

# **Charge Transfer Spectra of Coordination Complex Compound**

**M. Sc. : CC – VI / CSIR / Ph. D. Course Work  
(Inorganic Chemistry)**

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Visible light wavelength 400-750nm appears "white", it is made up of a series of colours. White light consists of three primary colours (red, yellow and blue). These primary colours can be mixed to make three secondary colours (orange, green and violet).

Red + Yellow makes Orange

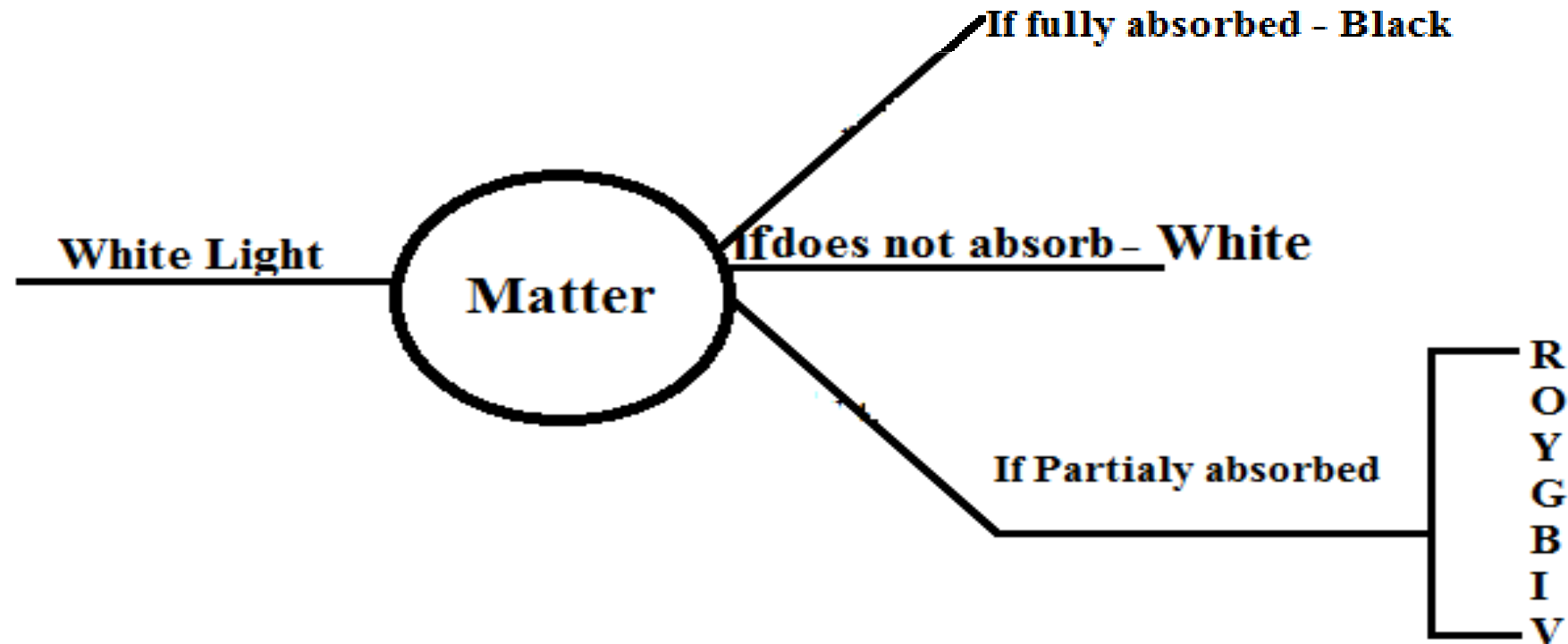
Yellow + Blue makes Green

Blue + Red makes Violet

If a sample absorbs all wavelength of visible light, none reaches our eyes from that sample, and then the sample appears black.

If the sample absorbs no visible light, it is white or colorless.

