M.Sc Chemistry
Inorganic Chemistry
Semester-II

UNIVERSITY OF DELHI

Course Title: Chemistry of d and f block elements

Course Code: 201-B

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Inorganic Group III and IV

REFERENCE BOOKS:

1. Electronic Spectra of Transition Metal Complexes by D. Sutton
2. Introduction to Ligand Field Theory: Figgis
3. Concise Inorganic Chemistry by J. D. Lee

Molecular Orbital Theory

VBT: Electronic Properties (X)
CFT: Spectrochemical Series (X)

MOLECULAR ORBITAL THEORY (MOT)

It encompasses a purely covalent as well as a purely electrostatic model & all possible intermediate situations.

According to the Molecular Orbital Theory, individual atoms combine to form molecular orbitals.

(i) Orbitals involved for bonding should have similar energy and overlap in the same region of space
(ii) Symmetry properties of combining orbitals should match
(iii) Number of molecular orbitals formed will the same as the number of atomic orbitals

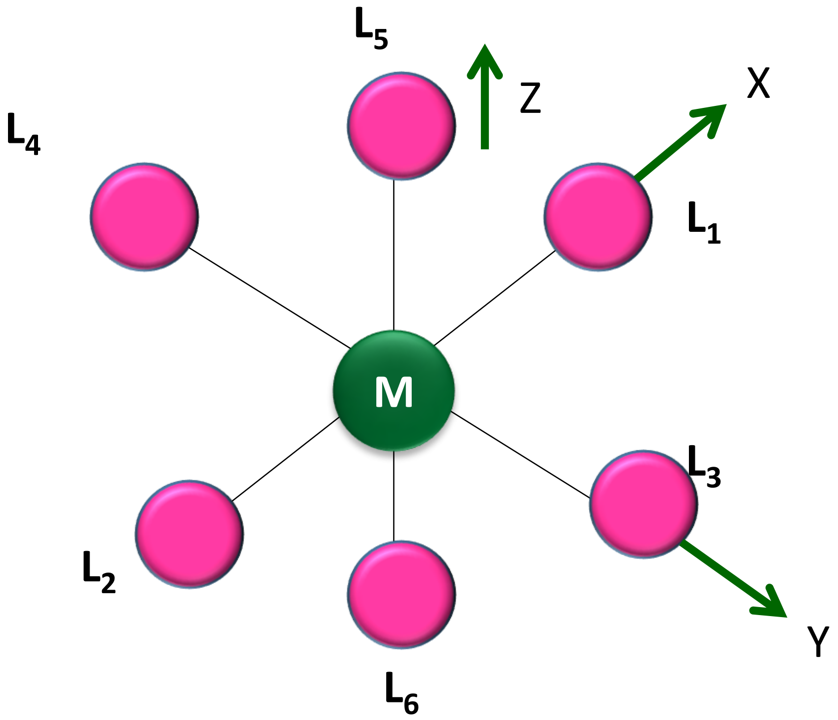
- Explains covalent bonding in complexes.

- Covalent bonds formed by the linear combinations of the metal atomic orbitals and ligand group orbitals.

- Symmetries of ligand group orbitals must match the symmetries of metal atomic orbitals such that there is positive overlapping of LGOs with metal orbitals along the bonding axes.

Sigma Bonding in octahedral complexes

In octahedral complexes, ligands are approaching the metal cation on x, y and z axes. Therefore, LGO's will overlap with metal orbital along the octahedral bonding axes to form σ bonds.



METAL (3d Transition metal)

4s, 4p and 3d

(only 6 out of 9 orbitals involved in σ bonding

Octahedral symmetry transforms **s orbital** into **a_{1g}**

Octahedral symmetry transforms **p orbital** into **t_{1u}**

Octahedral symmetry transforms **d_{xy}, d_{yz} and d_{xz}** into **t_{2g} and dx2-y2 and dz^2 into e_g sets**

Since a_{1g} orbital is spherical in shape, therefore it can overlap with LGO's along the axes.

These orbitals are pointing along axis and can form σ bonds by overlapping with LGOs

These orbitals lie between axis and are not capable of overlapping with LGO's to form σ bonds

Orbitals involved in σ bonding

a_{1g}

t_{1u}

e_g

t_{2g} orbitals lie in between the axes and therefore these orbitals are not capable of overlap with LGOs to form σ bonds. They are considered to be non-bonding orbitals.

