STUDY MATERIAL

VIVEKANANDA COLLEGE THAKURPUKUR

NAAC Accredited Grade—A

Topic: **Crystal field theory**

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Course Paper**: paper 4**

Unit: **NA**

Semester: **4**

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Name of the Department: **Chemistry**

Crystal field theory (CFT)

Syllabus:

Crystal field effect,octahedral symmetry.Crystal field stabilization energy(CFSE),Crystal field effects for weak and strong fields. Tetrahedral symmetry. Factors affecting the magnitude of D. Spectrochemical series. Comparison of CFSE for O_h and T_d complexes, Tetragonal distortion of octahedral geometry. Jahn-Teller distortion, Square planar coordination.

Crystal field theory

Crystal field theory (CFT) is a model developed by **Hans Bethe** and **John Von Vlech.** It explained the bonding in complex compounds and the stability of these compounds. It was based on the *degeneracies of d-orbitals.* According to it the d-orbitals splits when the ligands approach the central metal ion.

The following are the postulates of CFT :

i) VBT (valence bond theory) considers the metal ligand bond to be covalent, whereas CFT considers these bonds to be *ionic* arising purely due to ***electrostatic interaction*** between the metal ions and the ligands. Since these interactions are similar to this present in Crystals, hence the theory is called as crystal field theory.

ii) If the ligand is anion (negatively charged) then the metal ion has to be a cation (positively charged)and the force of attraction is due to opposite charges.

If the ligans is a neutral molecule like H_2O, NH_3, etc then the negative end of their dipoles are attached towards the central metal ion.

iii) It treated each ligand as a point of negative charge. The arrangement of these ligand around the central metal ion is such that the repulsion between the negative points (ligands) is minimum.

iv) It considers the effect of ligands on the relative energies of d-orbitals of the central metal ion.

In all free transition metal ion, all the five d-orbitals have equal energies (i.e they are degenerate). This degeneracy is maintained if the negative charges are present around the central metal ion in a spherical symmetrical field.

However if the negative field is due to the ligands which may be nagative ion or polar molecules with their nagative ends towards the central metal ion, then the field no longer remains symmetrical and the degeneracy is split.

The d-orbitals split into two parts (named as t_{2g} and e_g orbitals) depending on the number of ligands approaching the metal ion.

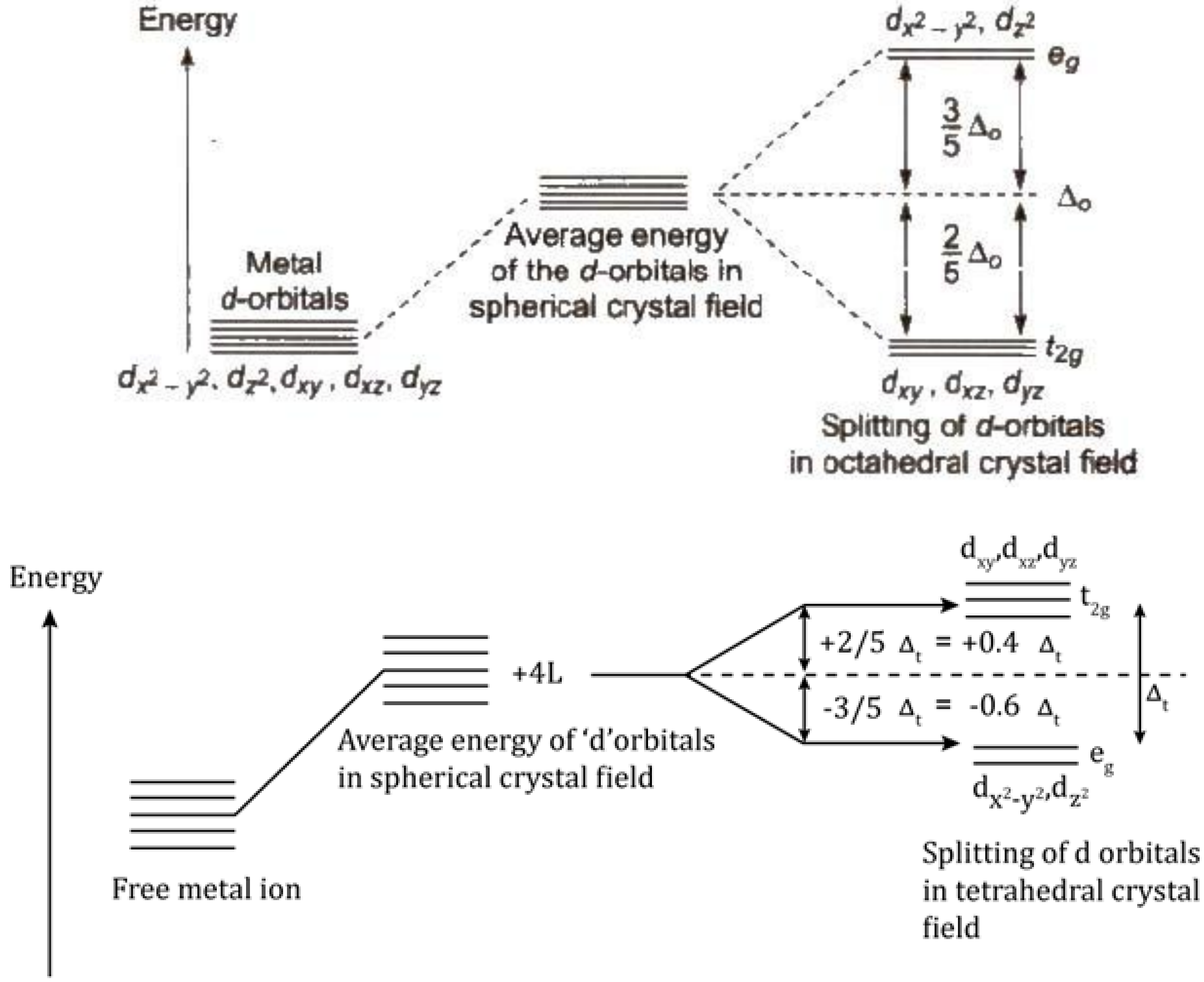


Figure: Crystal field splitting of octahedral and tetrahedral complex.