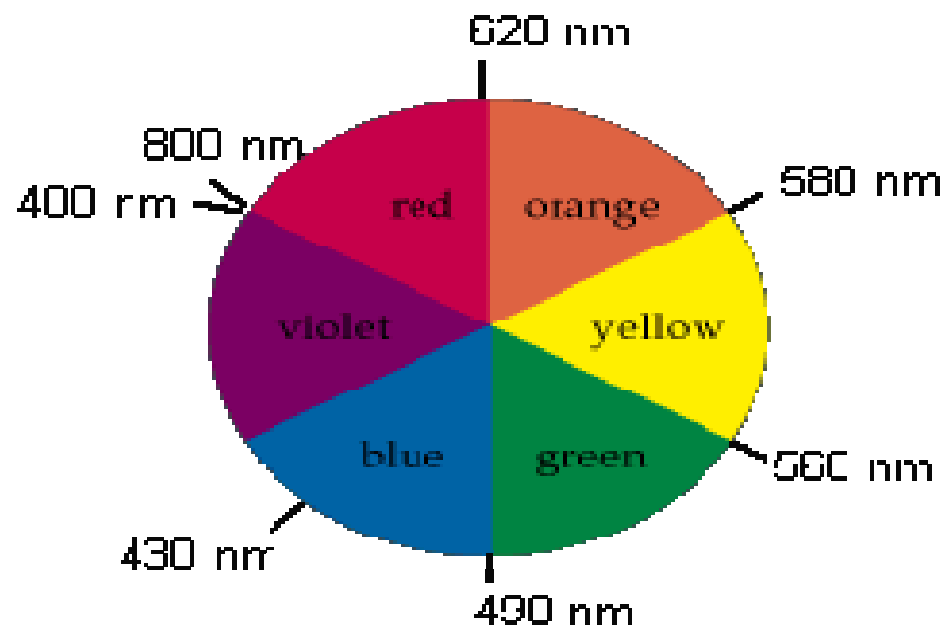
When the sample absorbs a photon of visible light, it is its complementary color we actually see.



If the sample absorbed orange colour, it would appear blue; blue and orange are said to be complementary colours.

**The Colour Wheel** The visible part of the electromagnetic spectrum contains light of wavelength 380-750 nm.

The colour wheel below gives information on the wavelength of different colour and also the complementary colour. For example: If red light is absorbed, the complex appears green.



Colour of Complex Compounds is due to

1. d-d transition (which have electron in d orbital)
2. Charge transfer (even does not have d electron)

d-d transition can explained by the help of CFT, Orgel diagram, Tanabe-Sugano diagram, Nephelauxetic effect etc but

## **Charge Transfer Spectra (CTS)**

Spectra obtained due to transfer of charge from one site to another site is called CTS.

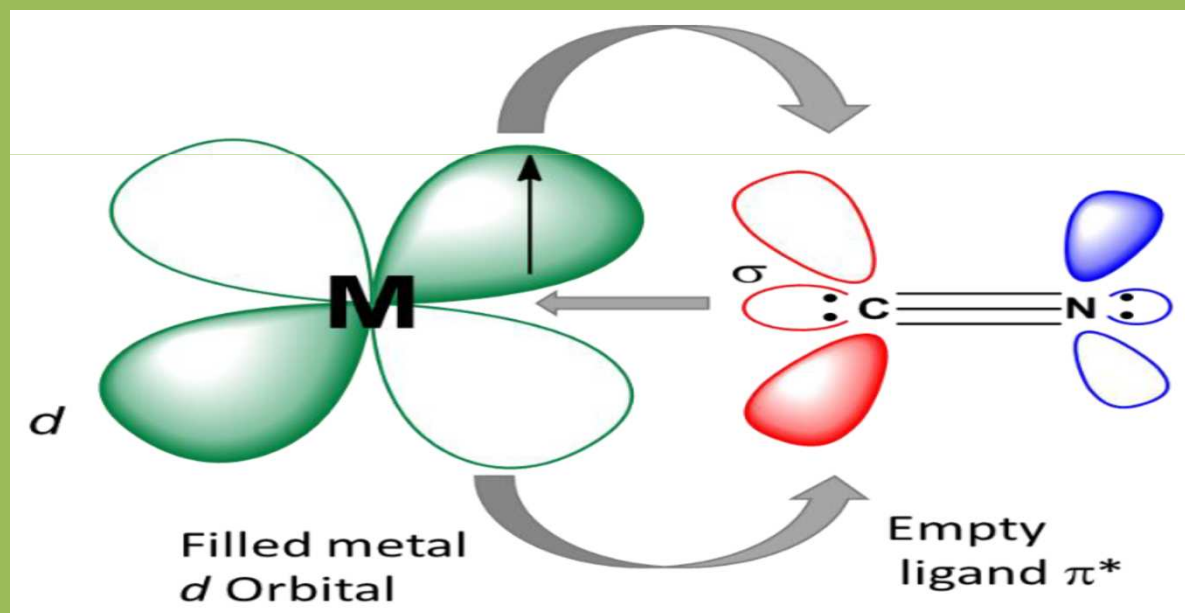
In complex compound metal atom or ion and ligands are present. It may have filled or vacant orbitals & there may be transfer of electron from filled orbital to vacant orbital & gives colour & spectral band. Since it is Laporte forbidden so its intensity is 1000 times  $<$  d-d transition.