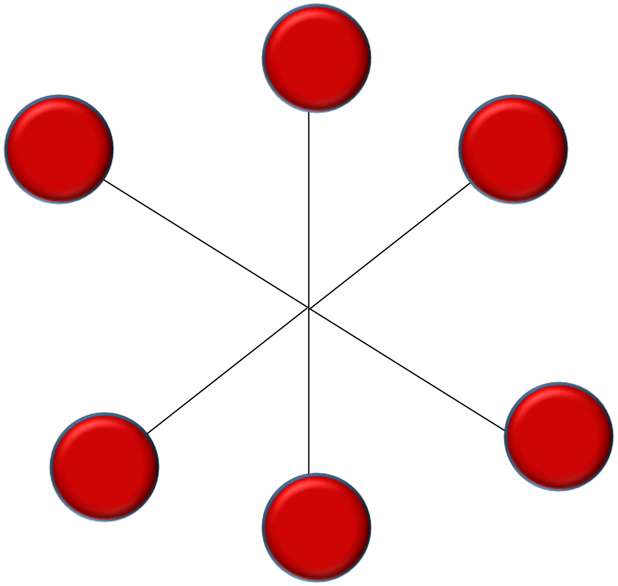
SYMMETRY ADOPTED LINEAR COMBINED LIGAND ORBITALS (SALO)

Ligands individually don't match symmetry.

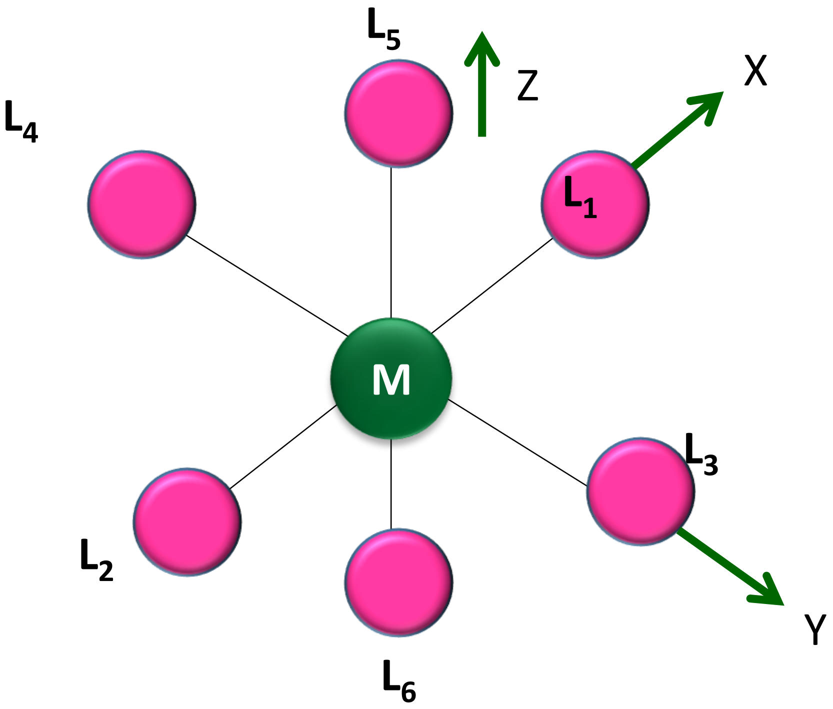
All ligands don't match symmetry of metal orbitals, but they adjust themselves by individually interacting with the metal center.

For eg:

4s



All six ligands interact equally with the metal center.



$$\sum_{a1g} (\psi_1) = \frac{1}{\sqrt{6}} \psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6$$

$$\sum p_z = \frac{1}{\sqrt{2}} (\psi_5 - \psi_6) \quad \sum p_x = \frac{1}{\sqrt{2}} (\psi_1 - \psi_2)$$

$$\sum p_y = \frac{1}{\sqrt{2}} (\psi_3 - \psi_4)$$

$$\sum dx^2\text{-}y^2 = \frac{1}{2} \psi_1 + \psi_2 - \psi_3 - \psi_4$$

$$\sum dz^2 = \frac{1}{\sqrt{12}} \left(2\psi_5 + 2\psi_6 - \psi_1 - \psi_2 - \psi_3 - \psi_4\right)$$

Metal orbitals	**Ligand orbitals**
a_{1g}	$\sum a_{1g}$
t_{1u}	$\sum t_{1u}$
e_g	$\sum e_g$

$\psi_M \longrightarrow$ Wave function of MO of metal

$\psi_L \longrightarrow$ Wave function of MO of ligand

$$\Psi_b = \alpha\psi_M + \beta\psi_L$$

$$\Psi_a = \beta\psi_M - \alpha\psi_L$$

α and β are co-efficients to make Ψ_a and Ψ_b normalized

$\alpha^2 + \beta^2 = 1$

(i) If $\alpha = \beta$

$\alpha = \beta = 1/\sqrt{2}$

Covalent character: Both M and L are involved in bonding i.e. sharing.