High Spin and Low Spin :

The complexion 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 Δo.

High spin – Maximum number of unpaired electrons. Example: $[CoF_6]^{3-}$

Low spin – Minimum number of unpaired electrons. Example: $[Co(CN)_6]^{3-}$

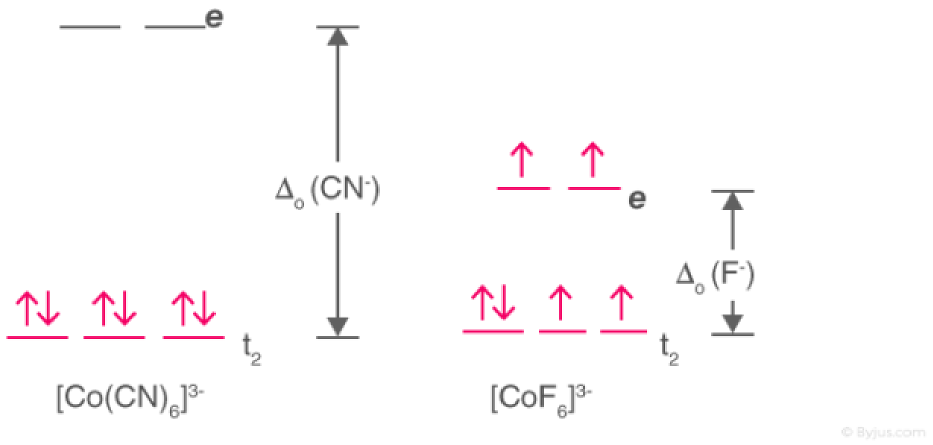


Figure: Low spin and high spin complex

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_{x2-y2} and d_{z2} 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_{x2-y2} and d_{z2}) with higher energy

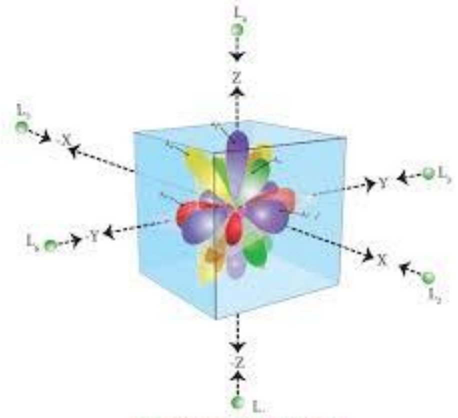
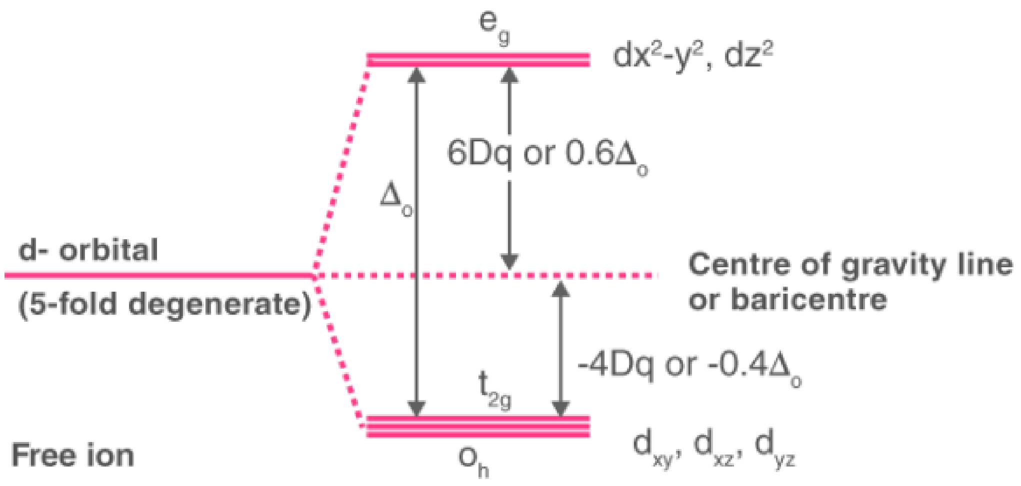


