nnection is not revealed by Pauling's theory.

CRYSTAL FIELD THEORY (CFT)

This theory advanced by Bethe and Van Vleck was originally applied mainly to ionic crystals and is therefore called **crystal field theory**.

It is mainly concerned with the interaction of *d* orbital of central metal with the surrounding ligands that produce crystal field effects.

Salient features: முக்கிய அடிகோள்கள்

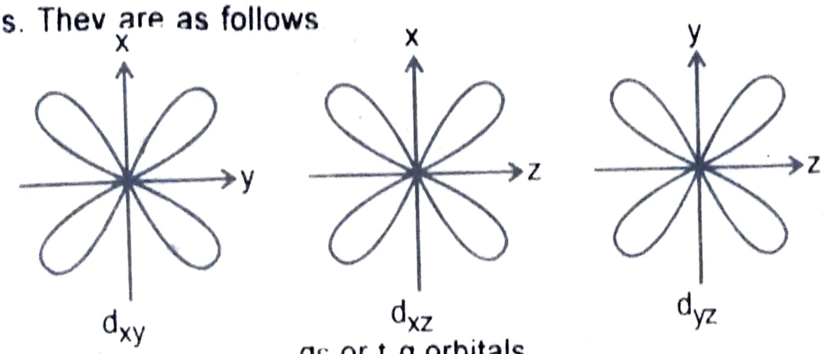
1) A complex is considered to be a combination of central metal ion surrounded by various ligands.
2) The interaction between the metal ion and ligands is purely electrostatic (ionic).
3) It does not consider any orbital overlap.
4) The ligands are either negatively charged ions e.g., F and CN or neutral molecules e.g., H_2O and NH_3. The ligands approach the central metal ions with negative poles closest to the metal ion. Neutral molecules are polarasied by the positive charge of the cation (δ $NH_3\delta^+$, δ $OH_2\delta^+$).
5) The interaction between the electrons of the metal ion and those of the ligand is purely repulsive. It is the repulsive forces that are responsible for causing the splitting of the *d* orbital of the metal into two groups t_2g and eg. This effect is known as **crystal field splitting**.

6) The number of ligands and their arrangement around the central ions will determine the crystal field.
7) Different crystal fields will have different effects on the relative energies of the five *d* orbitals.

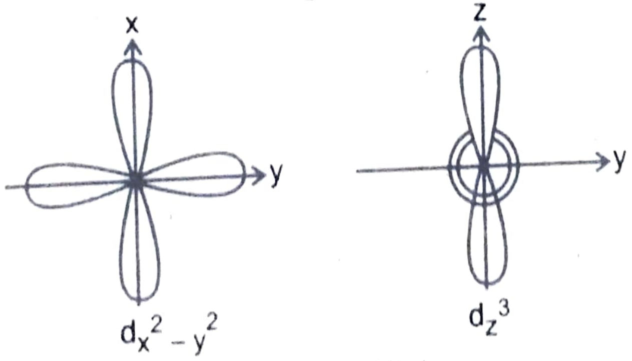
[illegible]

Crystal field splitting of *d*-orbitals:

The out come of crystal field theory is that degeneracy of the *d*- orbitals of the central metal ion is when the ligands approach it consequently the *d*-orbitals split into two groups. To understand this we recollect he shapes to *d*- orbitals. Thev are as follows



dε or t_2g orbitals



dγ or eg orbitals

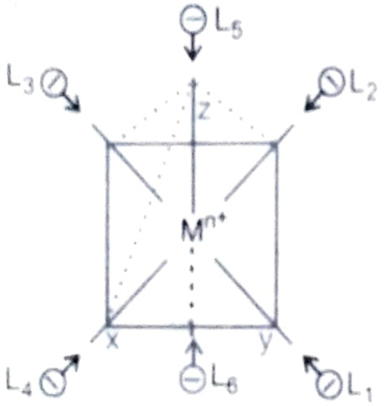
In a free (transition) metal ion all the five *d*- orbitals are degenerate i.e. have the same energy. An electron is free to occupy any of five *d*- orbitals .d_{xy}, d_{yz} d_{xz}, d_{z^2} and $d_{x^2-y^2}$, d_{xy}, d_{zy} and d_{zx} orbitals lie between xy, yz, zx axes respectively. They are known as dε or t_2g set of orbitals dz^2 orbital is oriented along the x-axis and y-axis. They are axials and are called d_y or eg set of orbitals.