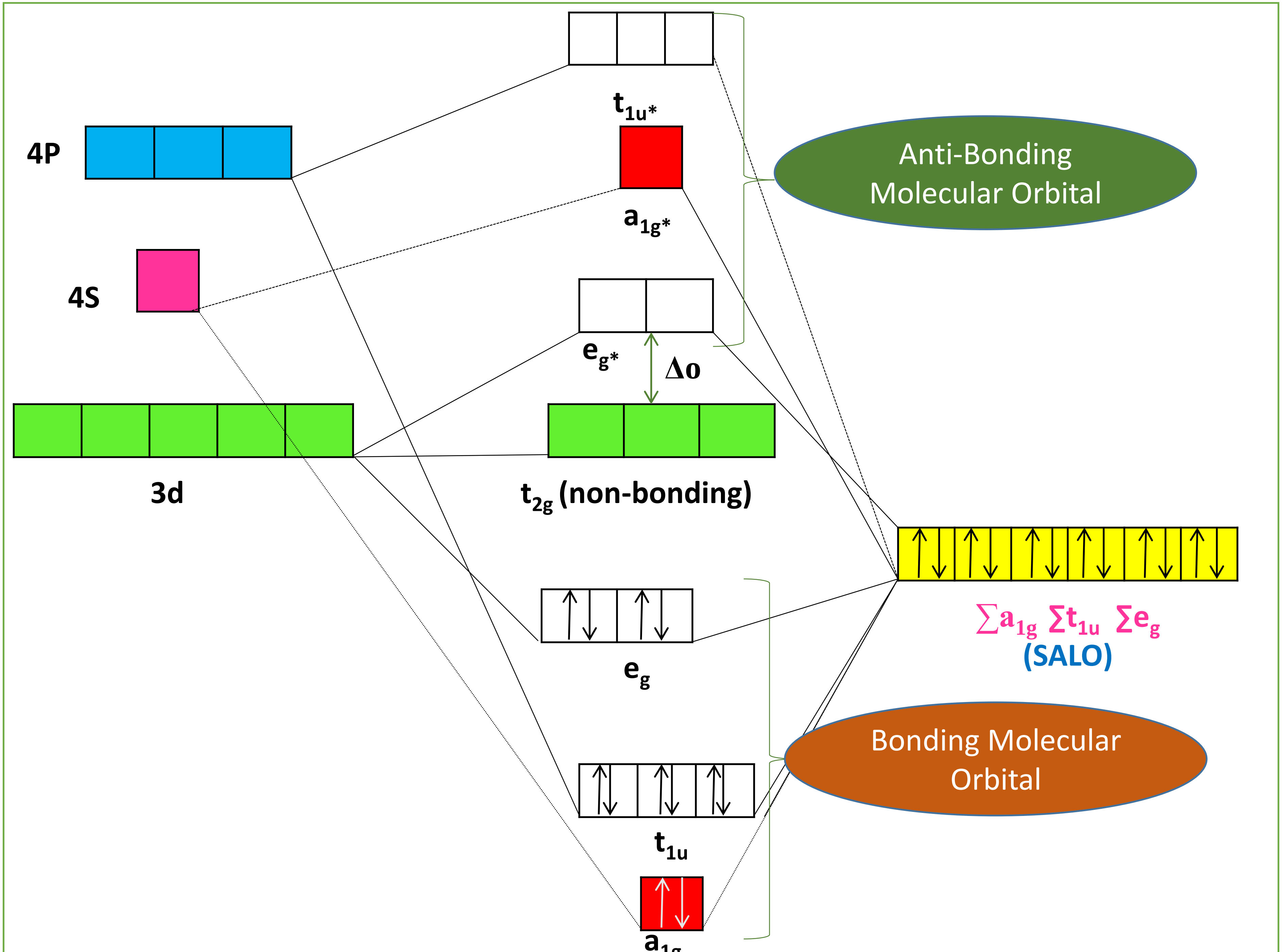
Nature of complex can be deduced from the values of α and β

(ii) If $\alpha = 0$ (ionic)

$\boldsymbol{0 < \alpha < 1/\sqrt{2}}$

Truly ionic

Truly covalent


4P
4S
3d
t_{1u*}
a_{1g*}
e_{g*}
Δo
t_{2g} (non-bonding)
e_g
t_{1u}
a_{1g}
Anti-Bonding Molecular Orbital
Bonding Molecular Orbital
$\sum a_{1g}$ $\sum t_{1u}$ $\sum e_g$
(SALO)

1.
   - From symmetry properties, metal and ligand a_{1g} orbitals overlap to give two molecular orbitals (one bonding a1g and one antibonding a_{1g}*)

2.
   - The triply degenerate metal and ligand t_{1u} orbitals will overlap to give six molecular orbitals (t_{1u} and $t_{1u*)}$

3.
   - Doubly degenerate metal and ligand eg orbitals will overlap to give four molecular orbitals (eg and eg*)

4.
   - t2g is non bonding and therefore has same energy as metal cation.