Figure 5.9 octahedral ligand field



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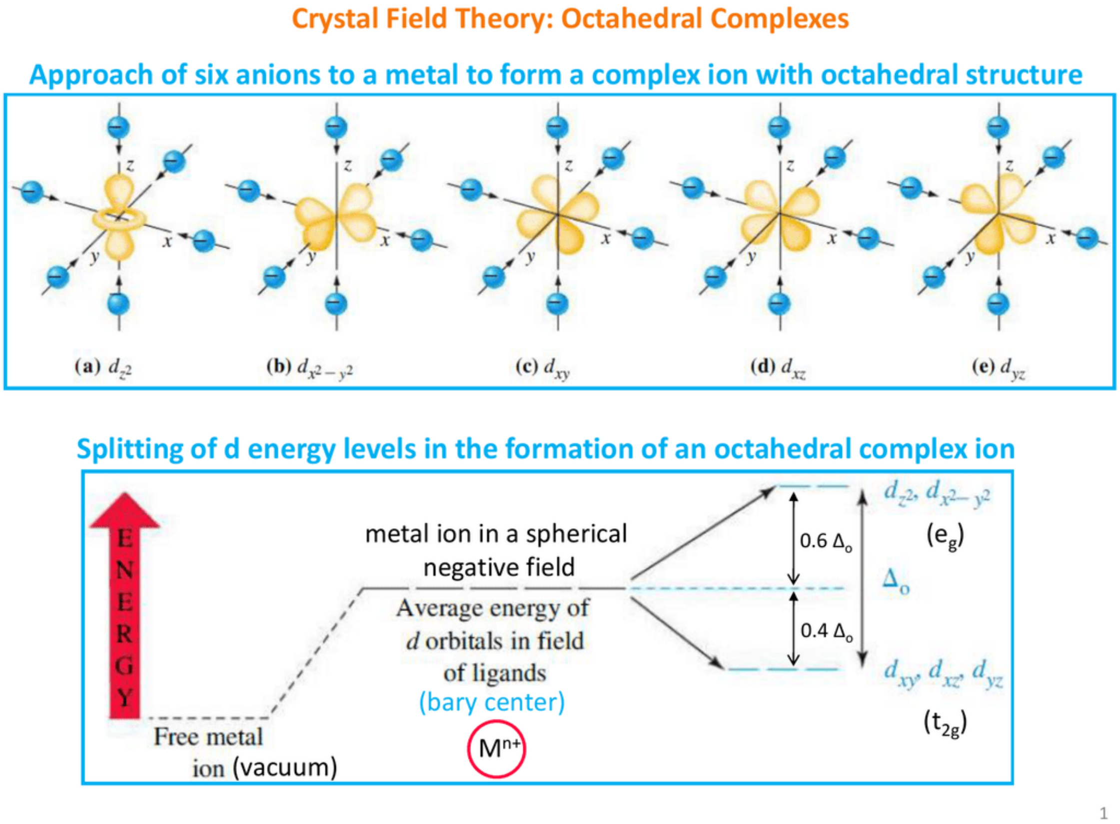


Crystal Field Theory: Octahedral Complexes

Approach of six anions to a metal to form a complex ion with octahedral structure

Splitting of d energy levels in the formation of an octahedral complex ion

Figure: Crystal field splitting in octahedral complex

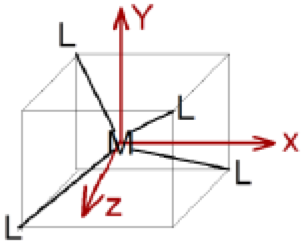
This splitting of degenerate level in the presence of ligand is known as **crystal field splitting**. The difference between the energy of **t_{2g} and e_g level is denoted by "Δo"** (subscript o stands for octahedral). Some ligands tend to produce strong fields thereby causing large crystal field splitting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

Crystal Field Splitting in Tetrahedral Complex

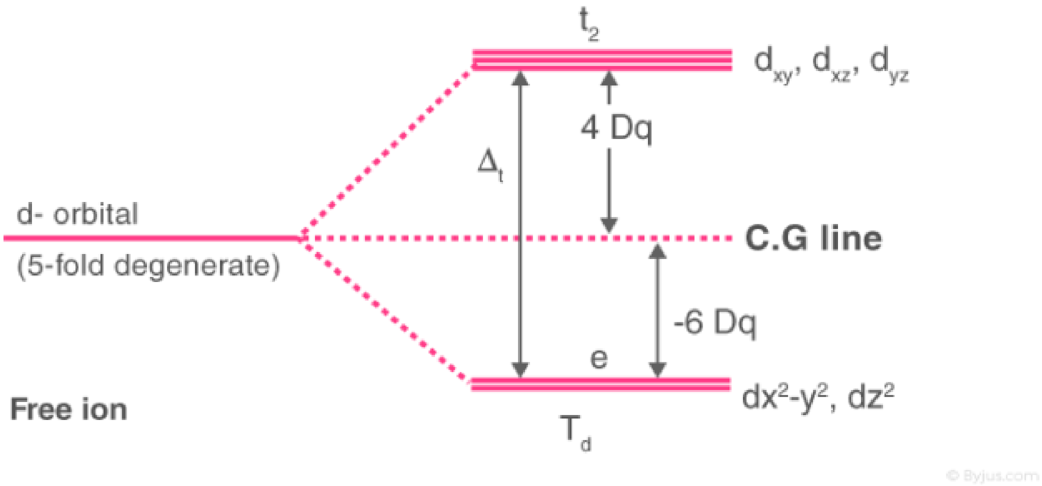
The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as T_d. The electrons in d_{x2-y2} and d_{z2} orbitals are less repelled by the ligands than the electrons present in d_{xy}, d_{yz}, and d_{xz} orbitals.

As a result, the energy of d_{xy}, d_{yz}, and d_{xz} orbital set are raised while the others d_{x2-y2} and d_{z2} orbitals are lowered.

There are only four ligands in Td 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. Thus, the repulsions in tetrahedral coordination compound yield two energy levels:



