

UNIT-II- COORDINATION COMPOUNDS-II

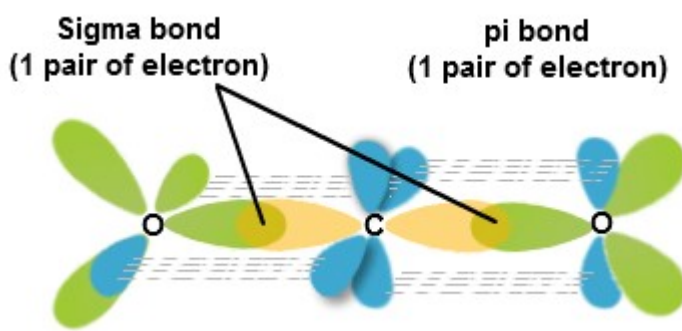
Theories of Coordination Compounds

Valence bond theory (VB Theory)

Valence bond theory, primarily the work of Linus Pauling regarded bonding as characterized by the overlap of atomic or hybrid orbitals of individual atoms.

The postulates of valence bond theory

1. The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number.
2. These vacant orbitals form covalent bonds with the ligand orbitals.
3. A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand, σ (sigma) bond.
4. Sigma bonds and pi bonds differ in the pattern that the atomic orbitals overlap in, i.e. pi bonds are formed from sidewise overlapping whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.



5. A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called 'hybridisation'. A hybridised orbital has better directional characteristics than an unhybridised one.

The following table gives the coordination number, orbital hybridisation and spatial geometry of the more important geometries.

Coordination number	Types of hybridization	Geometry
2	sp	linear
2	sp^3	tetrahedral
2	dsp^2	square planar
2	d^2sp^3	octahedral
2	sp^3d^2	octahedral

Magnetic moment

A species having atleast one unpaired electron, is said to be paramagnetic.

It is attracted by an external field. The paramagnetic moment is given by the following spin-only formula.

$$\mu_s = \sqrt{n(n+2)} \text{ BM}$$

μ_s = spin-only magnetic moment

n = number of unpaired electrons

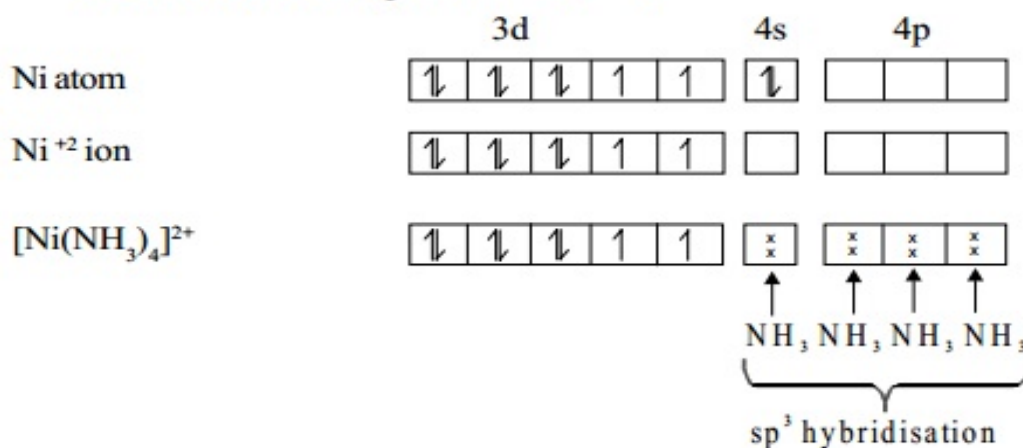
BM = Bohr magneton, the unit which expresses the magnetic moment. When the species does not contain any unpaired electron, it is diamagnetic.

Number of unpaired electrons	Spin-only moment (BM)
1	$\sqrt{1(1+2)} = 1.73$
2	$\sqrt{2(2+2)} = 2.83$
3	$\sqrt{3(3+2)} = 3.87$
4	$\sqrt{4(4+2)} = 4.90$
5	$\sqrt{5(5+2)} = 5.92$

Applications of valence bond theory

1) Nickel atom

Outer electronic configuration $3d^8 4s^2$



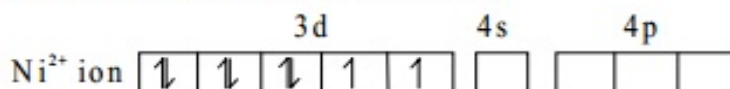
Number of unpaired electrons = 2

$$\therefore \mu_s = \sqrt{2(2+2)} = 2.83 \text{ BM}$$

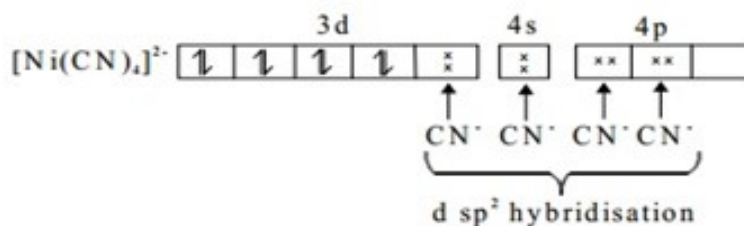
Since the hybridisation is sp^3 , the geometry of the molecule is tetrahedral.

2) [Ni(CN)₄]²⁻

Another possible geometry for the 4 coordinated complex is the square planar configuration involving dsp^2 hybridisation.



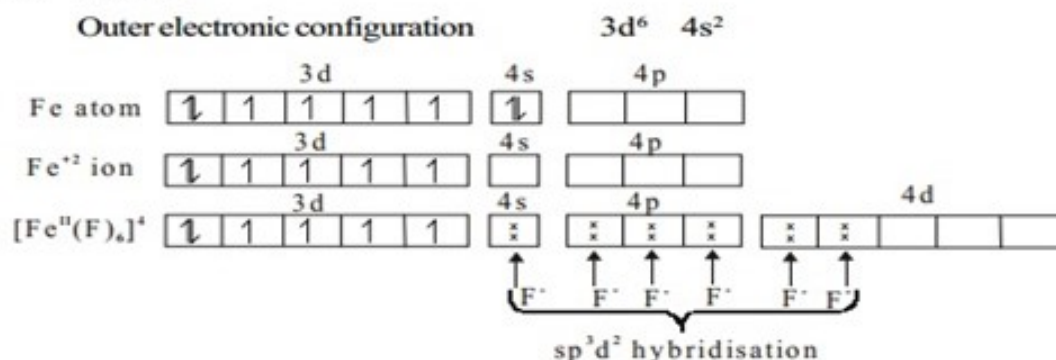
The ligand CN⁻ is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals. Hence this complex ion does not contain unpaired electrons. It is diamagnetic.



The geometry of the molecule is square planar.