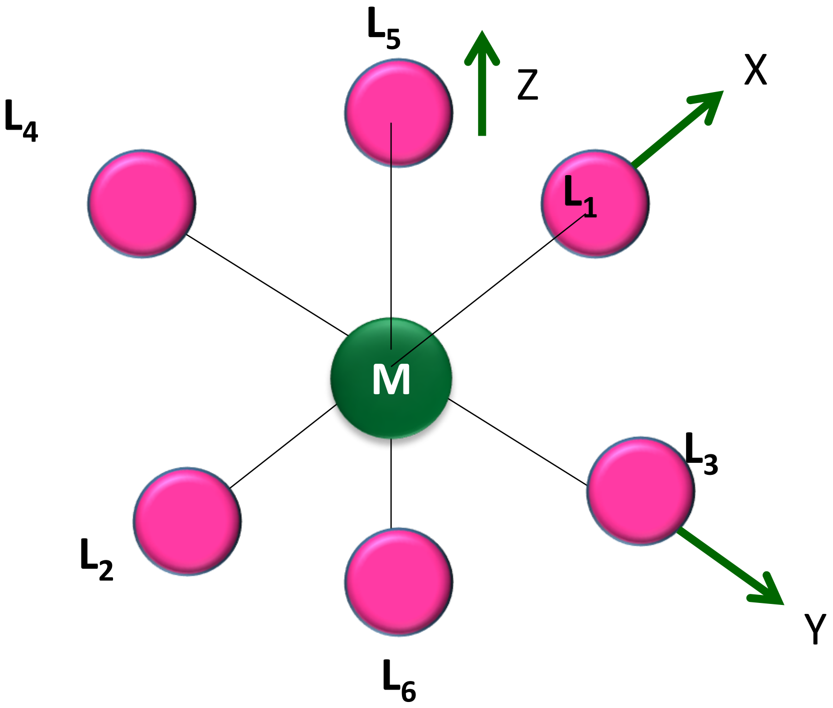
5.
   - Energy difference between t2g and eg* molecular orbitals is equal to Δo

6.
   - A given MO has the character associated with the atomic orbital nearest in energy. Therefore, six bonding MO's will have primarily the character of ligand orbitals while the antibonding MO's will have mainly the character of corresponding metal orbitals.

Π-bonding of octahedral complexes

Ligands which have orbitals with Π symmetry with respect to octahedral axis are capable of Π bonding interaction with the metal atom.

The metal and ligand orbitals involved in Π bonding are perpendicular to M-L axis.

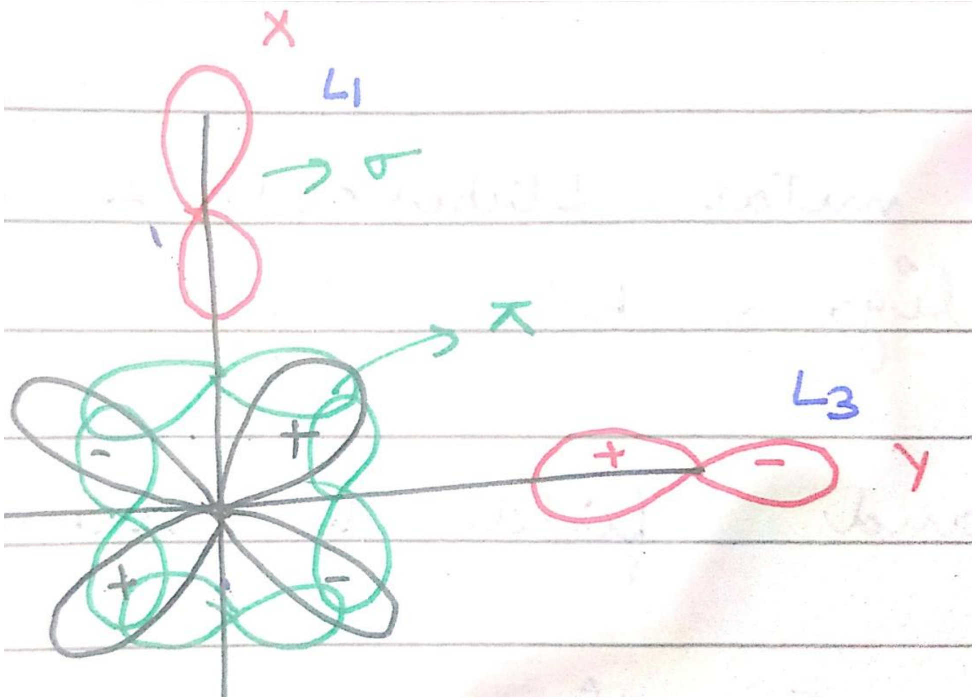


If we take L1:

p_x approaching in x direction (forms σ bond)

p_y and p_z are perpendicular to x axis (forms π bond)

t_{2g} is non bonding (dxy, dyz and dzx)



