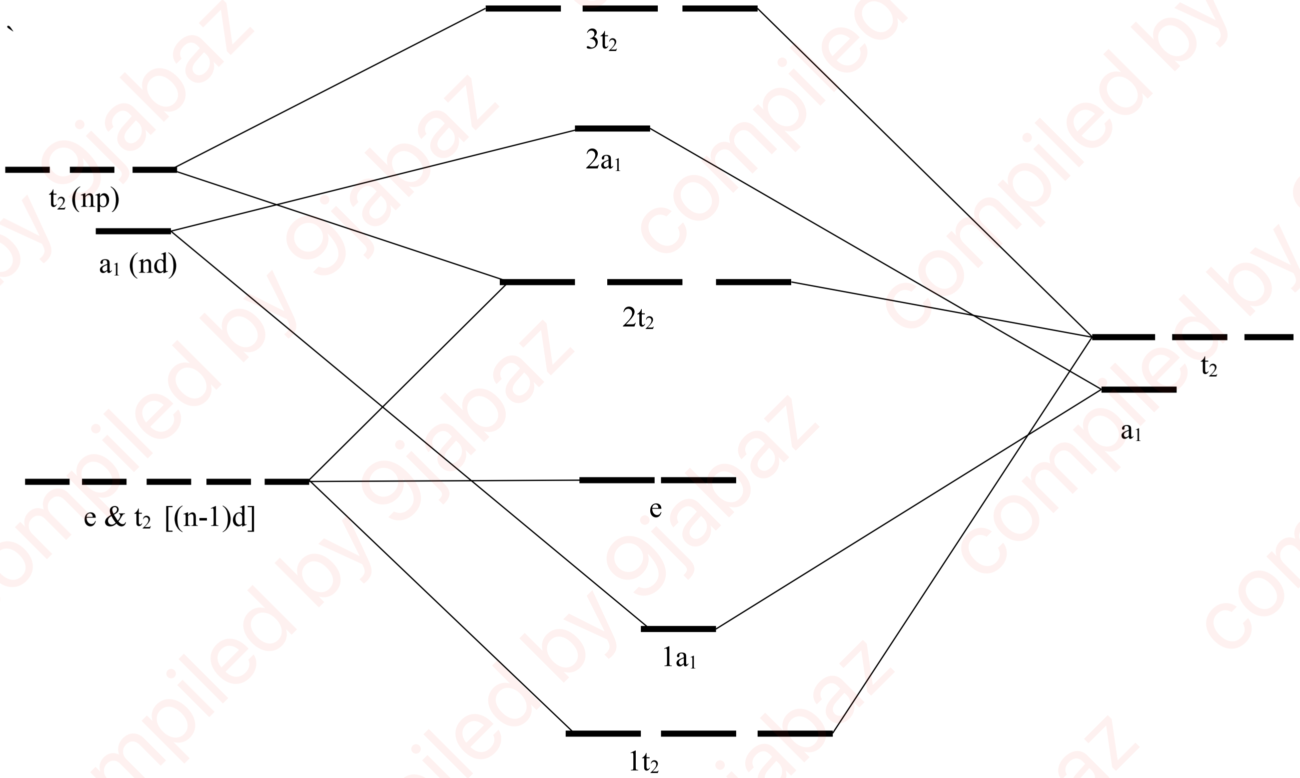


In a **tetrahedral environment** the symmetry of the molecule is T_d

Metal orbital	Symmetry	Degeneracy
s	a_1	1
p_x p_y p_x	t_2	3
d_{xy} d_{yz} d_{xz}	t_2	3
$d_{x^2-y^2}$ d_{z^2}	e	2

Notice that the (g) is gone. The LGO are **a_1** and **t_2** while for the metal **e** orbital is the non-bonding and the **t_2** from the metal (d-orbital) is very weakly anti-bonding. When these orbitals overlap the MO generated are ordered and labeled as:

$$\boldsymbol{1t_2, 1a_1, e, 2t_2, 2a_1, 3t_2}$$


`
3t₂
2a₁
t₂ (np)
a₁ (nd)
2t₂
t₂
a₁
e & t₂ [(n-1)d]
e
1a₁
1t₂

UNIT TWO - For Complexes only σ– Bonds and (σ & π)– Bonds Under O_h Symmetry

For Complexes only σ

So for a **low spin $Co(NH_3)_6]^{3+}$** a with a total of 18e$^-$ (6e$^-$ from Co^{3+}, 2 from each ligand) will occupy a_{1g}, t_{1u}, e_g, t_{2g} MOs. (Note there is forced pairing). The molecular orbital electronic configuration will be:

$$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6, e_g^{*0}, a_{1g}^{*0}, t_{1u}^{*0}$$

Notionally in σ-bonded octahedral complex the 12 electron supplied by the ligands are considered to fill in the a_{1g}, t_{1u} and e_g orbitals. The filling in of the t_{2g} and e_g^* level corresponds to the number of valence electron of the metal ion.

For **high spin complexes** forced pairing doesn't occur so the filling extends to the e_g^*.
NOTE: The t_{2g} and e_g^* are filled in singly before pairing e.g **$[Co(H_2O)_6]^{2+}$.** 12 electrons from the LGO and 7 electrons from Co^{2+} and so the molecular orbital electronic configuration is thus:

$$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^5, e_g^{*2}, a_{1g}^{*0}, t_{1u}^{*0}$$

For Complexes with π – Bonds

In these cases the t_{2g} in $(ML_6)^{2+}$ overlap with ligands of the correct symmetry which is t_{2g} to form π – bonds. There are 2 types of ligand; **π – donor** and **π – acceptors.**
A **π – donor ligand** donates e^- to the metal center in a bonding involving a filled ligand orbital and an empty metal orbital. Examples of π – donor ligand eg Cl^-, Br^- and I^-.
A π – acceptor ligand accepts e^- from the metal center in a bonding that involves a filled metal orbital and an empty ligand orbital e.g. CO, N_2, NO, alkenes. This is referred to as Back bonding.