tetrahedral geometry
having central metal M &
four ligands at the
corners



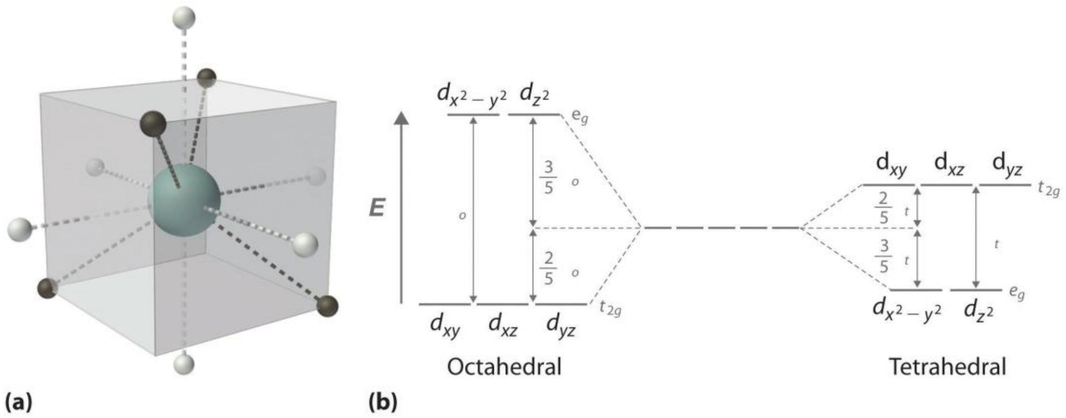


Figure: Crystal field splitting in tetrahedral complex

- t_2– set of three orbitals (d_{xy}, d_{yz}, and d_{xz}) with higher energy
- e – set of two orbitals (d_{x2-y2} and d_{z2}) with lower energy

The crystal field splitting in a tetrahedral complex is intrinsically smaller in an octahedral filed 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 (or $0.6\Delta_0$)and the destabilizing effect of 't_2' set will be +4Dq (or $0.4\Delta_0$)

Crystal Field Stabilization Energy

The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

The CSFE will depend on multiple factors including:

1. Geometry (which changes the d-orbital splitting patterns)
2. Number of d-electrons

3. Spin Pairing Energy
4. Ligand character (via Spectrochemical Series)

Factors affecting the magnitude of Dq:

This splitting is affected by the following factors:

1. the nature of the metal ion.
2. the metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.
3. the arrangement of the ligands around the metal ion.
4. the coordination number of the metal (i.e. tetrahedral, octahedral...)
5. the nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy d groups.

Spectrochemical series:

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 eg 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 eg level destabilizes the system by +6Dq. That is the t2g is lowered by 4Dq and the eg level is raised by +6Dq.

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:

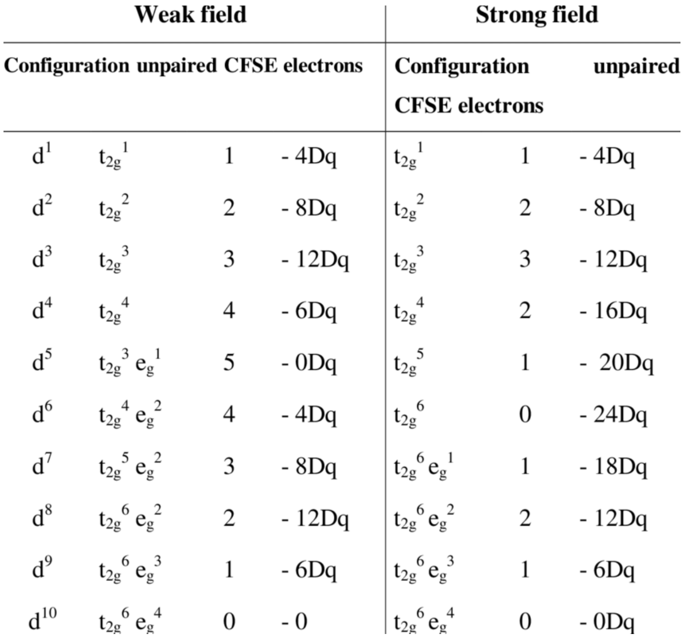
$$I^- < Br^- < Cl^- < SCN^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$$

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^0or can enter the eg orbital giving a configuration of t_{2g}^3 e_g^1. This depends on two parameters magnitude of crystal field splitting, Δo 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.

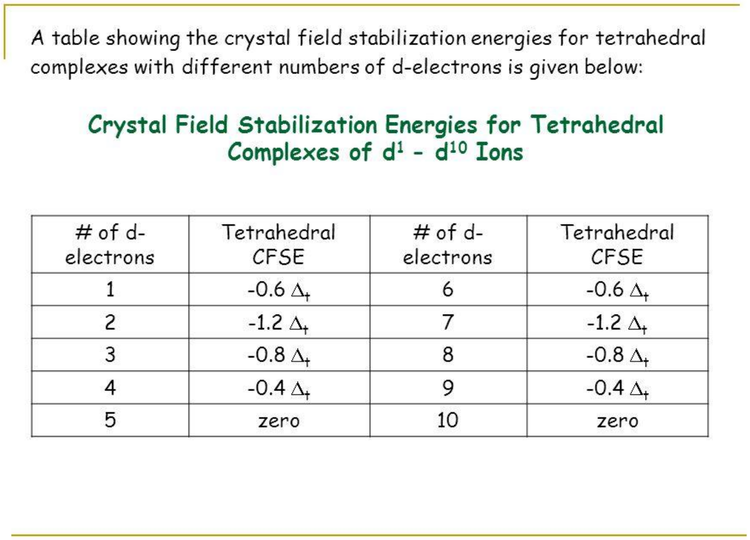
Comparison of CFSE for O_h andT_d complexes:

Table: CFSE calculation for octahedral complex.



	Weak field			Strong field		
	Configuration	unpaired	CFSE electrons	Configuration	unpaired	CFSE electrons
d^1	t_{2g}^1	1	- 4Dq	t_{2g}^1	1	- 4Dq
d^2	t_{2g}^2	2	- 8Dq	t_{2g}^2	2	- 8Dq
d^3	t_{2g}^3	3	- 12Dq	t_{2g}^3	3	- 12Dq
d^4	t_{2g}^4	4	- 6Dq	t_{2g}^4	2	- 16Dq
d^5	t_{2g}^3 e_g^1	5	- 0Dq	t_{2g}^5	1	- 20Dq
d^6	t_{2g}^4 e_g^2	4	- 4Dq	t_{2g}^6	0	- 24Dq
d^7	t_{2g}^5 e_g^2	3	- 8Dq	t_{2g}^6 e_g^1	1	- 18Dq
d^8	t_{2g}^6 e_g^2	2	- 12Dq	t_{2g}^6 e_g^2	2	- 12Dq
d^9	t_{2g}^6 e_g^3	1	- 6Dq	t_{2g}^6 e_g^3	1	- 6Dq
d^{10}	t_{2g}^6 e_g^4	0	- 0	t_{2g}^6 e_g^4	0	- 0Dq

Table: CFSE calculation for tetrahedral complex.