Intensity of colour depends upon feasibility of transition.  
Feasibility of CT is inversely proportional to energy gap.

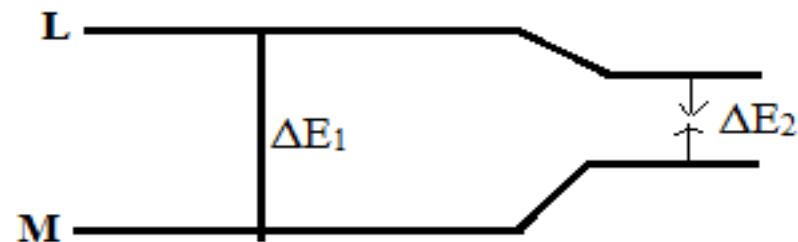
There are four types of CTS

1. Transfer of Charge (e) from M to L (MLCT)
2. Transfer of Charge (e) from L to M (LMCT)
3. Transfer of Charge (e) from M to M (MMCT or IVCT-inter valence)
4. Transfer of Charge (e) from ligand to ligand (LLCT/intra ligand-ILCT)

(MLCT) : Transfer of charge from metals d orbital to ligands orbital is called MLCT.



- It means metal have filled d orbital & ligands have vacant orbital.
- Energy level of metal is lower than ligands
- O.N. of metal is lower (-1 or 0)