For octahedral complexes with **π – donor** ligands the order of filling is

$$\boldsymbol{a_{1g}, t_{1u}, e_g, t_{2g}, t_{2g}^*, e_g^*, a_{1g}^*, t_{1u}^*}$$

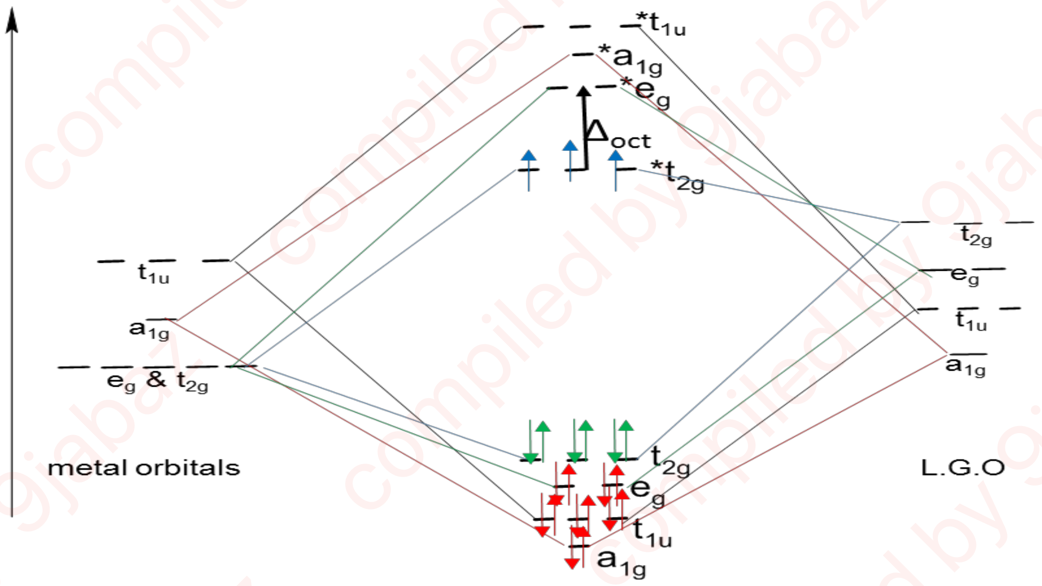
$[Cr(Cl)_6]^{3-}$
$6Cl^-$ = 12σ electrons + 6π electrons = 18 electrons
Cr^{3+} = 3σ electrons ($3d^3$, $4s^0$)
Total = 21 electrons

$$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6, t_{2g}^{*3}, e_g^{*0}, a_{1g}^{*0}, t_{1u}^{*0}$$

(PS: There are 18e for 6Cl^- because each Cl^- provides a lone pair with p-orbitals that overlap horizontally to form 6σ bonds (12σ electrons) while an extra electron in the p-orbitals that overlap vertically account for the 6π bonds (6π electrons). Remember that Cl^- is chlorine with 5e in its p orbital plus and additional electron that completes it octet.)

The 18 electrons from the donor ligands will occupy the a_{1g}, t_{1u}, e_g and t_{2g} and the t_{2g}^* and e_g^* will be occupied by the corresponding number of valence electrons of the metal. NOTE: The t_{2g}^* and e_g^* are filled in singly before pairing. The t_{2g} has the 6π electrons the a_{1g}, t_{1u} and e_g have 12σ electrons. For complexes with π-donor ligands the energy separations between the t_{2g}^* and e_g^* orbital corresponds to the Δ_{oct} in CFT ligands and the energy separation is small.

$[Cr(Cl)_6]^{3-}$



6Cl^- = 12σ electrons + 6π electrons = 18 electrons
Cr^{3+} = 3σ electrons ($3d^3$, $4s^0$)
Total = 21 electrons

In the case of ***π* -acceptor** ligand the order of filling is

$$\boldsymbol{a_{1g}, t_{1u}, e_g, t_{2g}, e_g^*, t_{2g}^*, a_{1g}^*, t_{1u}^*}$$

The π-acceptor ligands provide 12 electrons which occupy a_{1g}, t_{1u}, and e_g . The valence electrons from the metal then occupy the t_{2g} and e_g^* while the t_{2g}^* orbitals (π-orbitals) are empty

[Cr(CO)$_6$]

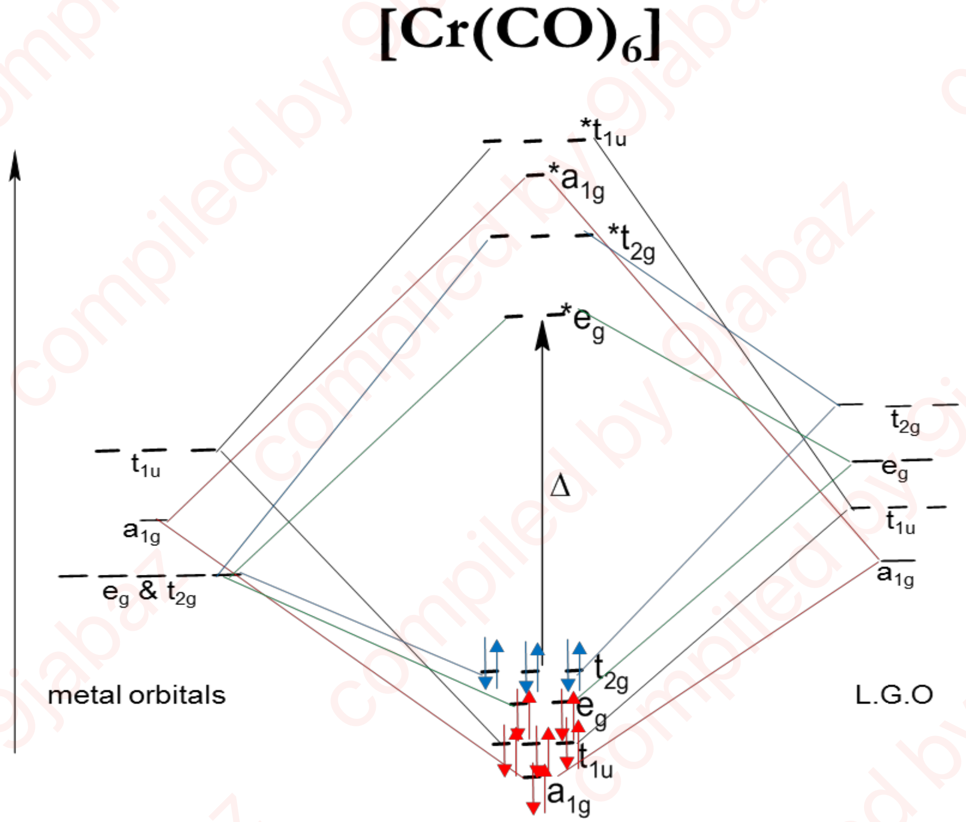
Oxidation state of Cr = 0

6CO = 12e

Cr^0 = 6e (3d^5, 4s^1)

Total = 18 electrons

$$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6,\ e_g^{*0}, t_{2g}^{*0},, a_{1g}^{*0}, t_{1u}^{*0}$$

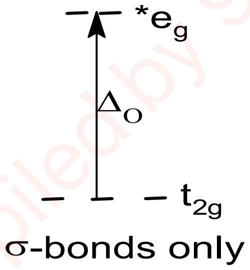


6CO = 12σ electrons

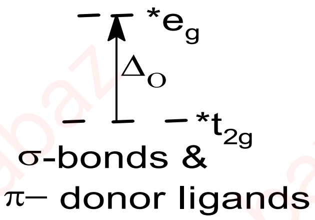
Cr^0= 6σ electrons (3d^5, 4s^1)

Total = 18 electrons

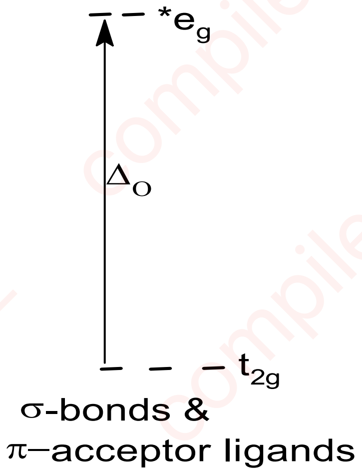
The lowering of the energy of the $e_g{}^*$ orbital is as a result of the stabilization due to decrease in the oxidation state of the metal complexes. For complexes with π-ligand acceptor the energy of the t_{2g}^* is very high, the so it is energy separation between t_{2g} *and* e_g^* that corresponds to Δ_{oct} and it is large.