A table showing the crystal field stabilization energies for tetrahedral complexes with different numbers of d-electrons is given below:

Crystal Field Stabilization Energies for Tetrahedral Complexes of d^1 - d^{10} Ions

# of d-electrons	Tetrahedral CFSE	# of d-electrons	Tetrahedral CFSE
1	$-0.6\ \Delta_t$	6	$-0.6\ \Delta_t$
2	$-1.2\ \Delta_t$	7	$-1.2\ \Delta_t$
3	$-0.8\ \Delta_t$	8	$-0.8\ \Delta_t$
4	$-0.4\ \Delta_t$	9	$-0.4\ \Delta_t$
5	zero	10	zero

Limitations of CFT:

The following points will clearly state the limitations of crystal field theory:

(i)The interaction between metal-ligand is purely electrostatic cannot be said to be very realistic.

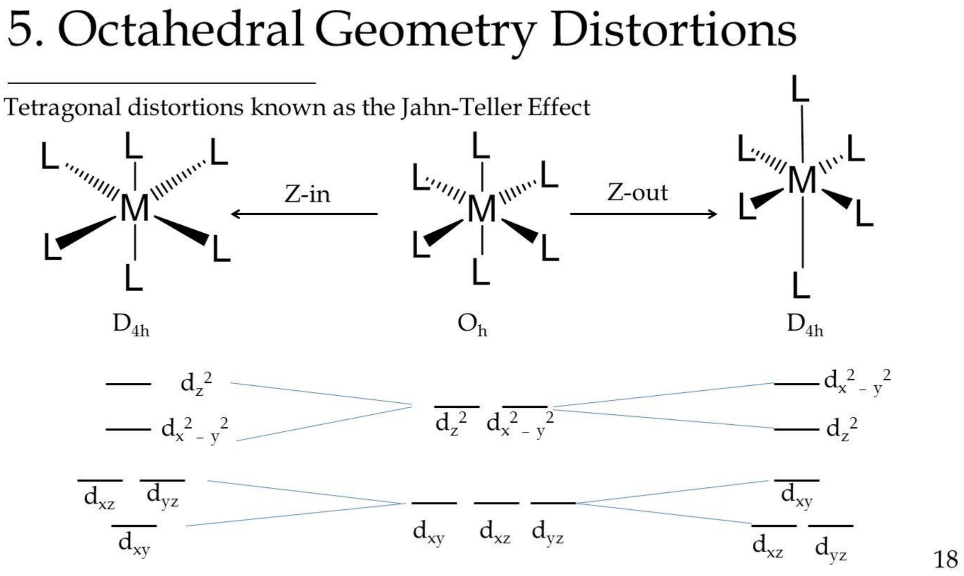
(ii)This theory is only applicable for d-orbital metal ions . The s and p orbits are not considered for study.

(iii)The theory fails to explain the behavior of certain metals which cause large splitting while others show small splitting.

(iv)The theory gives no idea about the covalent nature of the complexes. Therefore it cannot explain the overlap between the ligand orbitals and metal d orbitals.

Tetragonal distortion of octahedral geometry:

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_{xy}, d_{yz}, and d_{xz}) and e_g (d_{x2-y2} and d_{z2}). 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:



5. Octahedral Geometry Distortions

Tetragonal distortions known as the Jahn-Teller Effect

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) as shown in Figure:

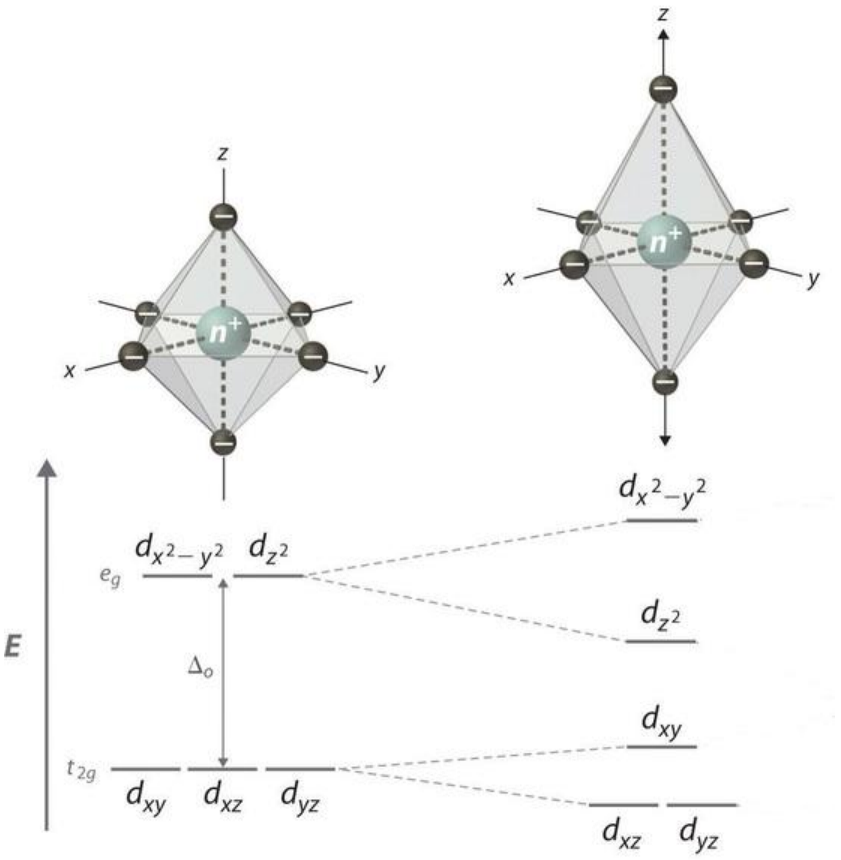


Figure: Tetragonal distortion (elongation) for an octahedral complex.