Perpendicular

Π bonding

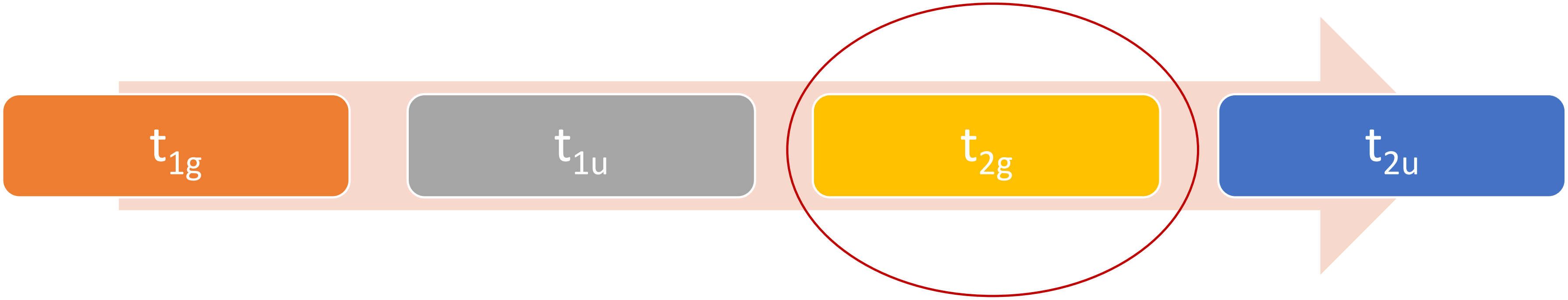
Along axis

σ Bonding

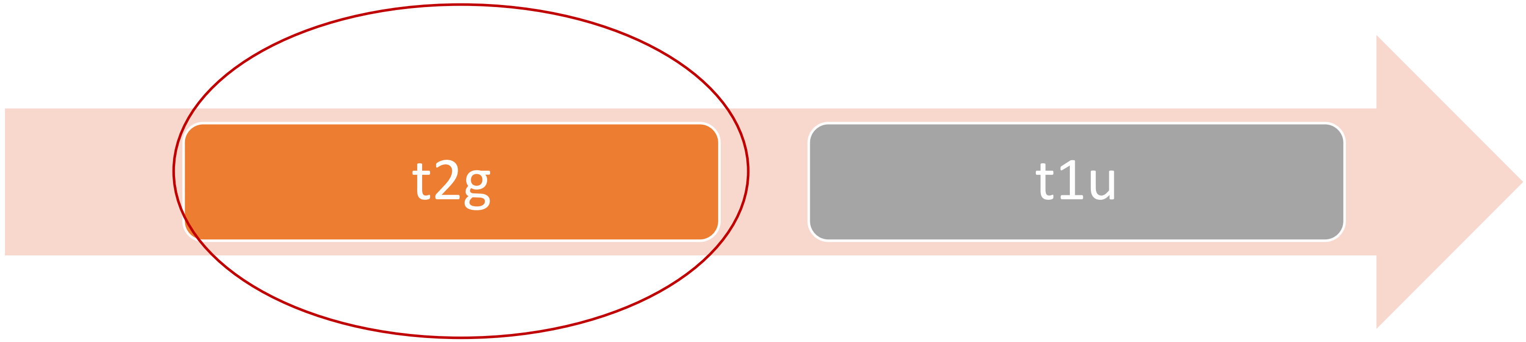
Three Symmetry adopted Π symmetry ligand

t_{2g}

LGO’s involved in Π bonding



Metal orbitals involved in Π bonding



- t_{1g} and t_{2u} ligand orbitals are non bonding because there are no metal orbitals of these symmetries.
- Metal orbitals of t_{1u} symmetry are directed at the ligands and therefore involved in σ bonding and not in Π bonding.
- **t_{2g} ligand and metal orbitals can only undergo Π bonding.**