Octahedral complexes

1) Fe atom



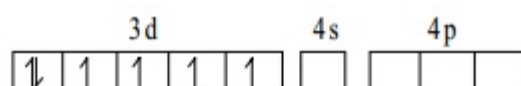
Number of unpaired electron = 4

$$\therefore \mu_s \sqrt{4(4+2)} = \sqrt{24} = 4.90 \text{ BM}$$

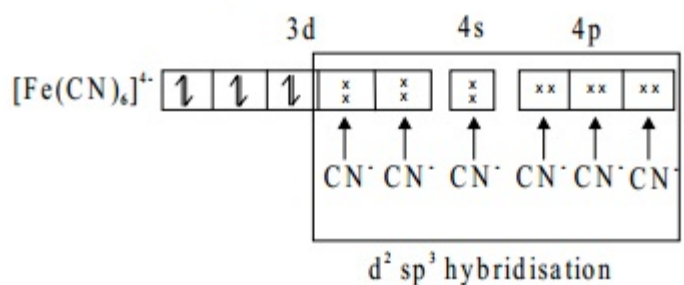
The molecule is paramagnetic. The geometry of the molecule is octahedral.

(n)d orbital involved in hybridisation is called as a Outer orbital complex

2) Fe^{+2} ion



In $[Fe(CN)_6]^{4-}$ complex the CN^- ligand is a powerful ligand, it forces the unpaired electrons in 3d level to pair up inside. Hence the species has no unpaired electron. The molecule is diamagnetic.



(n-1) d orbital involved in hybridisation is called as a Inner orbital complex

Defects of Valence bond theory

Although VB theory was the principal way in which chemist visualized coordination compounds until the 1950s, it has fallen into disfavour due to its inability to account for various magnetic, electronic and spectroscopic properties of these compounds.

(or)

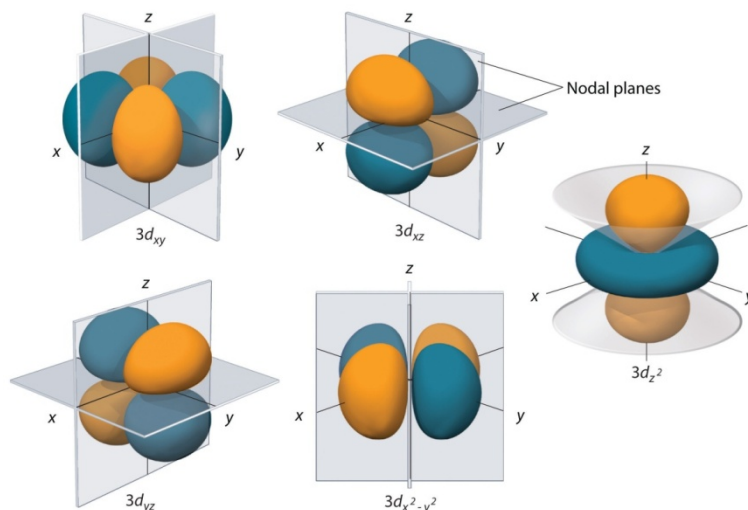
Limitation of the VB theory

- It does not tell anything about the spectral properties of the complexes.
- It does not give quantitative interpretation of magnetic data.
- It does not distinguish between strong and weak ligands.
- It does not explain the colour exhibited by coordination compounds.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

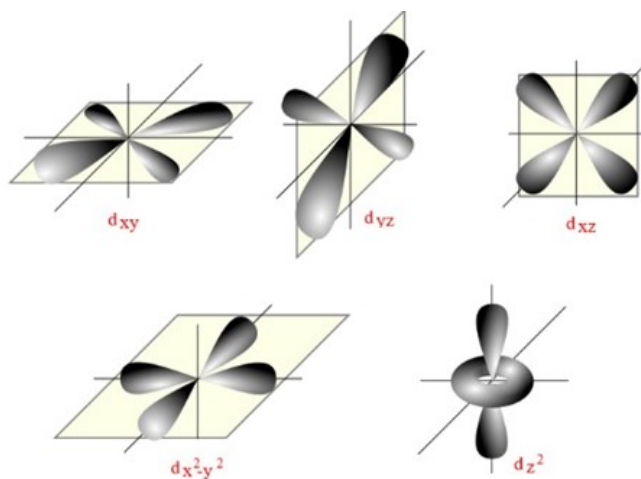
Crystal field theory:

Before go to CFT, must understand Shape of d-Orbitals

All of the d orbitals have four lobes of electron density, except for the d_{z^2} orbital, which has two opposing lobes and a doughnut of electron density around the middle. The d orbitals can also be divided into two smaller sets. The $d_{x^2-y^2}$ and d_{z^2} all point directly along the x, y, and z axes. They form an e_g set. On the other hand, the lobes of the d_{xy} , d_{xz} , and d_{yz} all line up in the quadrants, with no electron density on the axes. These three orbitals form the t_{2g} set. In most cases, the d orbitals are degenerate, but sometimes they can split, with the e_g and t_{2g} subsets having different energy. The CFT accounts for this.



(OR)



CFT:

The valence bond theory could not explain the stability of the coordination compounds. It also failed to throw a light on the differences between strong and weak ligands. Therefore, scientists proposed the crystal field theory.

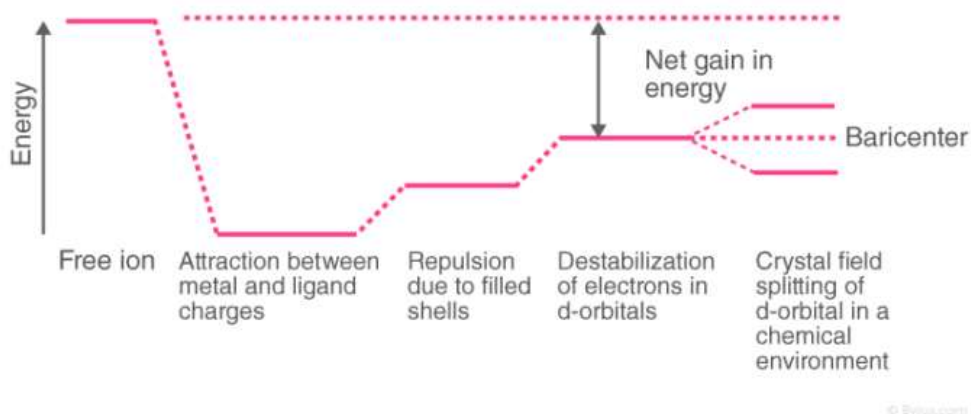
According to this theory, the metal-ligand bond acts as an ionic bond arising purely from the electrostatic interactions between the metal ions and ligands. This theory takes anions as point charges and neutral molecules as dipoles. When the transition metals do not bond to any ligand, their d orbitals degenerate. This means that they have the same amount of energy.

When they start bonding with other ligands, the d orbitals split apart and become non-degenerate. This bonding occurs mainly due to different symmetries of the d orbitals and the inductive effect of the ligands on the electrons. The pattern of the splitting of d orbitals depends on upon the nature of crystal field.

Overview of Crystal Field Theory

In order to understand clearly the crystal field interactions in transition metal complexes, it is necessary to have knowledge of the geometrical or spatial disposition of d orbitals. The d-orbitals are fivefold degenerate in a free gaseous metal ion. If a spherically symmetric field of negative ligand field charge is imposed on a central metal ion, the d-orbitals will remain degenerate but followed by some changes in the energy of free ion.

A summary of the interactions is given below.



Crystal Field Splitting

Crystal field theory was proposed which described the metal-ligand bond as an ionic bond arising purely from the electrostatic interactions between the metal ions and ligands. Crystal field theory considers anions as point charges and neutral molecules as dipoles.