σ-bonds only



σ-bonds &
π– donor ligands



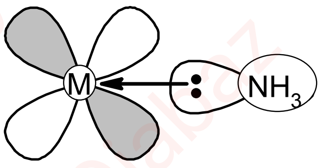
σ-bonds &
π–acceptor ligands

Write the molecular orbital electronic configuration of $[Mo(CO)_6]$ and $Na[V(CO)_6]$

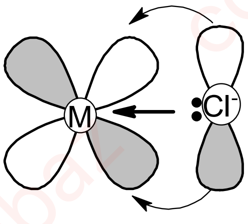
$[Mo(CO)_6]$		$Na[V(CO)_6] = Na^+ + [V(CO)_6]^-$	
Oxidation state of Mo = 0		Oxidation state of V = -1e	
6CO =	12e	6CO =	12e
Mo^0 =	6e ($3d^5$, $4s^1$)	V^0 =	5e ($3d^3$, $4s^2$)
Total =	**18 electrons**	V^{1-} =	6e ($3d^4$, $4s^2$)
		Total =	**18 electrons**
$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6,\ e_g^{*0}, t_{2g}^{*0},, a_{1g}^{*0}, t_{1u}^{*0}$		$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6,\ e_g^{*0}, t_{2g}^{*0},, a_{1g}^{*0}, t_{1u}^{*0}$	

UNIT THREE - Summary of LFT

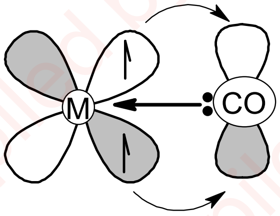
1. In LFT there are 3 types of ligands, σ-donor, π – donor and π – acceptors ligands.
2. All ligands form sigma donor but some have in addition to either accept or donate pi electrons.
3. Δ_{oct} decreases in going from a σ– bond only complex to one containing π – donor ligands.
4. For a complex with π–donor ligand, increased π–donation stabilizes the $\text{t}_{2\text{g}}$ level (lowers) and destabilizes (raises) the $\text{t}_{2\text{g}}^*$ level thus decreasing Δ_{oct} because the t_{2g}^* closer to e_g^*.
5. The value of Δ_{oct} is usually large for complexes containing π-acceptor ligands and such complexes are likely to be low spin.
6. Complexes with π-acceptor ligands increased π-acceptance stabilizes the $\text{t}_{2\text{g}}$ level (i.e. lowers it, hence increasing the distance from the e_g^*) increase Δ_{oct}.
7. This explains the spectrochemical series on π- donor s such as $\text{I}^-, \text{Br}^-, \text{Cl}^-$ are weak field while π- acceptors ligands like CO and CN^- are strong field ligands.
8. π-accepting ligands have empty π-orbitals where the metal can donate electrons into. This is back bonding. There are two kinds of back bonding: when the π-acceptor ligand vacant orbital is a p-orbital **dπ-pπ bond** for example M-CO. when the π-acceptor ligand vacant orbital is a d-orbital then then it is a **dπ-dπ bond.** An example is **:**PPh_3 (triphenylphosphine) the 3d orbital of phosphorus is vacant and would therefore be involved in back bonding.
9. π-donor ligands donate electrons into vacant d-orbitals.



σ– ligand only



σ– ligand + π- donor ligand



σ– ligand + π-acceptor ligand

$I^- < Br^- < Cl^- < F^- < OH^- < RCO_2^-$	$< H_2O < NCS < NH_3 < en$	$< NO_2 < Phen < CN \cong CO$
π-donor ligands	**σ-only ligands**	**π-acceptor ligands**

MODULE SIX

ELECTRONIC SPECTRA (in LFT)

UNIT ONE – Intro
UNIT TWO – Calculating electron quantum numbers S, L, J
UNIT THREE – Application in interpreting electronic spectra of complexes

UNIT ONE - Intro

The major deviation of LFT from CFT is that it takes into account the interaction between the electrons and their orbitals. Take for instance an electron in a p-orbital p^1. There are 3 degenerate p-orbitals **p_x, p_y, p_z,** and there is no way of knowing which of these orbitals the electron is in. Furthermore, the direction of the spin of the electron is also unknown.

All the possible arrangements of a p^1electron in a p-orbitals

p_x	p_y	p_z
↑		
	↑	
		↑
		↓
	↓	
↓		

Although the orbitals have the same energy, the electrons(s) present in them interact with each other and with the orbitals via

i. Electrostatic repulsion between electrons.
ii. Interaction or coupling of the magnetic field generated by the spinning motion of the electrons – (spin angular momentum). Spin – spin coupling for more than 1 electron system.
iii. Coupling of the fields produced by the orbital motion of the electron (orbital angular momentum). This can be referred to as orbit-orbit coupling.

iv. The coupling of the spin and the orbital (spin-orbit coupling) is also referred to as Russell Saunders coupling.

These interactions create a loss of degeneracy resulting in the formation of a ground state. (Lowest energy) and one or more excited states within the atom or ion. This in turn affects the specific orbital that electronic transitions will occur, hence it is used to explain the electron spectra of d-metal complexes.

The different ways in which the electrons can occupy the orbitals are called microstates of that specific configuration.

We can determine the number of microstate by using the expression

$$\frac{[2(2l+1)]!}{x!\,[2(2l+1)-\ x]!}$$

Where value of l is dependent on the specific orbital eg s = 0; p = 1 and d = 2

x = number of electrons

for p^1 l = 1 and x = 1 substituting in the expression above we have,

$$\frac{[2(2\times 1+1)]!}{1!\,[2(2\times 1+1)-1]!}$$

$$\frac{[2(3)]!}{1!\,[2(3)-1]!}$$

$$\frac{[6]!}{1!\,[5]!}$$

$$\frac{6\times \cancel{5\times 4\times 3\times 2\times 1}}{1\times \cancel{5\times 4\times 3\times 2\times 1}}=6$$

That there are 6 possible ways to arrange one electron in a p-orbital. We saw that earlier on. Hence p^1 has 6 microstates.