Intensity of spectra  $\propto$  1/ feasibility of transition

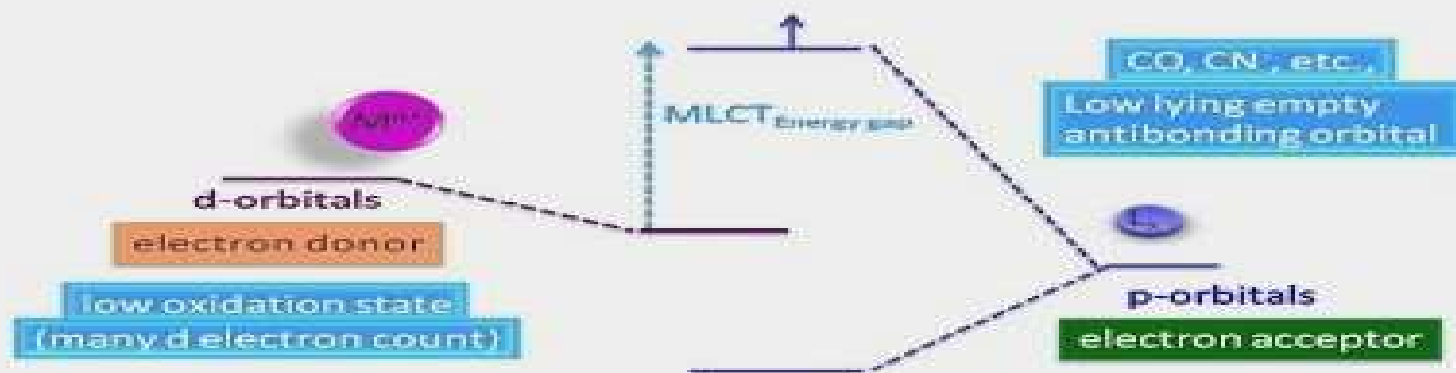
Here,

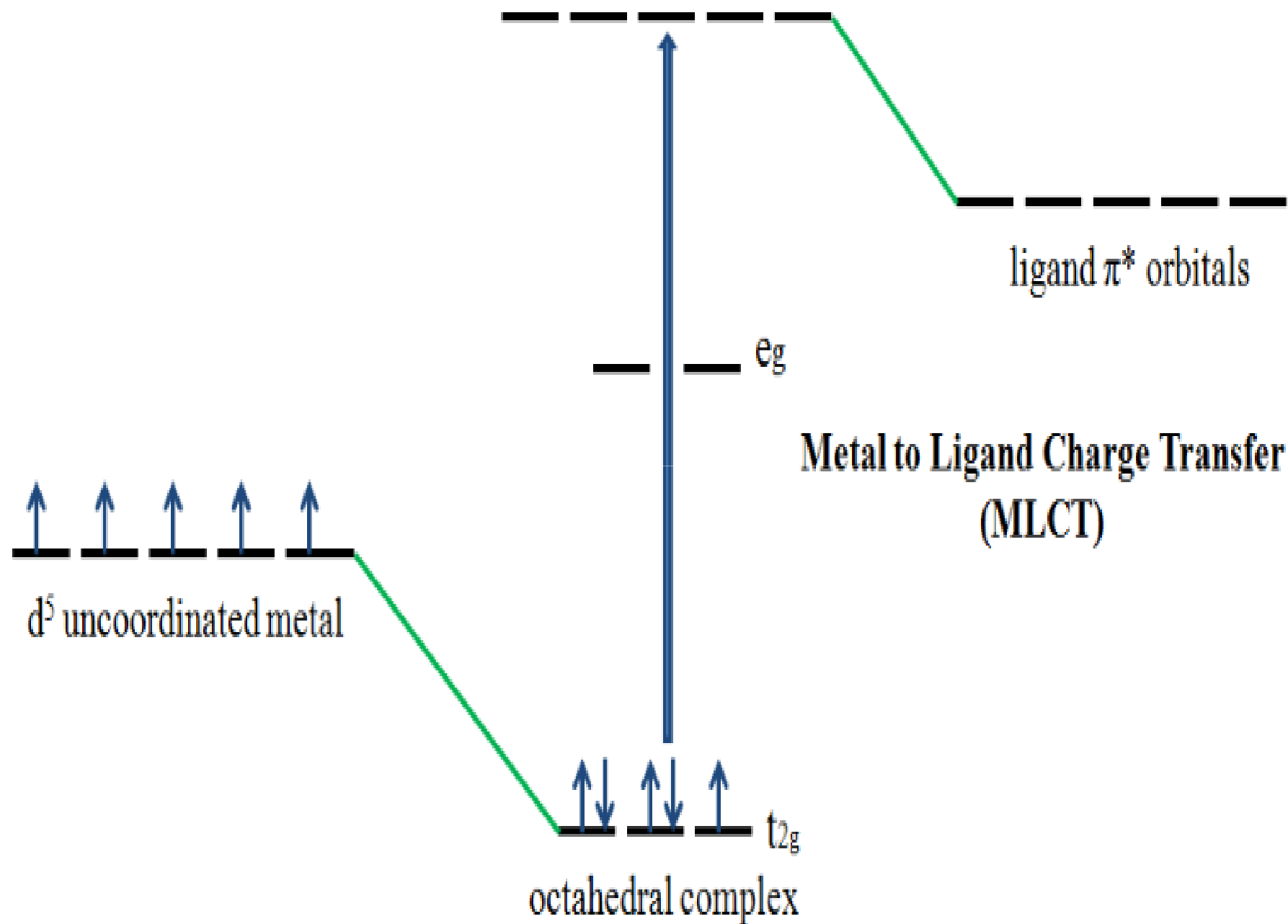
$\Delta E_1 > \Delta E_2$  So feasibility of CT  $\propto$  1/ $\Delta E$ .

So feasibility in  $\Delta E_2$  is

### Molecular Orbital Picture of Charge Transfer Transition

#### Metal to Ligand Charge Transfer







$\Delta E \downarrow$  So wave no ( $\nu$ )  $\downarrow$  ;  $\nu$  (frequency)  $\downarrow$  ;  $\lambda \uparrow$   
 In back bonding (Py, BiPy, Aromatic ligand having MLCT ( $\uparrow$ ) ;  
 Backbonding ( $\uparrow$ )  $\pi$  M.O bond length ( $\downarrow$ ) ; bond strength ( $\uparrow$ ) B.O ( $\uparrow$ ),  
 stretching frequency ( $\nu$ )  $\uparrow$  rotational barrier ( $\uparrow$ )

## Characteristics of MLCT

### Ligand side

1. Ligand should have low energy orbital
2. Ligand should have vacant orbital
3. Ligand should have high O.S.
4. Ligand accept  $e^-$  easily i.e. should be easily reducible. Ex-Co, CN-, Pyridine, Bi Py, Aromatic ligand which have vacant  $\pi^*$  M.O

## Metal side

Metal should have low energy orbital

Metal should have filled d orbital

Metal should have low O.S. (0, -1, -2)

Metal donate e- easily i.e. should be easily oxidizing.

## Significance of MLCT

Due to MLCT there is intense colour, change in wave no. bond length, bond strength, stretching frequency etc.