When transition metals are not bonded to any ligand, their d orbitals are degenerate that is they have the same energy. When they start bonding with other ligands, due to different symmetries of the d orbitals and the inductive effect of the ligands on the electrons, the d orbitals split apart and become non-degenerate.

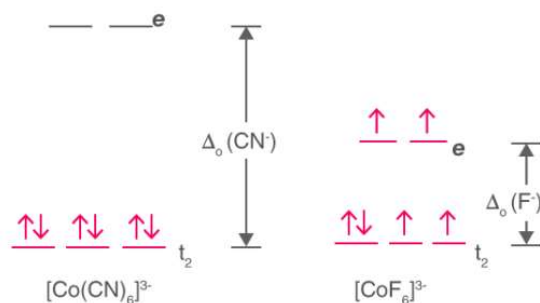
High Spin and Low Spin

The complex with the greater number of unpaired electrons is known as the high spin complex, the low spin complex contains the lesser number of unpaired electrons. High spin

complexes are expected with weak field ligands whereas the crystal field splitting energy is small Δ . The opposite applies to the low spin complexes in which strong field ligands cause maximum pairing of electrons in the set of three t_2 atomic orbitals due to large Δ_o .

- **High spin** – Maximum number of unpaired electrons.
- **Low spin** – Minimum number of unpaired electrons.

Example: $[\text{Co}(\text{CN})_6]^{3-}$ & $[\text{CoF}_6]^{3-}$



High Spin and Low Spin Complex

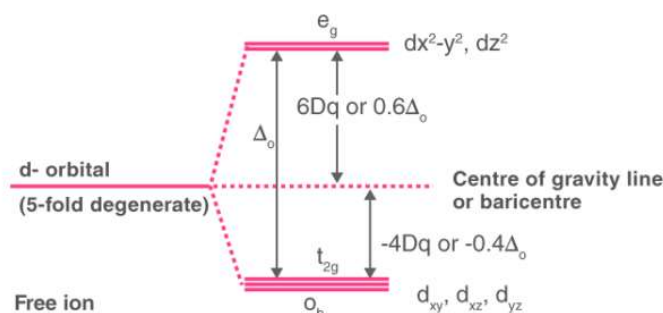
- $[\text{Co}(\text{CN})_6]^{3-}$ – Low spin complex
- $[\text{CoF}_6]^{3-}$ – High spin complex

Crystal Field Splitting in Octahedral Complex

- In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.
- This repulsion is experienced more in the case of $d_{x^2-y^2}$ and d_{z^2} orbitals as they point towards the axes along the direction of the ligand.
- Hence, they have higher energy than average energy in the spherical crystal field.
- On the other hand, d_{xy} , d_{yz} , and d_{xz} orbitals experience lower repulsions as they are directed between the axes.
- Hence, these three orbitals have less energy than the average energy in the spherical crystal field.

Thus, the repulsions in octahedral coordination compound yield two energy levels:

- t_{2g} – set of three orbitals (d_{xy} , d_{yz} and d_{xz}) with lower energy
- e_g – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with higher energy



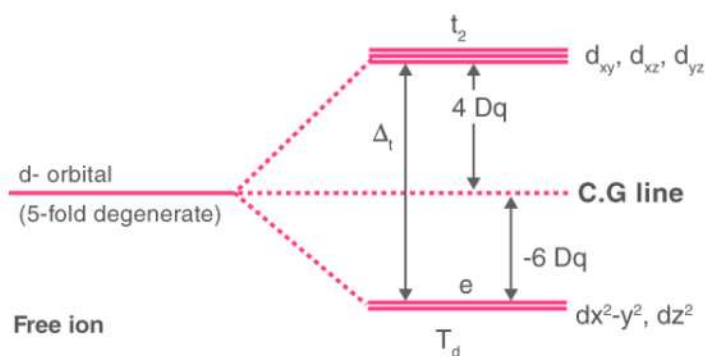
Crystal Field Splitting in Octahedral Complex

This splitting of degenerate level in the presence of ligand is known as **crystal field splitting**. The difference between the energy of t_{2g} and e_g level is denoted by " Δ_o " (subscript o stands for octahedral). Some ligands tend to produce strong fields thereby causing large crystal field splitting whereas some ligands tend to produce weak fields thereby causing small crystal field splitting.

Crystal Field Splitting in Tetrahedral Complex

The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as T_d . The electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals are less repelled by the ligands than the electrons present in d_{xy} , d_{yz} , and d_{xz} orbitals. As a result, the energy of d_{xy} , d_{yz} , and d_{xz} orbital set are raised while that $d_{x^2-y^2}$ and d_{z^2} orbitals are lowered.

- There are only four ligands in T_d complexes and therefore the total negative charge of four ligands and hence the ligand field is less than that of six ligands.
- The direction of the orbitals does not coincide with the directions of the ligands approach to the metal ion.



Crystal Field Splitting in Tetrahedral Complex

Thus, the repulsions in tetrahedral coordination compound yield two energy levels:

- t_2 – set of three orbitals (d_{xy} , d_{yz} and d_{xz}) with higher energy
- e – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with lower energy

The crystal field splitting in a tetrahedral complex is intrinsically smaller in an octahedral field because there are only two thirds as many ligands and they have a less direct effect of the d orbitals. The relative stabilizing effect of e set will be $-6Dq$ and the destabilizing effect of t_2 set will be $+4Dq$

Crystal Field Stabilization Energy

In a chemical environment, the energy levels generally split as directed by the symmetry of the local field surrounding the metal ion. The energy difference between the e_g and t_{2g} levels is given as or $10Dq$. It states that each electron that goes into the lower t_{2g} level stabilizes the system by an amount of $-4Dq$ and the electron that goes into e_g level destabilizes the system by $+6Dq$. That is the t_{2g} is lowered by $4Dq$ and the e_g level is raised by $+6Dq$.

For example, the net change in energy for d^5 and d^{10} systems will be zero as shown below.

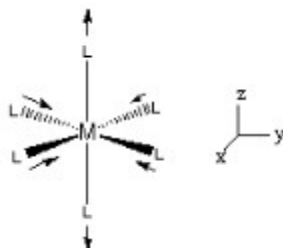
$$d^5 :- 3(-4Dq) + 2(+6Dq) = -12Dq + 12Dq = 0$$

$$d^{10} :- 6(-4Dq) + 4(+6Dq) = -24Dq + 24Dq = 0$$

The decrease in energy caused by the splitting of the energy levels is called the **“Ligand Field Stabilization Energy (LFSE)”**.