As a result of these inter-electronic interactions, the microstate would have different energy levels called TERMS. We can identify the Terms of an atom or ion and arrange them in the order of increasing energy by arranging these microstates based on their: -

a. Total spin quantum no **S**
b. Total orbital angular momentum quantum no **L**.
c. Spin – orbit coupling described as the angular momentum quantum no **J**.

The next unit would cover how to determine these quantum numbers. We would use simple systems p-orbitals then apply to d-orbitals

UNIT TWO - Calculating Electron Quantum Numbers S, L, J

SPIN QUANTUM No S

S = Total spin quantum no of a multi-electron system

s = Spin quantum no of an individual electron has a value of ½

m_s = Magnetic spin quantum no for a single electron & has values -½ & +½ (spinning anticlock wise and clock wise respectively)

M_s = Magnetic spin quantum no. of a multi-electron system

$$M_s = \sum m_s$$

a) S cannot have negative value

b) For an atom with odd no of electrons S = $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$... and for even no. of electrons S = 0, 1, 2…

c) For each value of S there are (2S + 1) value of M_s.
If S = 2, then there are (2S + 1) allowed values of M_s i.e. ([2 x 2] + 1) = 5 values of M_s $-2, -1, 0, 1, 2$.
If S = ${}^3/_2$, then there are $\left(\left[2 \text{ x } \frac{3}{2}\right] + 1\right) = 4$ values of M_s which are $-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

d) Terms for which (2S+1) = 1, 2, 3, 4…… (Corresponding to S = $0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$) are called singlet, doublet, triplet, quartet,…..

p^2 - System

p_x	p_y	p_z	$M_s = \Sigma m_s$
↑	↑		${}^1/_2 + {}^1/_2 = \mathbf{1}$
	↑	↑	${}^1/_2 + {}^1/_2 = \mathbf{1}$
↑		↑	${}^1/_2 + {}^1/_2 = \mathbf{1}$
↓	↓		$-{}^1/_2 - {}^1/_2 = \mathbf{-1}$
	↓	↓	$-{}^1/_2 - {}^1/_2 = \mathbf{-1}$
↓		↓	$-{}^1/_2 - {}^1/_2 = \mathbf{-1}$
↑		↓	${}^1/_2 - {}^1/_2 = 0$
↑	↓		${}^1/_2 - {}^1/_2 = 0$
	↑	↓	${}^1/_2 - {}^1/_2 = 0$
↓		↑	$-{}^1/_2 + {}^1/_2 = 0$
	↓	↑	${}^1/_2 - {}^1/_2 = 0$
↑↓			$-{}^1/_2 + {}^1/_2 = 0$
	↑↓		${}^1/_2 - {}^1/_2 = 0$

		↑↓	${}^{1}/_{2} - {}^{1}/_{2} = 0$
↓		↑	${}^{1}/_{2} - {}^{1}/_{2} = 0$

So far p^2– system M_s has values = 1, 0, -1 and since S cannot have a negative value S can only be 0, 1
When S = 0
Then 2S + 1 = 1 – a singlet state

When S = 1
Then 2S +1 = 3 – triplet state

What about the influence of the orbital?

ORBITAL ANGULAR QUANTUM No L

L = Subsidiary/Azumithal quantum no describes the shape as well as the orbital angular quantum no = m_l. Recall that $l = n - 1$

$\boldsymbol{l}$
s = 0
p = 1
d = 2
f = 3

For every value of l, there $(2l + 1)$ values of m_l
So for a p-orbital $l = 1$, then there are $(2 \, x \, 1 + 1)$ values of m_l. The values of m_l = –1, 0, +1. This is represented as p_x, p_y, p_z
Similarly, for M_L (i.e. a multi-electron system) it becomes (2L + 1) values of M_L. When we find the value of M_L, we can determine L, L just like l has values 0, 1, 2, 3… and these are energy states, which be known as S P D, F….. respectively and are called Term Symbols.

So for p^2 system, lets calculate the number of microstates

$$\frac{[2(2l+1)]!}{x!\,[2(2l+1) - x]!}$$

for p^2 l = 1 and x = 2 substituting in the expression above we have,

$$\frac{[2(2 \times 1 + 1)]!}{2!\,[2(2 \times 1 + 1) - 2]!}$$

$$\frac{[2(3)]!}{2!\,[2(3) - 2]!}$$

$$\frac{[6]!}{2!\,[4]!}$$

$$\frac{6\times 5\cancel{\times 4\times 3\times 2\times 1}}{2\times 1\times \cancel{4\times 3\times 2\times 1}} = \frac{30}{2} = 15\ microstates$$

p^2 system there are 15 possible arrangement

m_l = -1	m_l = 0	m_l = +1	M_L	M_S
↑	↑		**-1**	**1**
	↑	↑	**+1**	**1**
↑		↑	**0**	**1**
↓	↓		**-1**	**-1**
	↓	↓	**+1**	**-1**
↓		↓	**0**	**-1**
↑		↓	**0**	**0**
↑	↓		-1	0
	↑	↓	+1	0
↓		↑	0	0
	↓	↑	+1	0
↓	↑		-1	0
↑↓			-2	0
	↑↓		0	0
		↑↓	+2	0

The 15 microstates would be grouped so that there is no set containing repetition. Grouping M_L with the same M_S values

- Group all the M_L with M_S = -1 you will have M_L -1, 0, 1
- Group all the M_L with M_S = +1 you will have M_L -1, 0, 1
- Group all the M_L with M_S = 0 you will have 3 M_L
    a. -2, -1, 0, 1, 2
    b. -1, 0, +1 and then a
    c. **0**

Grouping M_L with the same M_S values and determine L and S

Grouping M_L	L	Term symbols	Grouping M_S	S	(2S+1)
+2, +1, 0, -1,-2	2	D	0	0	1 singlet
+1, 0, -1	1	P	-1	1	3 triplet
+1, 0, -1	1	P	0	1	3 triplet
+1, 0, -1	1	P	+1	1	3 triplet
0	0	S	0	0	1 singlet

Term symbols are written as $^{(2S+1)}L$

The term symbols for a p^2 system is $^1D,\ ^3P,\ ^1S$

There are 3 P terms but are they degenerate (equal)? The total angular momentum would answer that.

TOTAL ANGULAR MOMENTUM No J

This has values: (L + S), ([L + S]-1), ([L + S]-2) ... (L – S)

The full term symbol will include all the information L, S, J written as $^{(2S+1)}\boldsymbol{L}_{J\ value}$.