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) as shown in Figure:

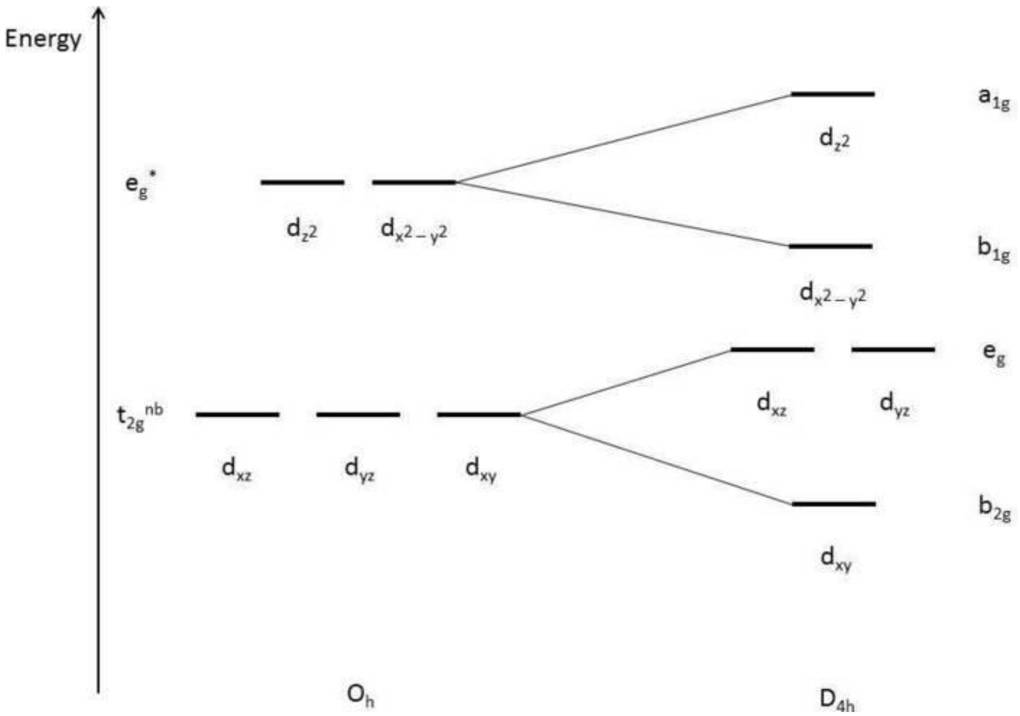


Figure: Tetragonal distortion (compression) for an octahedral complex.

Jahn-Teller Distortions.

The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds.

Jahn-Teller Theorem: In a nonlinear molecule, if degenerate orbitals are asymmetrically occupied, a distortion will occur to remove the degeneracy.

(or)

In an electronically degenerate state, a nonlinear molecule undergoes distortion to remove the degeneracy by lowering the symmetry and thus by lowering the energy.

Z-out distortion: In this case, the energies of d-orbitals with z factor (i.e., dz2, dxz, dyz) are lowered since the bonds along the z-axis are elongated. This is the most preferred distortion and occurs in most of the cases, especially when the degeneracy occurs in eg level.

E.g. Usually the octahedral d^2, d^4 high spin, d^7 low spin, d^8 low spin & d^9 configurations show the z-out distortion.

Theoretically it is not possible to predict the type of distortion occurs when the degeneracy occurs in eg level. However it is observed that z-out distortion is more preferred.

Z-in distortion: In this case the energies of orbitals with z factor are increased since the bonds along the z-axis are shortened. This type of distortion is observed in case of octahedral d1 configuration. The only electron will now occupy the dxy orbital with lower energy.

E.g. The octahedral d^1 configurations like Ti(III) in $[Ti(H_2O)_6]^{3+}$ can show z-in distortion In this case, the z-out distortion do not remove the degeneracy since even after distortion there are still two degenerate orbitals i.e., dxz and dyz available for the electron to occupy.