Square Planar Complexes:

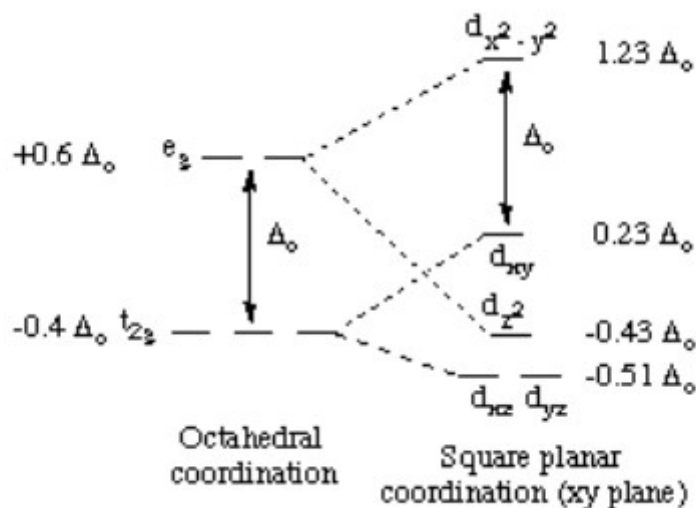
Square Planar Complexes d-Orbital Splitting in Square Planar Coordination. Square planar coordination can be imagined to result when two ligands on the z-axis of an octahedron are removed from the complex, leaving only the ligands in the x-y plane. As the z-ligands move away, the ligands in the square plane move a little closer to the metal. The orbital splitting diagram for square planar coordination can thus be derived from the octahedral diagram.



As ligands move away along the z-axis, d-orbitals with a z-component will fall in energy. The dz^2 orbital falls the most, as its electrons are concentrated in lobes along the z-axis.

The d_{xz} and d_{yz} orbitals also drop in energy, but not as much. Conversely the dx^2-y^2 and the d_{xy} orbitals increase in energy.

The splitting diagram for square planar complexes is more complex than for octahedral and tetrahedral complexes, and is shown below with the relative energies of each orbital.



Spectrochemical Series

Thus, the crystal field splitting depends on the field produced by the ligand and the charge on the metal ion. An experimentally determined series based on the absorption of light by coordination compound with different ligands known as spectrochemical series has been proposed.

Spectrochemical series arranges ligands in order of their field strength as:



Filling of d-orbitals takes place in the following manner; the first three electrons are arranged in t_{2g} level as per the Hund's rule. The fourth electron can either enter into t_{2g} level giving a configuration of $t_{2g}^4 e_g^0$ or can enter the e_g orbital giving a configuration of $t_{2g}^3 e_g^1$. This depends on two parameters magnitude of crystal field splitting, Δ_o and pairing energy, P. The possibilities of two cases can better be explained as:

- $\Delta_o > P$ – Electron enters in the t_{2g} level giving a configuration of $t_{2g}^4 e_g^0$. Ligands producing this configuration are known as strong field ligands and form low spin complexes.
- $\Delta_o < P$ – Electron enters in the e_g level giving a configuration of $t_{2g}^3 e_g^1$. Ligands producing this configuration are known as weak field ligands and form high spin complexes.

Factors affecting CFSE

There are several factors that affect the magnitude of splitting (Δ_o) of d-orbitals by the surrounding ligands.

1. Oxidation State of the Metal Cation:

The higher the oxidation state of the metal cation, the greater will be the magnitude of Δ . The higher the oxidation state of the metal causes the ligand to approach more closely to it and, therefore the ligand causes more splitting of metal d-orbitals.

For example Δ_o for $[\text{Co}(\text{H}_2\text{O})_6]^{2+} = 9200 \text{ cm}^{-1}$
and Δ_o for $[\text{Co}(\text{H}_2\text{O})_6]^{3+} = 20760 \text{ cm}^{-1}$

2. Same Oxidation State of Metal Cation but the number of d-electrons is Different:

In general, for a given series of transition elements (say 3d-series), in complexes having the metal cation with the same oxidation state but the different number of electrons in the d-orbitals, the magnitude of Δ_o decreases with increase in the number of d-electrons. It is due to the fact that the higher number of d-electrons prevents the ligands to come closer to the metal cation.

For example Δ_o for $[\text{Co}(\text{H}_2\text{O})_6]^{2+} = 9200 \text{ cm}^{-1} (3d^7)$
and Δ_o for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} = 8500 \text{ cm}^{-1} (3d^8)$

3. Principal Quantum Number(n) of the d-orbital of the Metal Cation:

In case of complexes having the metal cation with the same oxidation states and the same number of d-electrons, the magnitude of for analogous complexes within a given group increases about 30% to 50% from 3d to 4d and by about the same amount from 4d to 5d. It is because:

(1) On moving from 3d to 4d and 4d to 5d, the size of the d-orbital increases and electron density decreases in them. Therefore the ligands can approach the metal cation with larger d-orbital more closely.

(2) There is less steric hindrance around a larger metal cation.

For example Δ_o for $[\text{Co}(\text{NH}_3)_6]^{2+} = 2300 \text{ cm}^{-1}$
 Δ_o for $[\text{Rh}(\text{NH}_3)_6]^{2+} = 34100 \text{ cm}^{-1}$
 Δ_o for $[\text{Ir}(\text{NH}_3)_6]^{2+} = 41200 \text{ cm}^{-1}$

4. Nature of Ligands:

The ligands are classified as a weak and strong ligand. The ligand which causes a small degree of splitting of d-orbitals are called weak ligands and the ligands which cause a large splitting are called strong ligands. The common ligands have been arranged in order of their increasing

crystal field splitting power to cause splitting of d-orbitals from a study of their effects on the spectra of transition metal ions.

(weak end) $\text{O}_2^{2-} < \text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^-$ (S-bonded) $< \text{Cl}^- < \text{N}_3^- < \text{F}^- < \text{NCO}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^-$ (N-bonded) $< \text{CH}_3\text{CN} < \text{gly}$ (glycine) $< \text{py}$ (pyridine) $< \text{NH}_3 < \text{en}$ (ethylenediamine) $< \text{bipy}$ (2,2'-bipyridine) $< \text{phen}$ (1,10-phenanthroline) $< \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO} < \text{CH}_2$ (strong end)

This order is usually called as Spectrochemical series

The order of the field strength of common ligands is independent of the nature of the metal cation and the geometry of the complex.

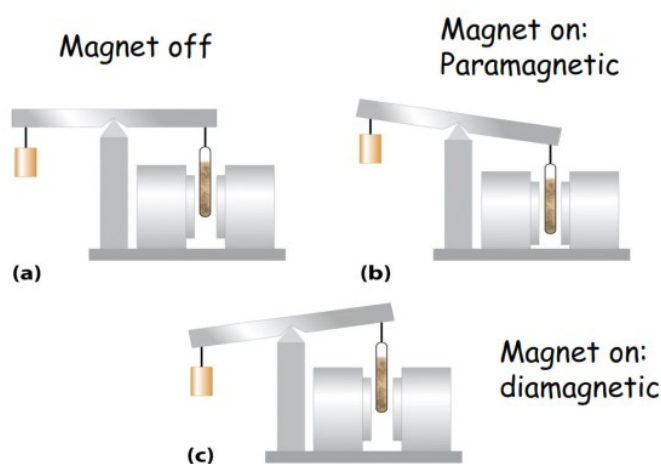
5. Number of Ligands:

The magnitude of crystal field splitting (Δ) increases with the increase of the number of ligands. For example $\Delta_0 > \Delta_t$

Though the number of ligands in a square planar complex is smaller than that of octahedral complexes, the magnitude of Δ_{sp} is greater than Δ_0 . It is because of the fact that square planar complexes are formed by much strong ligands with d^8 metal cation of 3d-series transition metal cation and 4d and 5d series d^8 metal cation with either weak or strong ligand. The very strong ligands and 4d or 5d series transition metal cations are responsible for higher crystal field splitting. Also in square planar complexes of d^8 metal cation, the d_{z^2} orbital with two electrons is stabilized and the vacant $d_{x^2-y^2}$ orbital is destabilized.