For p^2

L	**S**	**J**	**Values of J-**
1	1	2	its multiplicity is triplet (2S + 1) therefore J values are 2, 1, 0
2	0	2	because it multiplicity is singlet (2S + 1); only 2 is allowed
0	0	0	multiplicity is singlet only 0 is allowed

The full term symbols are $\boldsymbol{^1D_2,\ ^3P_2,\ ^3P_1,\ ^3P_0,\ ^0S_0}$

To be able to arrange these term symbols in order of increasing energy. The following rules are followed

1. The term with the highest spin (2S+1) has the lowest energy (hence the ^3P, has the lowest energy).
2. If 2 or more terms have the same multiplicity (e.g. $^3F\ and\ ^3P$) then the term with highest value of L has the lowest energy, hence ^3F has a lower energy than ^3P.

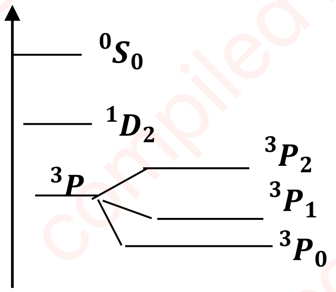
3. If 2 or more terms have the same multiplicity and value of, L, 3 conditions are considered
    (a) if the sub-level is less than half filled, the lowest value of J has the lowest energy
    (b) if the sub-level is more than half filled, the highest value of J has the lowest energy
    (c) if the sub level is half – filled L = 0 & J = S

For our $p^2 \Rightarrow$ ${}^1\boldsymbol{D_2},\ {}^3\boldsymbol{P_2},\ {}^3\boldsymbol{P_1},\ {}^3\boldsymbol{P_0},\ {}^0\boldsymbol{S_0}$

${}^3\boldsymbol{P_2},\ {}^3\boldsymbol{P_1},\ {}^3\boldsymbol{P_0},\ {}^1\boldsymbol{D_2},\ {}^0\boldsymbol{S_0}$ - Highest value of multiplicity

${}^3\boldsymbol{P_2},\ {}^3\boldsymbol{P_1},\ {}^3\boldsymbol{P_0},\ {}^1\boldsymbol{D_2},\ {}^0\boldsymbol{S_0}$- highest value of L

Since p is less than half filled $\underset{\text{increase in energy}}{\underrightarrow{{}^3\boldsymbol{P_0},\ {}^3\boldsymbol{P_1},\ {}^3\boldsymbol{P_2},\ {}^1\boldsymbol{D_2},\ {}^0\boldsymbol{S_0}}}$



So that the ground state energy of p^2 is ${}^3\boldsymbol{P_0}$ term

Class work – Determine the terms of d¹ configuration

- First calculate the number of microstates.
- Since you know the orbital you know the value of l and then make a table with and make all the possible arrangements of the electrons into the various ml values.
- Add all the m_l to get M_L
- Add all the m_s to get M_S
- Then group all the M_L with the same value of MS
- Determine L and S values
- Determine J values
- Arrange in order of increasing energy.

No of microstates l = 2, x = 1 $\frac{[2(2\cdot2+1)]!}{1![2(2\cdot2+1)-1]!} = \frac{[10]!}{1![9]!} = 10$

-2	-1	0	+1	+2	M_L	M_S	
↑					-2	$+½$	L = 2 S = $^1/_2$
	↑				-1	$+½$	
		↑			0	$+½$	
			↑		+1	$+½$	
				↑	+2	$+½$	
				↓	+2	$-½$	L = 2 S = $^1/_2$
			↓		+1	$-½$	
		↓			0	$-½$	
	↓				-1	$-½$	
↓					-2	$-½$	

With L = 2 the term will be D and

the multiplicity {(2S + 1) as S = $^1/_2$} = 2 i.e. it's a doublet, ^2D

Therefore there are only two values of J which (2 +$^1/_2$), [(2 + $^1/_2$) − 1] = $^5/_2, ^3/_2$

The full term symbols of the d^1 are $^2D_{3/2}$, $^2D_{5/2}$

UNIT THREE – Electronic Transitions

It has been shown from group theory that in an octahedral or tetrahedral field, the term symbols D, F G, H, & I spilt while, S and P do not.

The table below shows the splitting

Term	**Component in an octahedral field**
S	A_{1g}
P	T_{1g}
D	$\mathbf{T_{2g} + E_g}$
F	$\mathbf{A_{2g} + T_{2g} + T_{1g}}$
G	$A_{1g} + E_g + T_{2g} + T_{1g}$
H	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	$A_{1g}+ A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Similar splitting occurs in a tetrahedral field but the ‘g’ labels are no longer applicable. For d-orbitals the only ground state terms of significance are the D and F terms. These would be explained later.

Calculating Ground State Terms for d-ions

d^n	2	1	0	-1	-2	S	(2S+1)	L	Ground State Term
d^1	↑					½	2	2	^2D
d^2	↑	↑				1	3	3	^3F
d^3	↑	↑	↑			$^3/_2$	4	3	^4F
d^4	↑	↑	↑	↑		2	5	2	^5D
d^5	↑	↑	↑	↑	↑	$^5/_2$	6	0	^6S
d^6	↑↓	↑	↑	↑	↑	2	5	2	^5D
d^7	↑↓	↑↓	↑	↑	↑	$^3/_2$	4	3	^4F
d^8	↑↓	↑↓	↑↓	↑	↑	1	3	3	^3F
d^9	↑↓	↑↓	↑↓	↑↓	↑	$^1/_2$	2	2	^2D

A hole is created with the absence of an electron and is described as being positive. The d^1 and d^9 configurations are related by a positive hole concept:

- d^1 has one electron while the d^9 has one hole as it is obtained by removing an electron from d^{10} leaving behind a hole.

↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑□

d^{10} **d^9**

Similar relationships exist between d^4/d^6; d^2/d^8; d^3/d^7 (inverse relationship). They have the same ground term and multiplicity.

Starting d^0 (adding ė)	Starting d^{10} (adding hole)
d^1 1 electron ↑	d^9 1 hole ↑↓ ↑↓ ↑↓ ↑↓ ↑□
d^2 2 electrons ↑ ↑	d^8 2 holes ↑↓ ↑↓ ↑↓ ↑□ ↑□
d^3 3 electrons ↑ ↑ ↑	d^7 3 holes ↑↓ ↑↓ ↑□ ↑□ ↑□
d^4 4 electrons ↑ ↑ ↑ ↑	d^6 4 holes ↑↓ ↑□ ↑□ ↑□ ↑□

Due to this relationship there is an **inversion of the splits terms**. The d^1/d^9 ions have the same ground state term of ^2D. This term in an octahedral environment splits into two $\boldsymbol{T_{2g}}$ & $\boldsymbol{E_g}$.

- For d^1 the transition is $\boldsymbol{E_g} \leftarrow \boldsymbol{T_{2g}}$, while for d^9 its $\boldsymbol{T_{2g}} \leftarrow \boldsymbol{E_g}$. Similarly, these inversions occur between d^4/d^6; d^2/d^8; d^3/d^7.