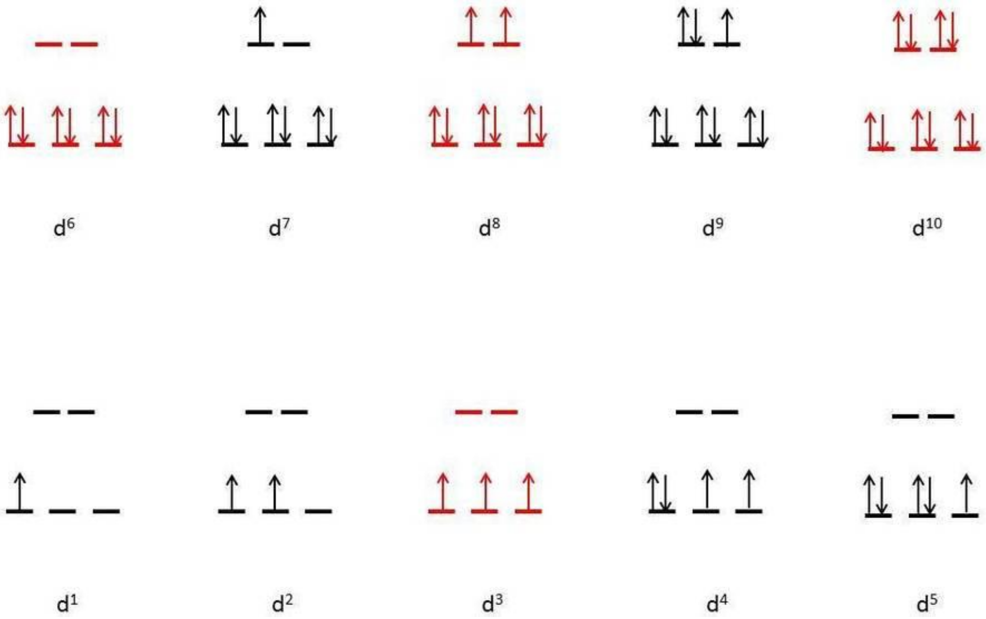


Figure : Electron configuration diagram of octahedral complexes (red indicates no degeneracies possible, thus no Jahn-Teller effects).

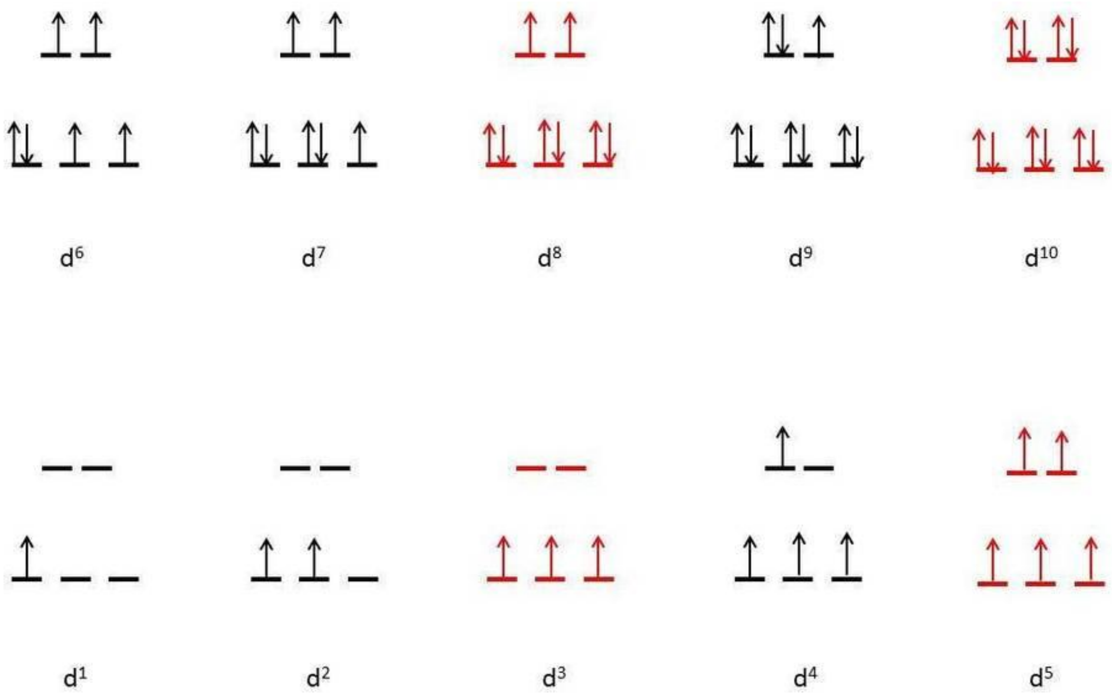


Figure : High spin octahedral coordination diagram (red indicates no degeneracies possible, thus no Jahn-Teller effects).