Magnetic Properties of Coordination Complexes

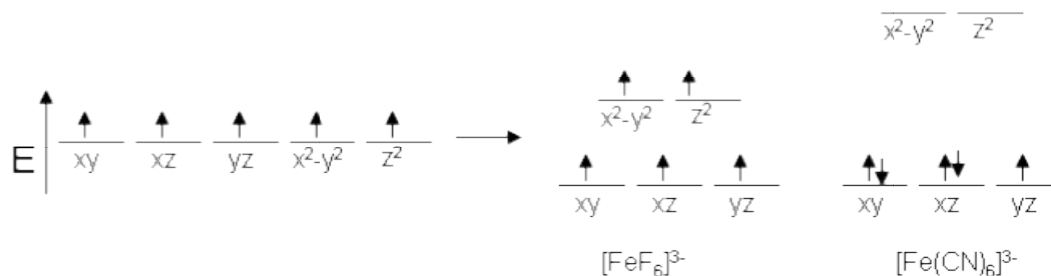
- Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic.



- Molecules such as N_2 and ions such as Na^+ and $[\text{Fe}(\text{CN})_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment

is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[\text{Fe}(\text{CN})_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.



- Tetrahedral complexes have naturally weaker splitting because none of the ligands lie within the plane of the orbitals. As a result, they have either have too many or too few d electrons to warrant consideration about high or low spin configurations.
- Square planar compounds, on the other hand, stem solely from transition metals with eight d electrons. $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$, and $[\text{PtCl}_4]^{2-}$ are all diamagnetic.
- Since this encompasses the full spectrum of ligand strength, we can conclude that square planar compounds are always low spin and therefore are weakly magnetic.

Colour:

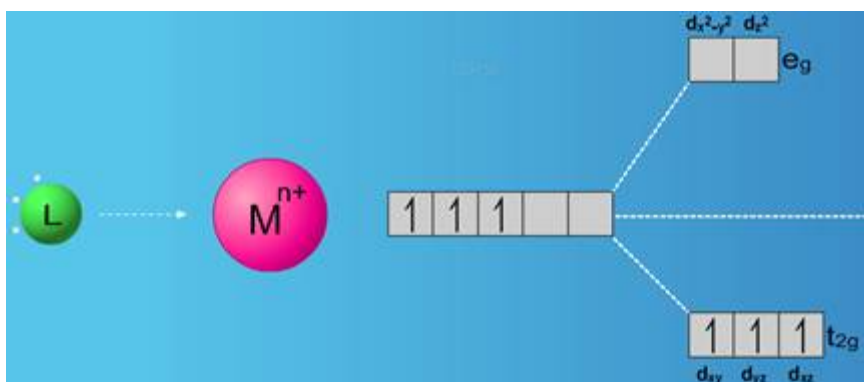
Transition metal atoms (or) ions with one (or) more unpaired electrons and their complexes exhibit colour both in their solid and in solution states.

If absorption occurs in the visible region of the spectrum, then the transmitted light bears a colour complementary to the colour of the light absorbed. The relationship between the absorbed and transmitted wavelengths can be readily understood from the following,

Coordination Entity	Wavelength of Light Absorbed (nm)	Colour of Light Absorbed	Colour of Coordination Entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green	Purple

The origin of the colour of coordination compounds can be readily explained in terms of the crystal field theory.

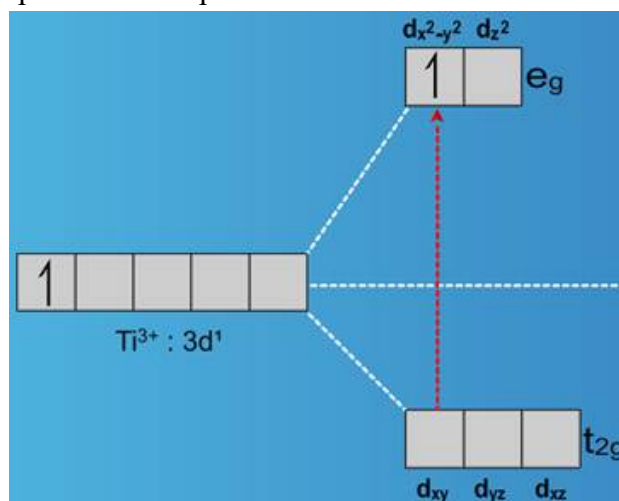
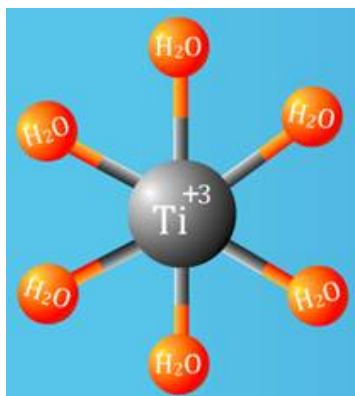
When a ligand approaches the metal ion containing unpaired electrons the five degenerate d-orbitals separate into two distinct energy levels t_{2g} and e_g .



The colour of coordination compounds arises from the electron transition between the split d-orbital energy levels.

When light passes through a solution of the complex, the electron in the lower t_{2g} level is promoted to a higher e_g level by absorbing light with energy equal to the energy difference between the t_{2g} and e_g levels.

Ex: Hexa Aqua Titanium(III) is coloured due presence of unpaired electron.



The colour of gem stones like ruby and emerald is due to the d-to-d transition of electrons within the d orbitals of the transition metal ion.

Ruby is a pink to blood red coloured gem stone of aluminium oxide.

Emerald is a green variety of beryl. The green colour of emerald is due to the presence of chromium three plus ions.

In the absence of a ligand, crystal field splitting does not occur and the substance remains colourless.

The Limitations Of Crystal Field Theory

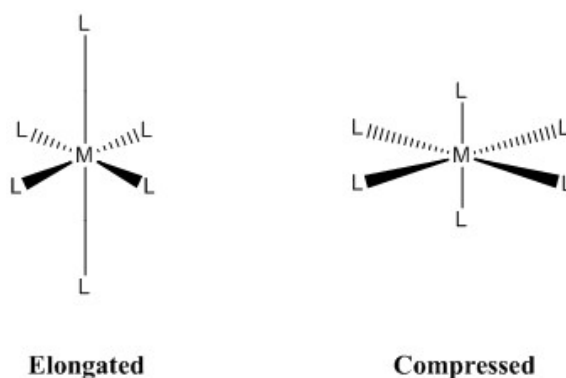
The crystal field theory is highly useful and more significant as compared to the valence bond theory. Even after such useful properties, it has many limitations. The following points will clearly state the limitations of crystal field theory:

1. The assumption that the interaction between metal-ligand is purely electrostatic cannot be said to be very realistic.
2. This theory takes only d-orbitals of a central atom into account. The s and p orbits are not considered for the study.
3. The theory fails to explain the behaviour of certain metals which cause large splitting while others show small splitting. For example, the theory has no explanation as to why H_2O is a stronger ligand as compared to OH^- .