CASE 1

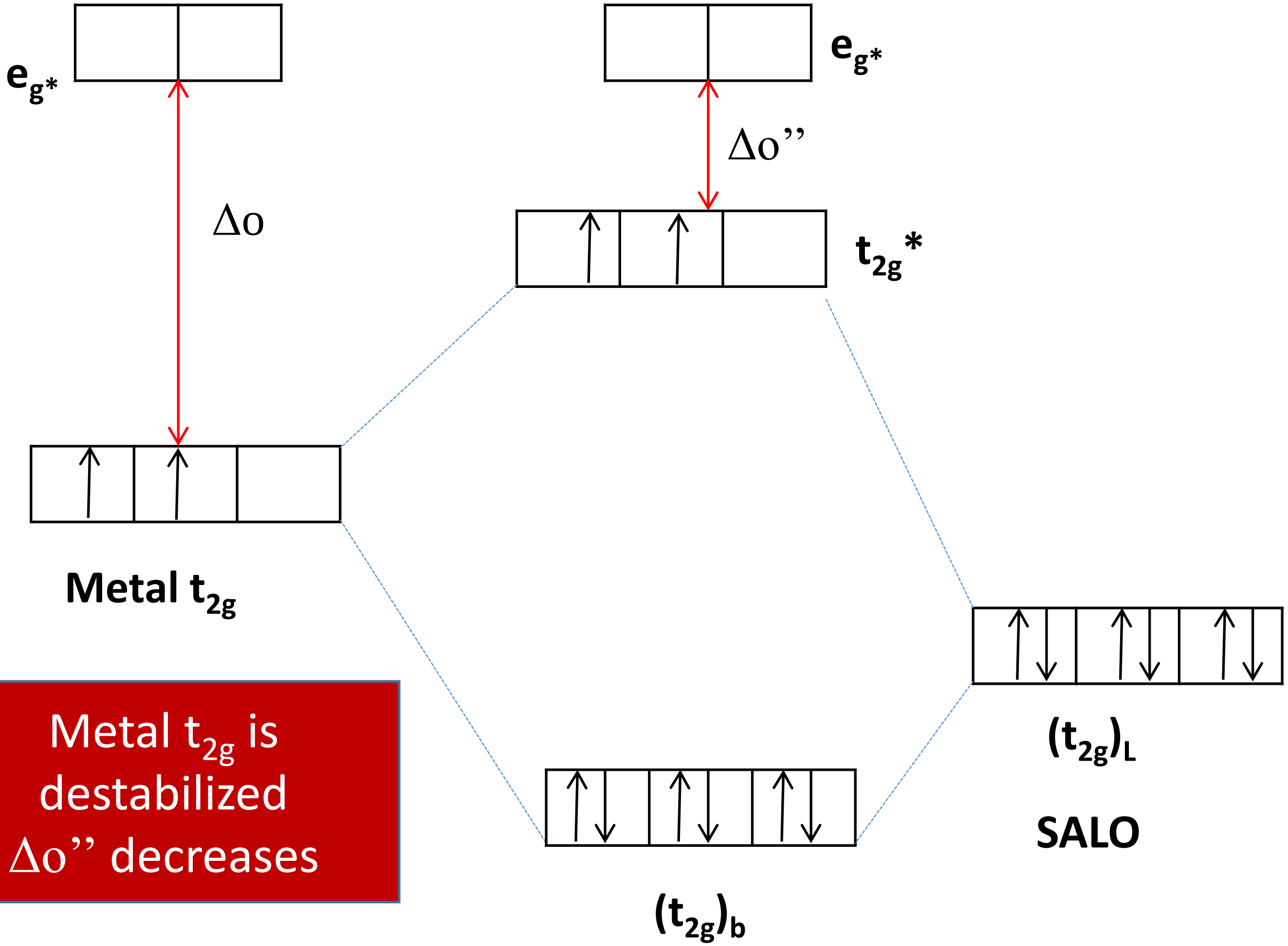
- Ligand t_{2g} orbitals are filled and are of lower energy than partly filled metal t_{2g} orbitals

CASE 2

- If t2g orbitals are empty and of higher energy than the metal partly filled t_{2g} orbitals.