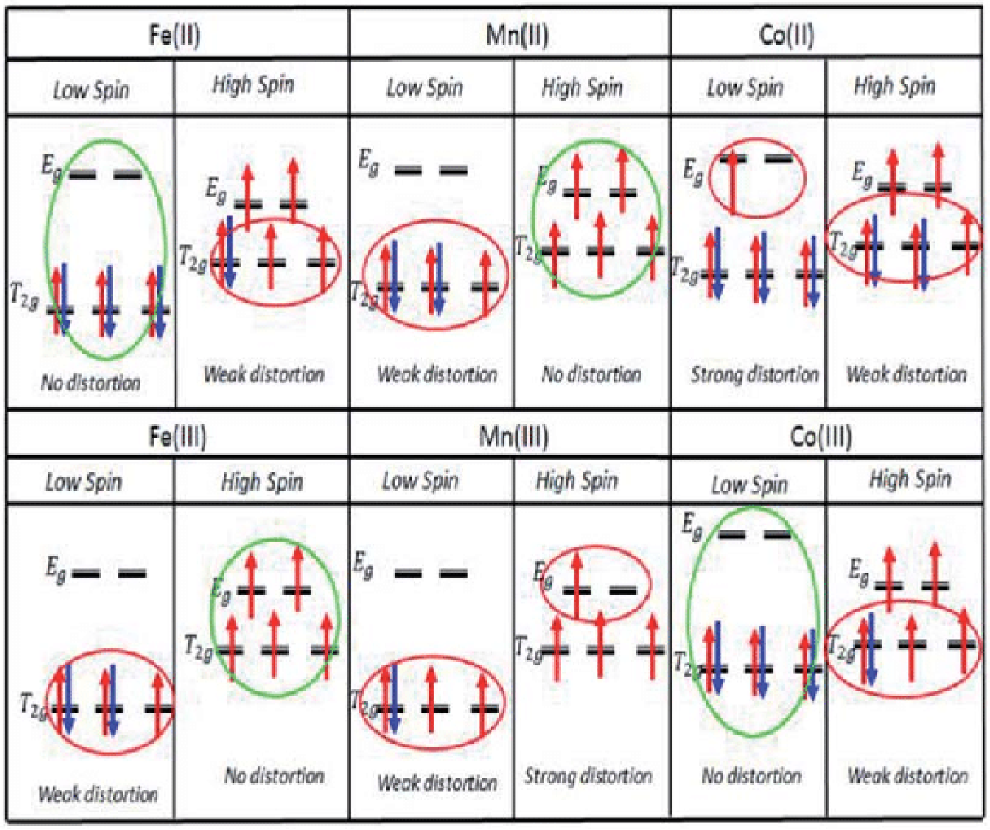


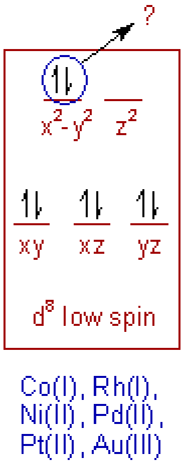
Figure: Jahn Teller Distortion.

Square planar coordinations:

The complexes formed by low spin d^8 systems, like Ni(II), are electronically degenerate in the octahedral environment since the strong field ligands around the metal ion force the two electrons in the e_g orbitals to pair up. Hence they also undergo Jahn Teller distortion by completely eliminating the ligands on the z-axis to become square planar.

E.g. $[Ni(CN)_4]^{2-}$ is a square planar complex.

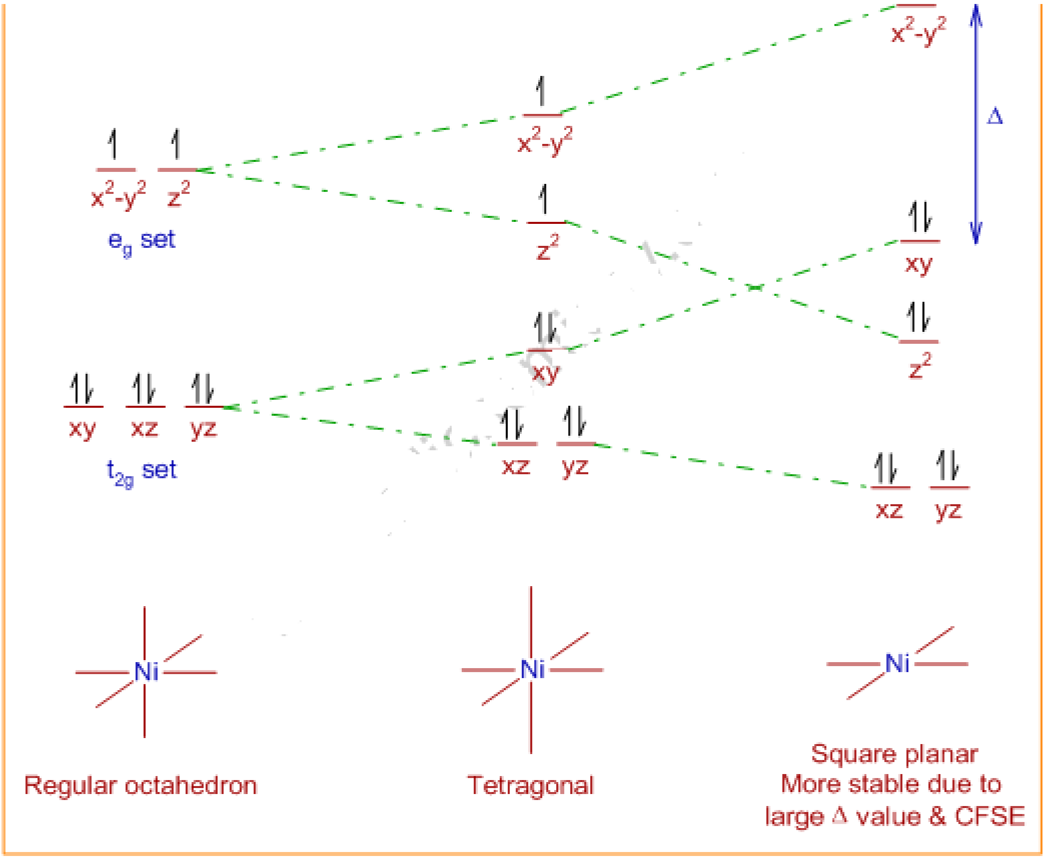
The same arguments are also applicable to the square planar complexes formed by Pt, Pd etc.



But this argument is debatable since the pairing of electrons is against the Hund's rule.

According to another school of thought, the low spin d8 systems are not at all electronically degenerate in the octahedral environment. Therefore no question of Jahn-Teller distortion. They exhibit square planar geometry simply because the crystal field splitting energy, Δ in this geometry is very high since the ligands are of strong field. This will also increases the CFSE value.

The square planar geometry is thought to be resulted due to infinite distortion of octahedral geometry along the z-axis (see the diagram below).



On the other hand, the high spin Ni(II) complexes, like NiCl42-, are tetrahedral. It is because the Δ value in presence of weak field ligands is low and does not favor the square planar geometry. Its geometry is tetrahedral because in this configuration, the ligands are placed as far away as possible from each other.

But all types of complexes of Pt, Pd; irrespective of whether they are high spin or low spin, are square planar.

The reasons are:

1) As we move down the group, the Δ value increases by about 50% in all cases.

2) Ligand replulsions are minimized due to large size of the metal. This favors square planar geometry.

3) Due to the π-interactions of d-orbitals of metals with the orbitals of ligands the stability of square planar geometry increases.

References: 1. https://byjus.com.

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3. https://chem.libretexts.org.