4. The theory rules out the possibility of having p bonding. This is a serious drawback because it is found in many complexes.
5. The theory gives no significance to the orbits of the ligands. Therefore, it cannot explain any properties related to ligand orbitals and their interaction with metal orbitals

Jahn-Teller Distortions

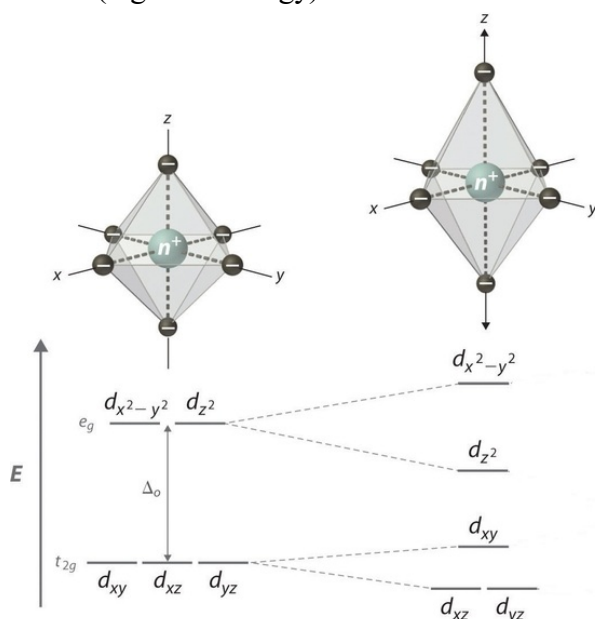
For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t_{2g} (d_{xz} , d_{yz} , d_{xy}) and e_g (d_{z^2} and $d_{x^2-y^2}$). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the z ligand bonds as shown in Figure given below:



When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse

Elongation

Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, while the orbitals without a z component are destabilized (higher in energy)

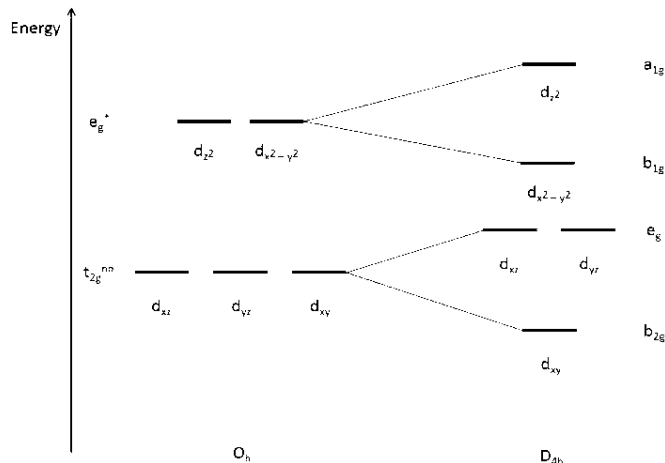


This is due to the d_{xy} and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding, but is destabilized due

to the interactions. Jahn-Teller elongations are well-documented for copper(II) octahedral compounds.

Compression

Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals *without* a z component, while the orbitals with a z component are destabilized (higher in energy)



This is due to the z-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the d_{z^2} orbital is antibonding, it is expected to increase in energy due to compression. The d_{xz} and d_{yz} orbitals are still nonbonding, but are destabilized due to the interactions.

Molecular orbital theory

The crystal field theory takes no account of possible covalent bonding in complexes.

According to MOT, the metal-ligand σ -bonding in octahedral complexes results from the overlap of suitable atomic orbitals of the metal ion with ligand σ -orbitals. The formation of six-metal-ligand σ -bonds in an octahedral complex takes place through the following steps.

1) The central metal cation of 3d-series contains nine valence-shell atomic orbitals, which are 4s, 4p_x, 4p_y, 4p_z, 3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x²-y²} and 3d_{z²}. Of them, only six suitable atomic orbitals may overlap along the axis with ligand σ -orbitals to form six metal-ligand σ -bonds. All the nine atomic orbitals have been grouped into four symmetry classes, which are given below.

$$4s \rightarrow A_{1g} \text{ or } a_{1g}; \quad 4p_x, p_y, p_z \rightarrow T_{1u} \text{ or } t_{1u};$$

$$3d_{x^2-y^2}, 3d_{z^2} \rightarrow E_g \text{ or } e_g \text{ and } 3d_{xy}, d_{yz}, d_{zx} \rightarrow T_{2g} \text{ or } t_{2g}$$

The atomic orbitals 4s, 4p_x, 4p_y, 4p_z, 3d_{x²-y²} and 3d_{z²} have their lobes lying along the axes along

which the six σ -orbitals of the six ligands are approaching towards the central metal cation to form six metal-ligand σ -bonds. The remaining three AO's 3d_{xy}, 3d_{yz} and 3d_{zx} do not participate in σ -bonding process, since these have their lobes oriented in space between the axes. These are called non-bonding orbitals. However, these can overlap sidewise with filled or unfilled π -orbitals of the same ligands to form metal-ligand π -bonds.

3) The six atomic orbitals of the central metal cation 4s, 4p_x, 4p_y, 4p_z, 3d_{x²-y²} and 3d_{z²} overlap with six-group ligand σ -orbitals i.e., Σ_s , Σ_x , Σ_y , Σ_z , $\Sigma_{x^2-y^2}$, and Σ_{z^2} respectively to form six sigma bonding and six sigma anti-bonding molecular orbitals.

4) Thus twelve molecular orbitals (six bonding and six antibonding) and three non-bonding orbitals 3d_{xy}, 3d_{yz} and 3d_{zx} (i.e.) totally fifteen orbitals are available for electron filling.