- In a weak field, a d^5 ion is high spin and it spherically symmetrical and in this regard is similar to a d^0 and d^{10}.

- By adding an electron to the high spin d^5 ion to give a d^6 configuration it is similar to going from a d^0 to d^1.

- Likewise, a d^4 is achieved by adding four electrons to a d^0 which is then similar to obtaining the d^9 by adding four electrons to a d^5.

- This means then that the d^4 and d^9 will have the same splitting pattern and the d^1 and d^6 too.

Direct relationship between d^1/d^6; d^2/d^7; d^3/d^8; d^4/d^9;

Starting d^0 (adding ė to make a d^5)	Starting d^5 (adding ė to make a d^{10})
d^1 1 electron ↑ □ □ □ □	d^6 1 electron ↑↓ ↑□ ↑□ ↑□ ↑□
d^2 2 electrons ↑ ↑ □ □ □	d^7 2 electrons ↑↓ ↑↓ ↑□ ↑□ ↑□
d^3 3 electrons ↑ ↑ ↑ □ □	d^8 3 electrons ↑↓ ↑↓ ↑↓ ↑□ ↑□
d^4 4 electrons ↑ ↑ ↑ ↑ □	d^9 4 electrons ↑↓ ↑↓ ↑↓ ↑↓ ↑□

- These relationships are shown in an Orgel diagram (Figure 1), however the Orgel diagram cannot show the crystal field relationship between Δ_{oct} and Δ_{tet}. The Orgel diagram above shows that only one electronic transition from ground state to the excited state is possible.

- The electronic transitions

  d^1 in an octahedral field is ^2D term, This D term splits $\boldsymbol{^2E_g} \leftarrow \boldsymbol{^2T_{2g}}$

  d^1 has a direct relationship with d^6 which is a ^5D term $\boldsymbol{^5E_g} \leftarrow \boldsymbol{^5T_{2g}}$

  d^9 which is also a ^2D has an inverse relationship with d^1 so splits $\boldsymbol{^2T_{2g}} \leftarrow \boldsymbol{^2E_g}$

  d^4 which is also a ^5D has an inverse relationship with d^6 so splits $\boldsymbol{^5T_{2g}} \leftarrow \boldsymbol{^5E_g}$

- All of these transitions are spin allowed [no change in total spin S] and the electronic spectrum of each ion exhibits **one absorption band.**

- In a tetrahedral field, an inversion takes place for example the d^4 and d^9 in an octahedral field are the same as the d^1 and d^6 in the tetrahedral field (SEE Figure 1).

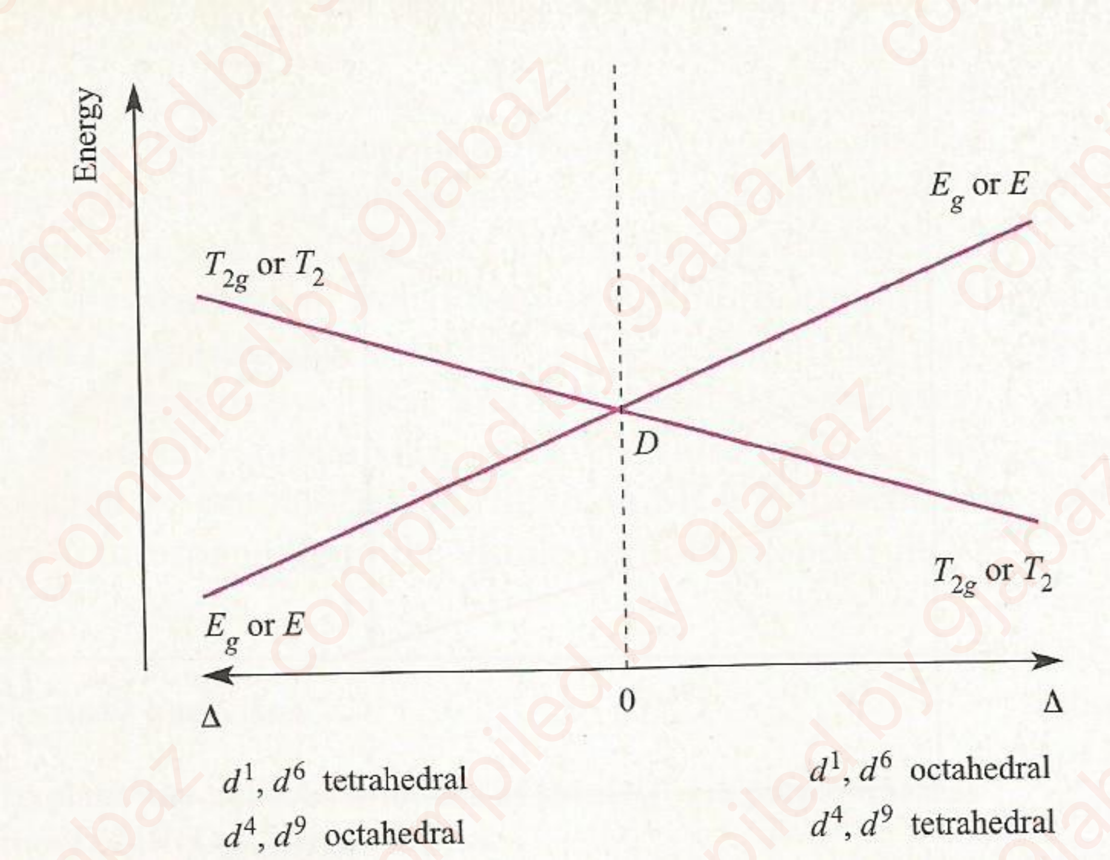


Figure 1: Orgel diagram d^1, d^6, d^4 and d^9

There are cases where more than one electron/hole (d^2, d^8; d^3, d^7) are involved in electronic transitions. The transitions that are being considered are only those from the ground state to one or more excited states. (Note that transitions from one excited state to another are possible but not probable hence are ignored).

Selection rules:

1. Only transitions between terms of the same multiplicity are allowed. (For full notation for these transition should include the multiplicities i.e. 2S+1).

2. The GROUND STATE TERMS will be one with the highest spin multiplicity.

→ Considering the d^2 it has 45 microstates and its term symbols are $^3F_2$, $^3F_3$, $^3F_4$, $^3P_0$, $^3P_1$, $^3P_2$, $^1G_4$, $^1D_2$, $^1S_0$.

→ The Ground State Term is ^3F (ignoring the J-values) and ^3P is one of the excited states. Others are $^1G_4$, $^1D_2$, $^1S_0$.

→ The allowed transition would be from ^3F to ^3P (same multiplicity)

→ F term splits into T_{1g}, T_{2g}, A_{2g}. Just like the D term splits into T_{2g} & E_g are illustrated in the Orgel diagram (Figure 3). The P term is also T_{1g}

Notice that the $T_{1g}(F)$ and $T_{1g}(P)$ are curved away from each other. That is because they have the same symmetry hence an interaction exist between them and as such they are not allowed to cross (non-crossing rule).