$\Delta E \downarrow$  So wave no ( $\nu$ )  $\downarrow$  ;  $\nu$  (frequency)  $\downarrow$  ;  $\lambda \uparrow$

In back bonding (Py, BiPy, Aromatic ligand having MLCT ( $\uparrow$ ) ;

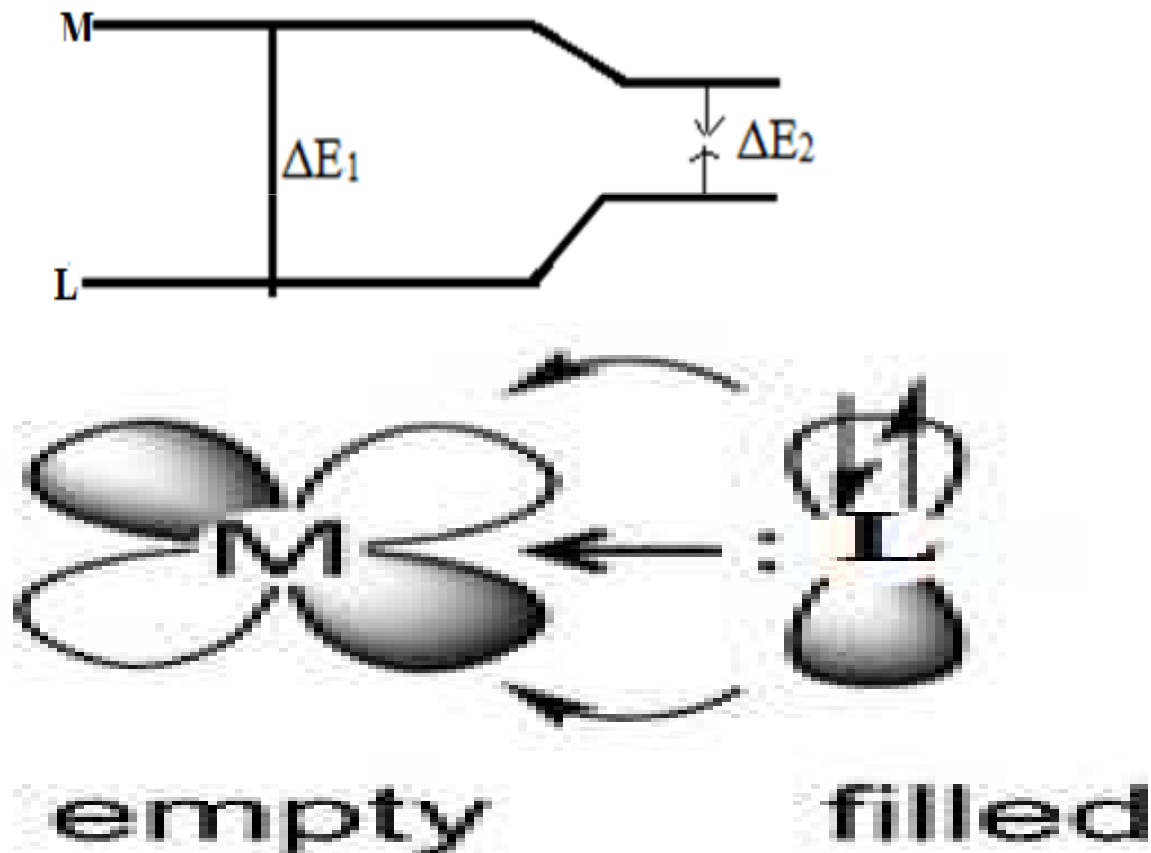
Backbonding ( $\uparrow$ )  $\pi$  M.O bond length ( $\downarrow$ ) ; bond strength ( $\uparrow$ ) B.O ( $\uparrow$ ),