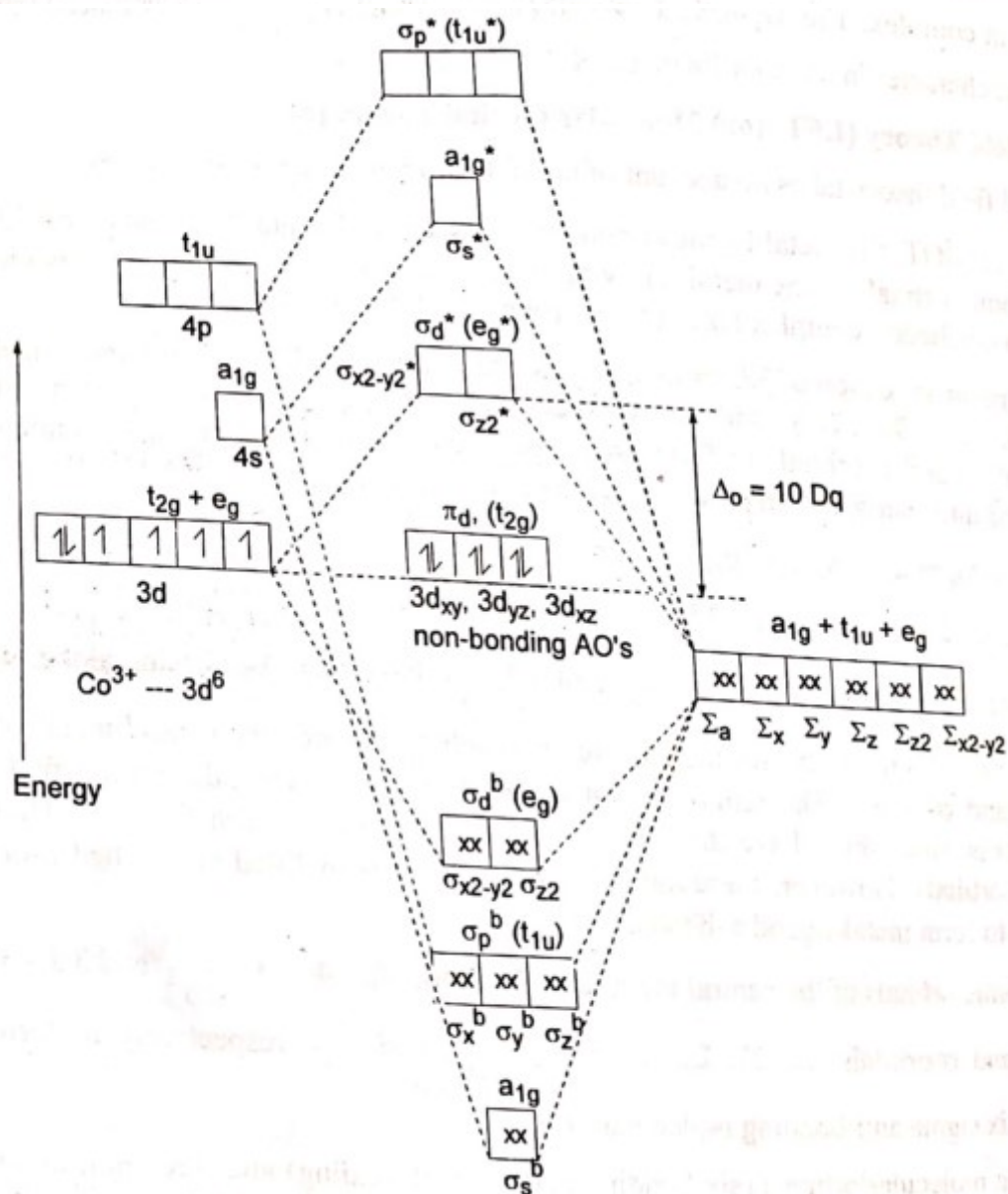
Energy order of orbitals and their filling with electrons

The order of energy of different orbitals formed in an octahedral complex depends upon the nature of the ligands i.e., whether the ligand are stronger or weaker ligands.

(i) *When the ligands are stronger:* Strong ligands such as NH_3 split the σ -bonding MO's namely $\sigma_x^b, \sigma_y^b = \sigma_z^b, \sigma_{x^2-y^2}^b = \sigma_{z^2}^b$, more widely and the energy difference Δ_o between the t_{2g} -set of non-bonding AO's and e_g^* set of MO's is greater than the electron pairing energy, P ($\Delta_o > P$). The σ^b MO's have the lowest energy and σ^* MO's have the highest energy while the non-bonding orbitals $3d_{xy}, 3d_{yz}$ and $3d_{zx}$ have an energy intermediate between the bonding and anti-bonding MO's.

Example:

$[\text{Co}(\text{NH}_3)_6]^{3+}$ contains strong ligands. This complex has Co as Co^{3+} (d^6 system). There are 18 electrons in it, 12 electrons from 6 ligands and 6 from d-orbitals of Co^{3+} ion. The distribution of 18 electrons in various orbitals is shown below:



The MOT configuration of $[\text{Co}(\text{NH}_3)_6]^{3+}$ can be represented as follows:

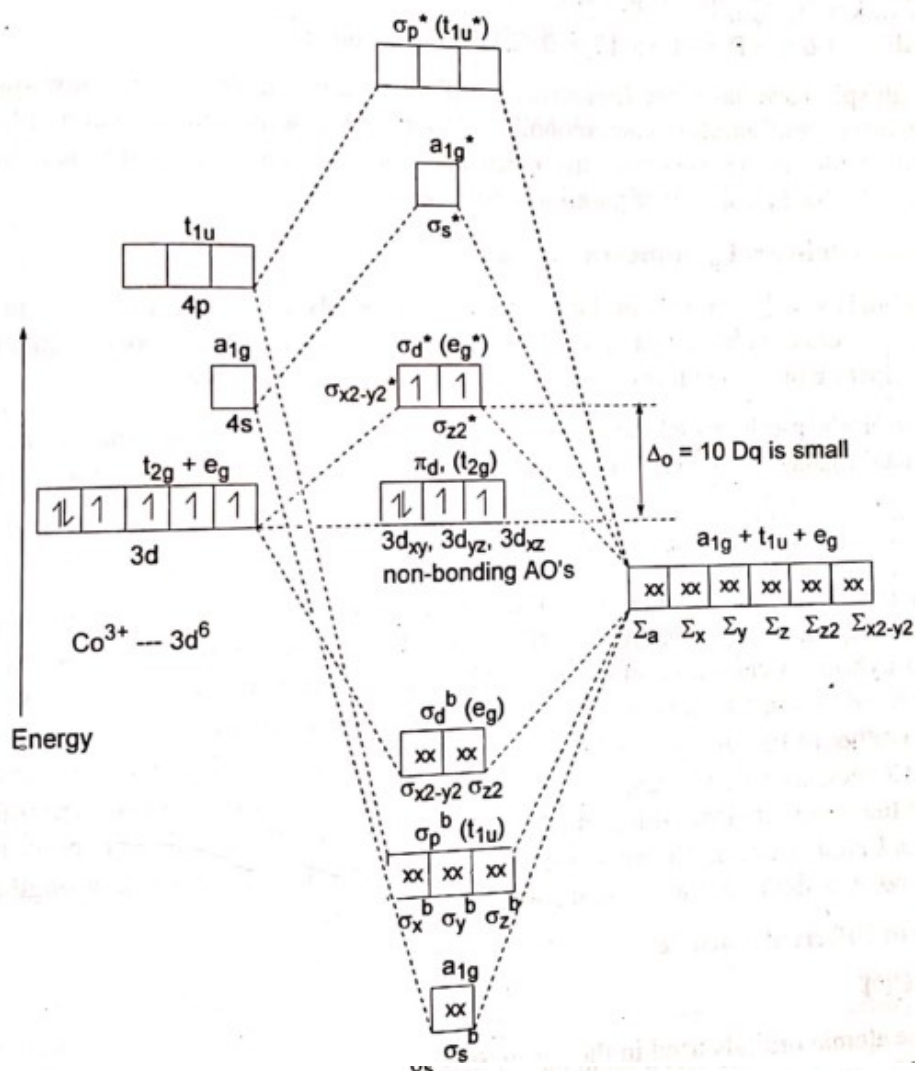
$$(\sigma_s^b)^2 (\sigma_x^b)^2 = (\sigma_y^b)^2 = (\sigma_z^b)^2 (\sigma_{x^2-y^2}^b)^2 = (\sigma_{z^2}^b)^2 (3d_{xy})^2 = (3d_{yz})^2 = (3d_{zx})^2$$

In connection with MOT energy level diagram, the following points may be noted.

a) Since the ligand orbitals are usually more electronegative than the metal AO's, the right hand energy levels are drawn below any of the left hand levels.

b) The crystal field splitting energy (Δ_o or $10Dq$) in an octahedral complex is the difference in energy between the t_{2g} and e_g .

ii) When the ligands are weak: In the case of weaker ligands such as F^- ion, the energy difference Δ_o between the t_{2g} and e_g set is smaller than P and hence the lowest energy anti-bonding MO's namely $\sigma_{x^2-y^2}^*$ and $\sigma_{z^2}^*$ have approximately the same energy as the non-bonding AO's, $3d_{xy}$, $3d_{yz}$, d_{zx} (t_{2g} set).