CASE 1: Π donor

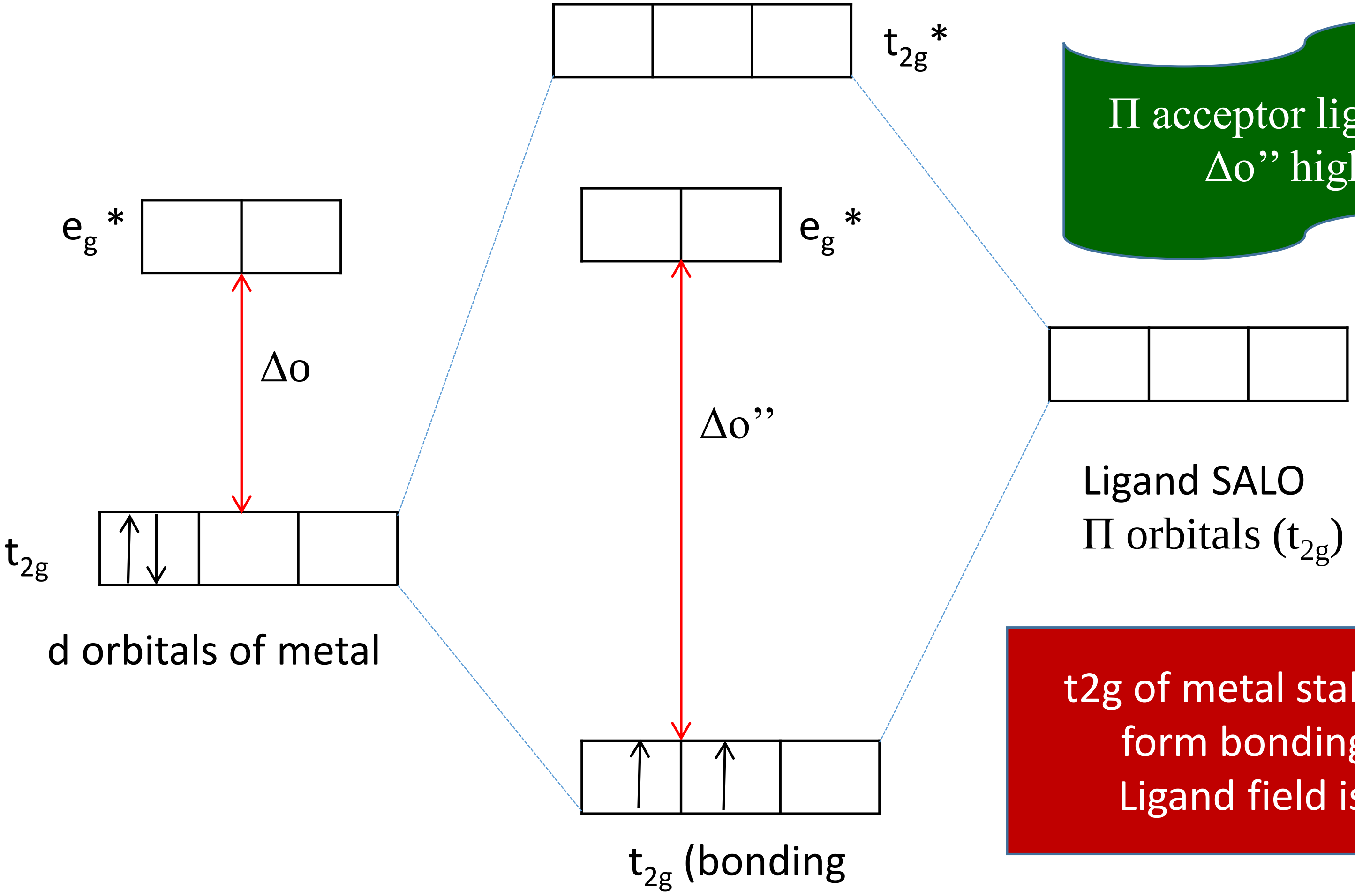
Ligand t_{2g} orbitals are filled and are of lower energy than partly filled metal t_{2g} orbitals



Metal t_{2g} is destabilized
Δo'' decreases

CASE 2: Π acceptor

If t_{2g} orbitals are empty and of higher energy than the metal partly filled t_{2g} orbitals



Π acceptor ligand CO
Δo” higher

t2g of metal stabilised and
form bonding ligand
Ligand field is strong

SPECTROCHEMICAL SERIES

Π donor	**<**	**weak Π donor**	**<**	**σ only**	**<**	**Π acceptor**
Cl^-, Br^-, F^-		OH^-, H_2O		NH_3		PR_3, CO, CN^-