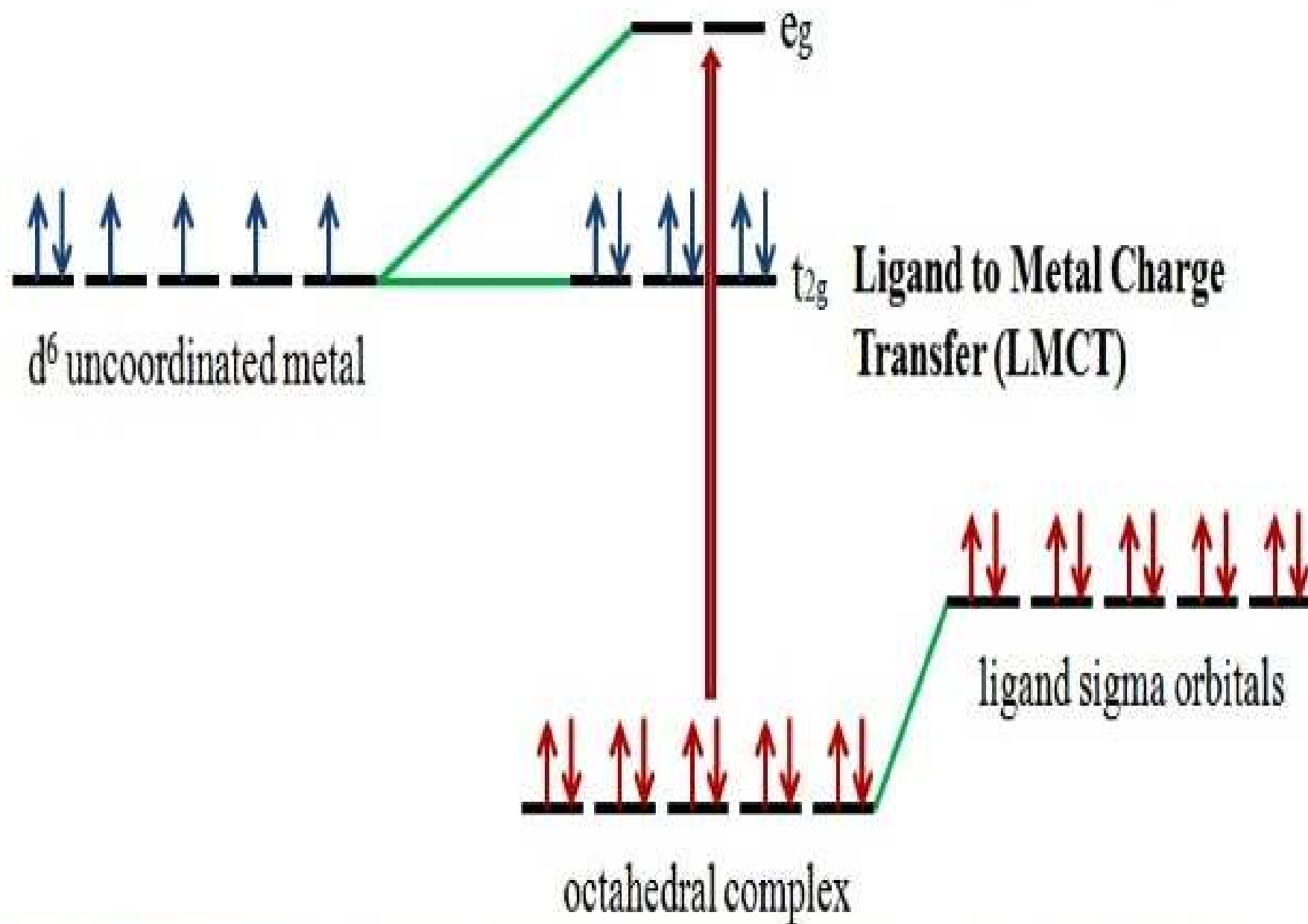
stretching frequency ( $\nu$ )  $\uparrow$  rotational barrier ( $\uparrow$ )

# LMCT

Spectra obtained due to transfer of electron from filled ligand orbital to vacant metal orbital is called LMCTS.

It means ligand have filled orbitals & metal have vacant d orbital





# Characteristics of LMCT

## Ligand side

1. Ligand should have low energy orbital
2. Ligand should have filled orbital,  $\pi$  donor ligand
3. Ligand should have low O.S.
4. Ligand can donate  $e^-$  easily i.e. should be easily oxidisable. Ex-  $X^-$ ,  $O^{2-}$ ,  $RO^-$ ,  $S^{2-}$ ,  $Se^{2-}$ ,  $N_3^-$  etc

## Metal side

Metal should have high energy orbital

Metal should have vacant d orbital

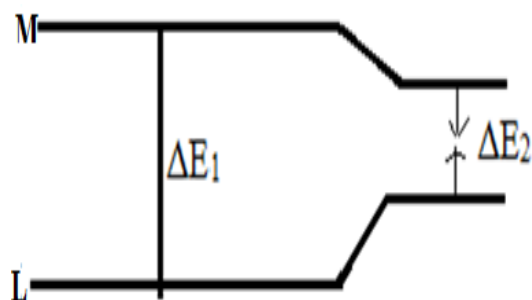
Metal should have high O.S.

Metal can accept  $e^-$  easily i.e. should be easily reducible.