The distribution of 18 electrons in $[\text{CoF}_6]^{3-}$ takes place in various orbitals in accordance with the above scheme. It clearly shows that in case of high-spin complexes, Hund's rule is obeyed. The MO configuration of this complex can be represented as follows:

$$(\sigma_s^b)^2 (\sigma_x^b)^2 = (\sigma_y^b)^2 = (\sigma_z^b)^2 (\sigma_{x^2-y^2}^b)^2 = (\sigma_{z^2}^b)^2 (3d_{xy})^1 = (3d_{yz})^1 = (3d_{zx})^1 = (\sigma_{x^2-y^2}^*)^1 = (\sigma_{z^2}^*)^1$$

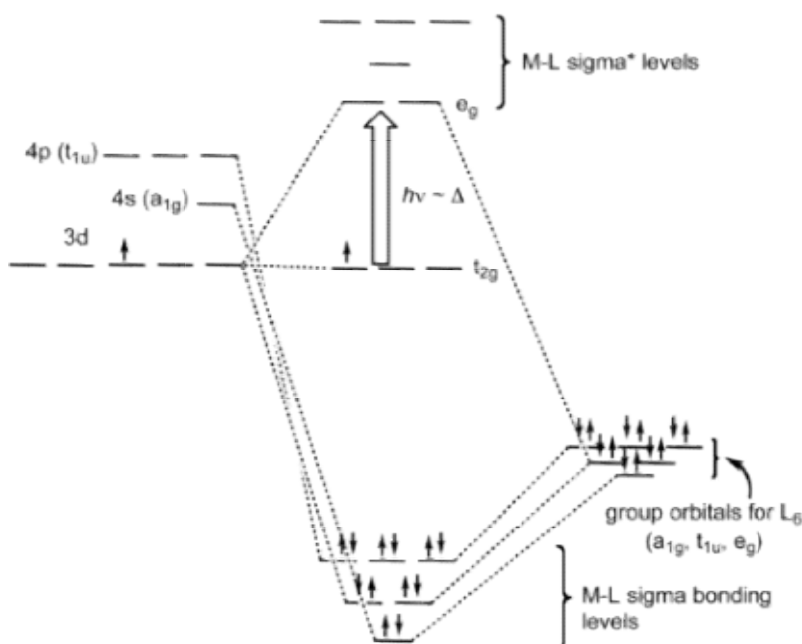
Ligand field theory (LFT)

Ligand field theory (LFT) describes the bonding, orbital arrangement, and other characteristics of coordination complexes. It represents an application of molecular orbital theory to transition metal complexes. A transition metal ion has nine valence atomic orbitals - consisting of five nd , one $(n+1)s$, and three $(n+1)p$ orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The LFT analysis is highly dependent on the geometry of the complex, but most explanations begin by describing octahedral complexes, where six ligands coordinate to the metal. Other complexes can be described by reference to crystal field theory.

Bonding

σ -bonding (sigma bonding)

In an octahedral complex, the molecular orbitals created by coordination can be seen as resulting from the donation of two electrons by each of six σ -donor ligands to the d -orbitals on the metal. In octahedral complexes, ligands approach along the x -, y - and z -axes, so their σ -symmetry orbitals form bonding and anti-bonding combinations with the d_z^2 and $d_{x^2-y^2}$ orbitals. The d_{xy} , d_{xz} and d_{yz} orbitals remain non-bonding orbitals. Some weak bonding (and anti-bonding) interactions with the s and p orbitals of the metal also occur, to make a total of 6 bonding (and 6 anti-bonding) molecular orbitals



In molecular symmetry terms, the six lone-pair orbitals from the ligands (one from each ligand) form six symmetry adapted linear combinations (SALCs) of orbitals, also sometimes called ligand group orbitals (LGOs). The irreducible representations that these span are a_{1g} , t_{1u} and e_g . The metal also has six valence orbitals that span these irreducible representations - the s orbital is labeled a_{1g} , a set of three p -orbitals is labeled t_{1u} , and the d_z^2 and $d_{x^2-y^2}$ orbitals are labeled e_g . The six σ -bonding molecular orbitals result from the combinations of ligand SALCs with metal orbitals of the same symmetry.

π -bonding (pi bonding)

- π bonding in octahedral complexes occurs in two ways: via any ligand p -orbitals that are not being used in σ bonding, and via any π or π^* molecular orbitals present on the ligand.
- In the usual analysis, the p -orbitals of the metal are used for σ bonding (and have the wrong symmetry to overlap with the ligand p or π or π^* orbitals anyway), so the π

interactions take place with the appropriate metal d -orbitals, i.e. d_{xy} , d_{xz} and d_{yz} . These are the orbitals that are non-bonding when only σ bonding takes place.

- One important π bonding in coordination complexes is metal-to-ligand π bonding, also called π backbonding. It occurs when the LUMOs (lowest unoccupied molecular orbitals) of the ligand are anti-bonding π^* orbitals.
- The other form of coordination π bonding is ligand-to-metal bonding. This situation arises when the π -symmetry p or π orbitals on the ligands are filled. This is called the HOMO (highest occupied molecular orbital) of the complex. For that reason, Δ_O decreases when ligand-to-metal bonding occurs.
- The greater stabilization that results from metal-to-ligand bonding is caused by the donation of negative charge away from the metal ion, towards the ligands.
- As each of the six ligands has two orbitals of π -symmetry, there are twelve in total. The symmetry adapted linear combinations of these fall into four triply degenerate irreducible representations, one of which is of t_{2g} symmetry.

High and low spin and the Spectrochemical Series

The energy difference between the latter two types of MOs is called Δ_O (O stands for octahedral) and is determined by the nature of the π -interaction between the ligand orbitals with the d -orbitals on the central atom. As described above, π -donor ligands lead to a small Δ_O and are called weak- or low-field ligands, whereas π -acceptor ligands lead to a large value of Δ_O and are called strong- or high-field ligands. Ligands that are neither π -donor nor π -acceptor give a value of Δ_O somewhere in-between.

The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ that they produce. It can be seen that the low-field ligands are all π -donors (such as Γ^-), the high field ligands are π -acceptors (such as CN^- and CO), and ligands such as H_2O and NH_3 , which are neither, are in the middle.

$\Gamma^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_3^- < \text{N}_3^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{CN} < \text{py}$
(pyridine) $< \text{NH}_3 < \text{en}$ (ethylenediamine) $< \text{bipy}$ (2,2'-bipyridine) $< \text{phen}$ (1,10-phenanthroline)
 $< \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$