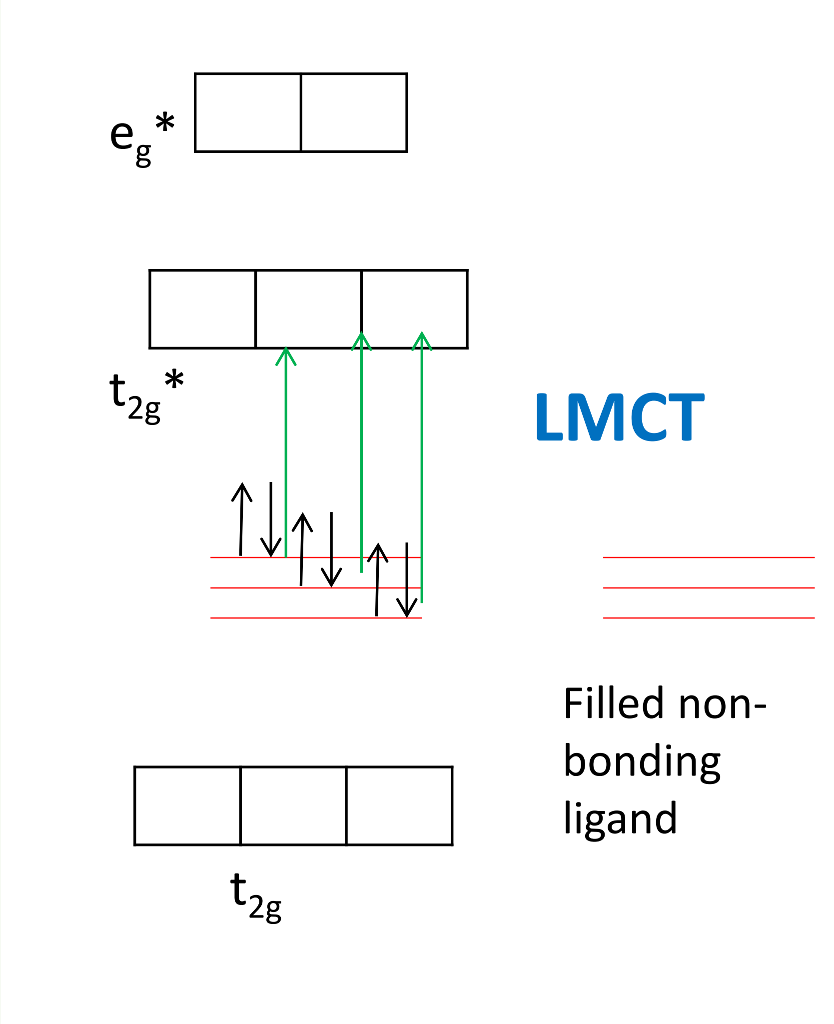
CHARGE TRANSFER

1. LMCT → Higher OS (MnO_4^-, $Cr_2O_7^{2-}$)
2. MLCT → Low OS, empty non-bonding orbitals eg: Bipyridine

(i) Nature of non-bonding ligand orbital

(ii) Oxidation State (OS) of metal

CHARGE TRANSFER



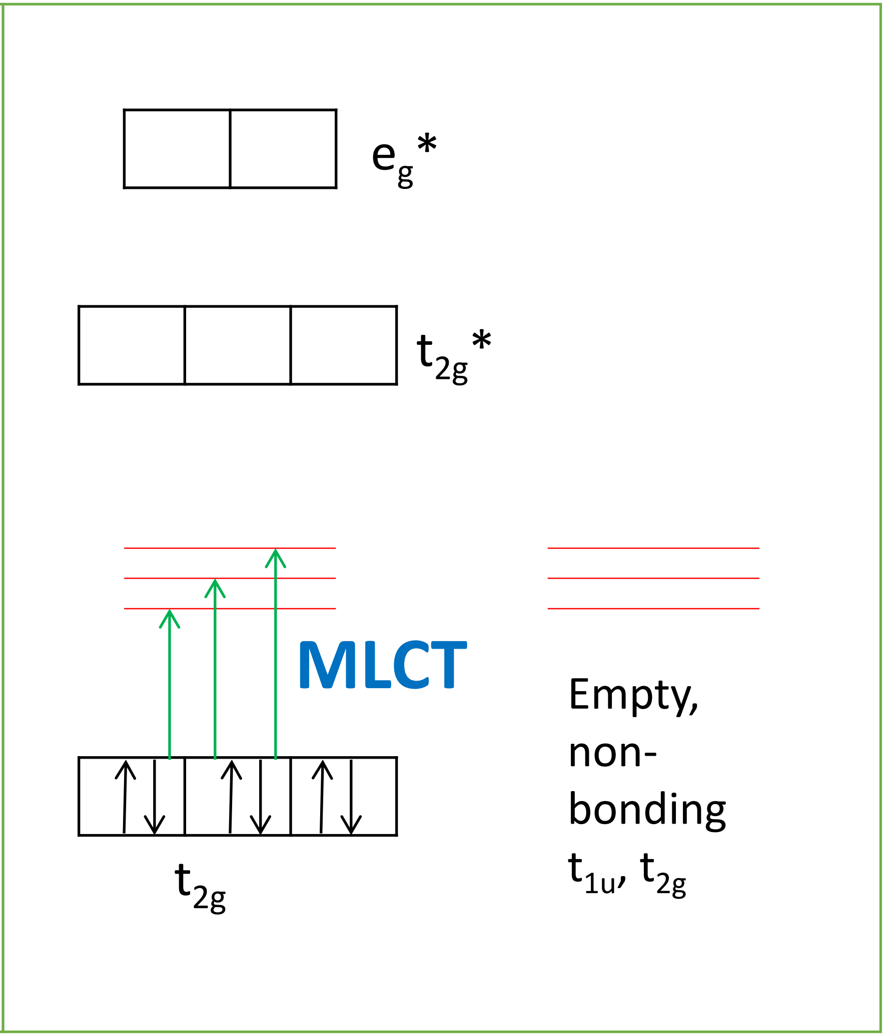
e_g^*

t_{2g}^*

LMCT

Filled non-bonding ligand

t_{2g}



e_g^*

t_{2g}^*

MLCT

Empty, non-bonding t_{1u}, t_{2g}

t_{2g}