Metal may be of main gr., TE, ITE

# Significance of LMCT

LMCT gives idea about feasibility intensity variation in group or period of periodic table



Intensity of spectra  $\propto 1/\text{feasibility of transition}$

Here,

$\Delta E_1 > \Delta E_2$  So feasibility of CT  $\propto 1/\Delta E$ .  
So feasibility in  $\Delta E_2$  is more

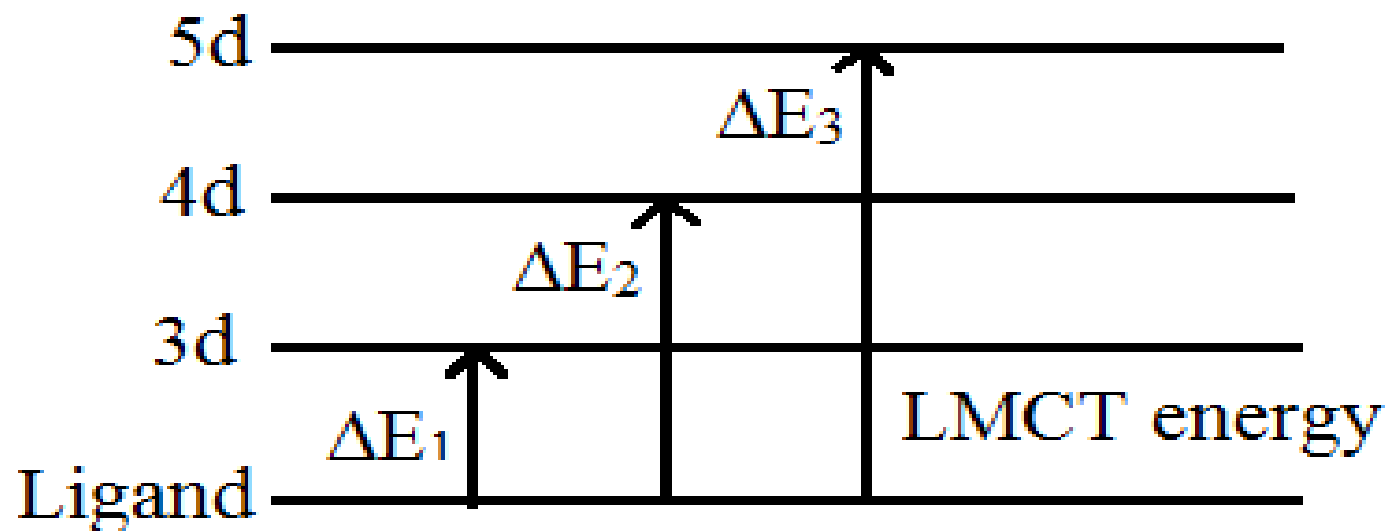
$\Delta E \downarrow$  So wave no ( $v$ )  $\downarrow$  ;  $v$  (frequency)  $\downarrow$  ;  $\lambda \uparrow$

In back bonding (Py, BiPy, Aromatic ligand having MLCT ( $\uparrow$ );

Backbonding ( $\uparrow$ )  $\pi$  M.O bond length ( $\downarrow$ ) ; bond strength ( $\uparrow$ ) B.O ( $\uparrow$ ),

stretching frequency ( $v$ )  $\uparrow$  rotational barrier ( $\uparrow$ )

## 2. Frequency also depends upon size of TEs



Here,

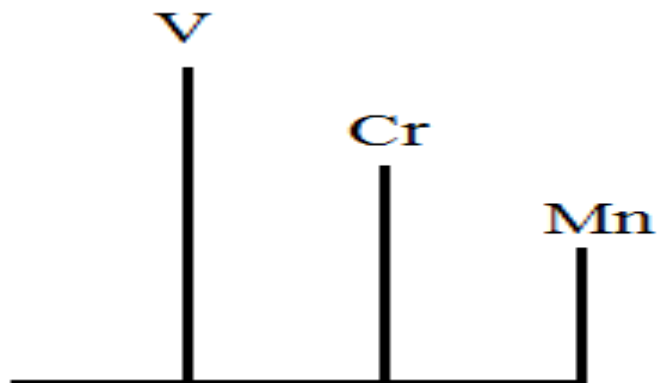
$\Delta E_1 < \Delta E_2 < \Delta E_3$  So  $\Delta E_1$  is easily feasible.

$\Delta E$  increases in group from top to bottom.

LMCT is increases from top to bottom..