- From the Orgel diagram the will be 3 transitions for d^2, d^3, d^7 and d^8 whether in an octahedral or tetrahedral field. Hence three absorption bands are expected (Figure 4).
- All transition from the ground state to the excited states are spin allowed.

For example octahedral d^2 ion has ^3F term, the F term splits to $^3T_{1g}(F)$, $^3T_{2g}$, $^3A_{2g}$ and the excited state is a P term $^3T_{1g}(P)$

$$E \uparrow \quad \begin{array}{c} ^3A_{2g} \leftarrow {}^3T_{1g}(F) \\ ^3T_{1g}(P) \leftarrow {}^3T_{1g}(F) \\ ^3T_{2g} \leftarrow {}^3T_{1g}(F) \end{array}$$

It has a direct relationship with d^7 which is a ^4F term

$$E \uparrow \quad \begin{array}{c} ^4A_{2g} \leftarrow {}^4T_{1g}(F) \\ ^4T_{1g}(P) \leftarrow {}^4T_{1g}(F) \end{array}$$

$$\boldsymbol{{}^{4}T_{2g} \leftarrow {}^{4}T_{1g}(F)}$$

For the high spin d^5 all the transitions are spin forbidden and the d-d transitions that are observed are between the ${}^6S$ ground state and quartet ${}^4G$ and the absorptions are extremely weak.

Class Work

${}^3F$ is a ground state term symbol of a transition metal, describe in details the significance of the term symbol.

The Tanabe-Sugano Diagram

Tanabe-Sugano diagrams is used to predict to an approximation to the ligand field splitting energy (Δ), generated by ligands attached to a metal center.

Racah parameters (A, B, and C) were generated as a means to describe the effects of electron-electron repulsion within the metal complexes. In the case of Tanabe-Sugano diagrams each electron configuration split has an energy that can be related by the B value.

$A =$ same value for any metal (hence ignored)

$C \approx \frac{1}{4}B$

$B \approx$ bond strength between the ligand and metal.

The ratio of B of a coordination complex to free ion B is called the Nephelauxetic ratio. It is a measure of the effect of reducing electron – electron repulsion by the ligands. This effect is what gave rise to the spectrochemical series of ligands

$$B = \frac{B_{complex}}{B_{free\ ion}}$$

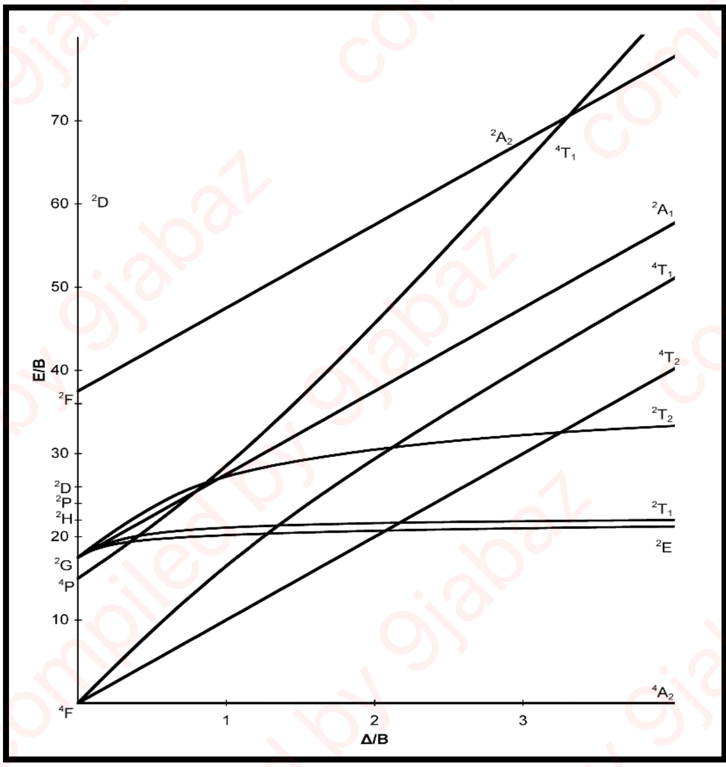
The x-axis in a Tanabe-Sugano diagram is the values of $\frac{\Delta_o}{B}$

The y-axis is the values of $\frac{E}{B}$ where E = energy of an electronic transition.

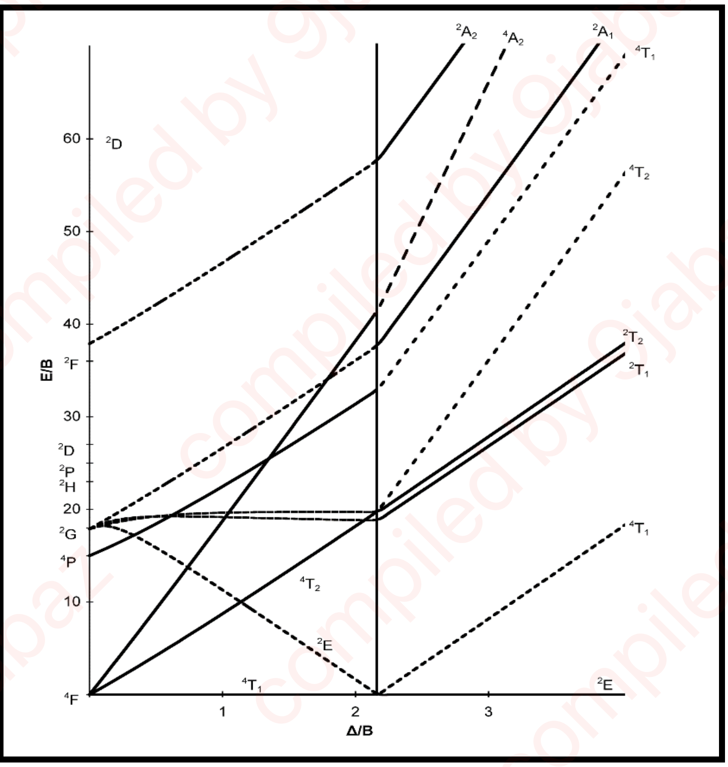
Each line represents the energy of an electronic state while varying the strength of octahedral ligand field.

Both spin allowed and spin forbidden transition are represented because spin forbidden transitions are seen in the UV-vis spectrum.

Each term symbol is created from the splitting of term symbols from spherical to octahedral symmetry. With the relative energy ordering of the states are determined via Hund's rules.



d^3



d^7

Diagrams for d^4, d^5, d^6, and d^7 metal ions have a discontinuity in energies as the ligand field, changing from high-spin to low-spin complexes. This is indicated by the straight line.

At the line, the spin pairing energy P is equal to the ligand field splitting energy Δ.