### 3. In same period of PT

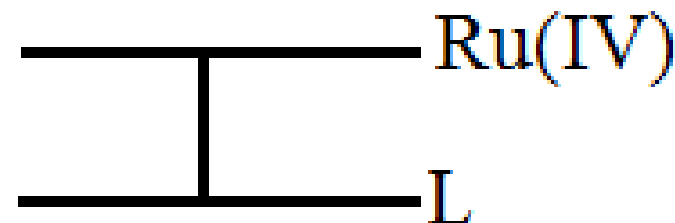
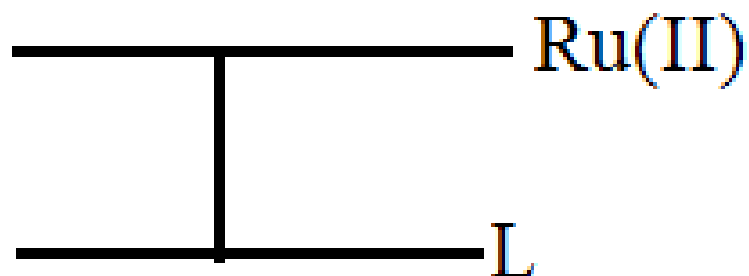
LMCT  $\propto$  effective nuclear charge



On moving in same period of periodic table from left to right size decreases due to effecting nuclear charge hence LMCT decreases (if ligands are same)

4. O. N. are different of same metal

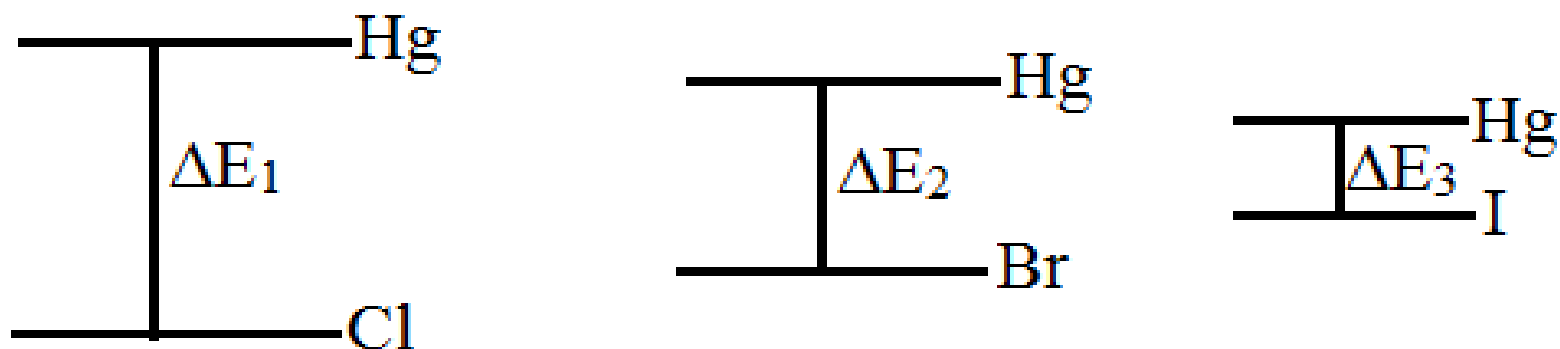
LMCT  $\propto$  1/ O.N



So LMCT of Ru(II) > Ru(IV)



## 5. When size of ligand are different but metal are same



Here,

$$\Delta E_3 < \Delta E_2 < \Delta E_1$$

$\text{HgI}_2$  is more intense.

In summary

1. LMCT increases in group decreases on moving top to bottom.
2. LMCT decreases on moving left to right in period.
3. LMCT decreases on increasing O.N. of metal.
4. LMCT decreases on increasing level of ligand.

## MMCT or IVCT

Transfer of  $e^-$  from filled orbital of 1 metal ion to vacant orbital of other metal ion of a complex compound is called MMCT or IVCT.

i.e. it contains two types of metal ion in one molecule. One has filled orbital and another have vacant orbital. Ex-

$K\{\overset{+3}{Fe}[\overset{+2}{Fe}(CN)_6]\}$  == Blue Colour due to transfer of  $e^-$  from +2 to +3

$\overset{+3}{Fe}_4[\overset{+2}{Fe}(CN)_6]_3$  == Blue colour due to transfer of  $e^-$  from +2 to +3

Rust is reddish due to transfer of  $e^-$  from  $Fe^{+2}$  to  $Fe^{+3}$  in  $Fe_3O_4$

If spinal is colour then MMCT occurs.

$Pb_3O_4$  is colour due to MMCT from  $Pb^{+2}$  to  $Pb^{+4}$

## LLCT or ILCT

Transfer of  $e^-$  from one ligand to another ligand of a complex compound is called intra ligand charge transfer it contains two types of ligands. One have vacant orbital and one have filled orbital it contains  $\pi$  donor ligand and  $\pi$  acceptor ligand i.e. it has charge transfer of  $e^-$  from  $\pi$  to  $\pi^*$  orbital.



*Thank You*