To the left of the line metal complexes are high-spin as $P > \Delta$.

To the right of the line metal complexes are low-spin as $P < \Delta$.

How to calculate Δ using the Tanabe-Sugano diagram

A Cr^{3+} metal complex has strong transitions and λ_{max} at 431.03 nm, 781.25 nm, and 1,250 nm. Determine the Δ_{oct} for this complex.

1. **Determine the d electronic configuration of the transition metal e.g. d^1, d^2, d^3 etc.**

   $Cr^0 = 3d^5, 4s^1$ $Cr^3 = 3d^3, 4s^0$
   Cr^{3+} had d^3 configuration

2. **From the UV-Vis spectrum determine the λ_{max} for each peak.**

In this case it was given

3. **Convert the λ_{max} to wavenumber**

$$\boldsymbol{wave\ number\ \bar{\upsilon}\ (cm^{-1}) = \frac{10^7 (nm/cm)}{wavelength\ \lambda\ (nm)}}$$

$\frac{10^7 (\cancel{nm}/cm)}{431.03\ (\cancel{nm})} = 23{,}200\ cm^{-}$	$\frac{10^7 (\cancel{nm}/cm)}{781.25\ (\cancel{nm})} = 13{,}600\ cm^{-}$	$\frac{10^7 (\cancel{nm}/cm)}{1250\ (\cancel{nm})} = 8{,}000\ cm^{-}$

4. **Determine E ratios relative to the lowest allowed transitions (e.g. $\frac{E_3}{E_1}, \frac{E_2}{E_1}$ where E_1 has the lowest value.**

$\frac{E_3}{E_1} = \frac{23200}{8000} = 2.9$	$\frac{E_2}{E_1} = \frac{13600}{8000} = 1.7$	$\frac{E_1}{E_1} = \frac{8000}{8000} = 1.0$

Remember $E\ (energy) = h\frac{c}{\lambda} = hc\bar{\upsilon}$, therefore the higher the value of $\bar{\upsilon}$, the greater the energy of the electronic transition and that means the larger splitting parameter Δ.

5. **Identify and assign the various E ($\bar{\upsilon}$) to each allowed transition.**

Energy

$^4T_{1g}(P) \leftarrow\ ^4A_{2g}$ $23{,}200\ cm^{-}$

$^4T_{1g}(F) \leftarrow\ ^4A_{2g}$ $13{,}600\ cm^{-}$

$^4T_{2g} \leftarrow\ ^4A_{2g}$ $8{,}000\ cm^{-}$

6. a. **Use appropriate Tanabe-Sugano diagram matching the d-configuration.**
The appropriate TS-diagram to use the d³

b. **Go to the Tanabe-Sunago diagram from each value of x-axis, trace the corresponding value on the y-axis, on the line of the each allowed transitions.** For example the line for $\frac{E_1}{B}$ will be $^4T_{2g}$, for $\frac{E_2}{B}$ will be $^4T_{1g}$ (F) and for $\frac{E_3}{B}$ will be $^4T_{1g}$ (P) (see slides)

$\frac{E_1}{B}$	$\frac{E_2}{B}$	$\frac{E_3}{B}$
@ $\frac{\Delta_o}{B} = 1$		
10	17	29
@ $\frac{\Delta_o}{B} = 2$		
20	31	45

@ $\frac{\Delta_o}{B} = 3$		
30	40	65

7. **Calculate ratios of $\frac{E}{B}$ relative to the least $\frac{E}{B}$**

$$\frac{\left(\frac{E_3}{B}\right)}{\left(\frac{E_1}{B}\right)} = \frac{29}{10} = 2.9$$

$\frac{E_1}{B}$	$\frac{E_2}{B}$	$\frac{E_3}{B}$
@ $\frac{\Delta_o}{B} = 1$		
10	17	29
1.0	1.7	2.9
@ $\frac{\Delta_o}{B} = 2$		
20	31	45
1.0	1.6	2.3
@ $\frac{\Delta_o}{B} = 3$		
30	40	65
1.0	1.3	2.2

8. **Comparing the values of the ratios in No 7 with that in No 4, for the one that is almost the same ratio will be the value of $\frac{\Delta_o}{B}$ that will be used to find Δ_o.**

In this case $\frac{\Delta_o}{B} = 1$ will be used.

9. **Substitute and get B then get Δ_o**

$E_3 = 23{,}200$ and $\frac{E_3}{B} = 29 \therefore B = \frac{23200}{29} = 800cm^{-}$

$$\frac{\Delta_o}{800} = 1 \therefore \Delta_o = 800cm^{-}$$

Similarly $E_2 = 13{,}600$ and $\frac{E_2}{B} = 17 \therefore B = \frac{13600}{17} = 800cm^{-}$

$$\frac{\Delta_o}{800} = 1 \therefore \Delta_o = 800cm^{-}$$

And $E_1 = 8{,}000$ and $\frac{E_1}{B} = 10 \therefore B = \frac{8000}{10} = 800cm^{-}$

$$\frac{\Delta_o}{800} = 1 \therefore \Delta_o = 800cm^{-}$$

ASSIGNMENT #2

CHM401

(1)

Sodium tetrachlorocobaltate(II) has a blue colour while tris(ethylenediammine)cobalt(III) chloride is orange in colour.

a. Calculate the crystal field stabilization energy of each.
b. These two complexes undergo d – d electronic transition. Explain why the molar absorptivity of sodium tetrachlorocobaltate(II) is $1.3 \times 10^3 \mathrm{dm^3 mol^{-1} cm^{-1}}$ while that of tris(ethylenediammine)cobalt(III) chloride is $1.3 \times 10^1 \mathrm{dm^3 mol^{-1} cm^{-1}}$ (Note: the concentration of both complexes are the same).

(2)

The oxidation state of nickel in the following complexes $[Ni(H_2O)_6]Cl_2$, $Na_2[NiCl_4]$ and $Na_2[Ni(CN)_4]$ is +2.

a) Draw the crystal field splitting pattern of each complex.
b) State for each complex which is centrosymmetric or non-centrosymmetric; and which would undergo symmetry allowed or forbidden; spin allowed or forbidden electronic transitions.

(3)

Consider this complex **$[Pt(en)_2Cl_2](NO_3)_2$**, its electronic spectra has absorption maximum at 410 nm. $[c = 3.0 \times 10^8\, m/s\, ;\ h = 6.63 \times 10^{-34} Js]$

a. Describe the bonding between the ligands and the metal according to crystal field theory.
b. What colour would this complex have and if **en** is a strong field ligand, would this colour be intense or weak? Give reason(s) for each of your answers.
c. In that case calculate the crystal field stabilization energy of this complex if **en** is a strong field ligand.
~~d. Would this be a complex with high stability? Give reasons for your answer.~~
~~e. How lability, do you think it would be labile? Provide reasons for your answer.~~