On the approach of the ligands, the electrons inn the *d*-orbitals of the central ion are repelled by the lone pairs of the ligands. As a result, a energy of the entire system will b raised. If the electric field arising from the ligands is spherically symmetrical, the energy of all the *d*-orbitals would be raised to the same extent, and they will still be degenerate. But the *d*-orbitals differ in their orientation. As a result, the energies of the larger extent than those of the orbitals lying in between the split up into the two sets of orbitals havi different energies. This splitting of five degenerate *d*-orbitals of the me ion under the influence of approaching ligands, into two sets of orbita having different energies is called **crystal field splitting or energy le splitting**.

The crystal field splitting depends on the number and the arrangeme of ligands around the central metal ion.

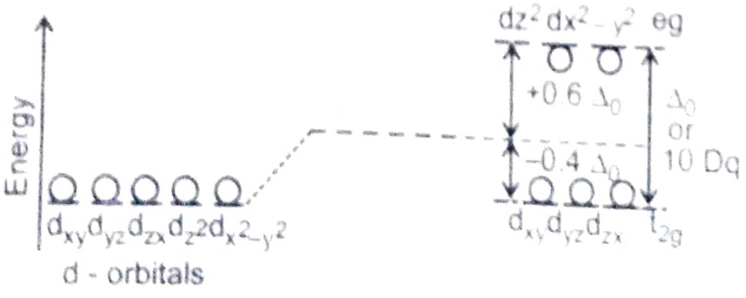
Crystal field splitting in octahedral complexes:

In the octahedral complex, the six ligands are arrangement octahedr around a central metal ion. In this arrangement the $d_{x^2y^2}$ and d_{z^2} orbitals along the x,y and z axes and point directly towards the ligands. So, the experience much more than the remaining d-orbitals d_{xy}, d_{yz}, and d_{zx}, whic are, directed in between the x, y and z-axes. Consequently the energies $d_{x^2-y^2}$ and d_{x^2} orbitals are increased much more in comparison to othe *d*-orbitals.



The *d*-sub shell thus splits up into two degenerate sets, one consistin of more stable [lower energy] orbitals d_{xy}, d_{yz} and d_{zx} and other less stab [higher energy] orbitals $d_{x^2-y^2}$ and d_{z^2}.

The energy difference between eg and t_2g sets, of orbitals is known a **crystal field stabilization energy [CFSE]** and this is represented by th symbol Δ_0 where σ indicates an octahedral arrangement of ligands. It i measured in terms of a parameter Dq. The magnitude of splitting is obitan set as 10 Dq.



Electrons will tend to occupy the lower energy t_2g orbitals to achieve stability. Each electron entering the t_2g orbitals stabilises the complex by 0.4 Δ_0 units and each electrons entering the higher energy orbitals [eg] introduces in the complex an instability unit of 6.0 Δ_0. The greater the amount of CFSE of the complex is, greater is its stability.

Since Δ_0=10Dq, each electron entering t_2g orbital stability by 4Dq, each electron entering eg orbitals destabilizes by 6Dq.

The magnitude of Δ_0 depends upon the following factors.

1) Size of he metal ion.
2) Oxidation state of the metals.
3) Nature of the ligand.
4) Stereochemistry of the complex.

Let us consider a d^x ion containing $t_{2g}^p e_g^q$ configuration where *p* is the number of electrons in t_{2g} level and q is the number of electrons in e_g level and x=p+q. For this system the CFSE is given by [-4p+6q] Dq.

In the above expression the pairing energy (p) is not taken into account. If we take that also into account their

CFSE = [-4p + 6q] Dq + mP

Here m is the total number of pairs of electrons in t_2g and eg levels put together

The following table gives of CFSE for various configurations are given below:

A High spin (spin-free/weak field) octahedral complexes

Configuration	P	Q	m	CFSE
d^0	0	0	0	0Dq
d^1	1	0	0	-4Dq
d^2	2	0	0	-8Dq
d^3	3	0	0	-12Dq
d^4	3	1	0	-6Dq
d^5	3	2	0	0Dq
d^6	4	2	1	4Dq+p
d^7	5	2	2	-8Dq+2p
d^8	6	2	3	-12Dq+3p
d^9		3	4	-6Dq+4p
d^{10}	6	4	5	0+5p

B Low spin(spin paired /strong field)Octahedral complexes

Configuration	P	Q	m	CFSE
d^0	0	0	0	0Dq
d^1	1	0	0	-4Dq
d^2	2	0	0	-8Dq
d^3	3	0	0	-12Dq
d^4	4	0	1	-16Dq+p
d^5	5	0	2	-20Dq+2p
d^6	6	0	3	-24Dq+3p
d^7	6	1	3	-18Dq+3p
d^8	6	2	3	-12Dq+3p
d^9	6	3	4	-6Dq+4p
d^{10}	6	4	5	-0Dq+5p

Analysis of the above two tables reveals.

i) When Δ_0=p i.e., p=10Dq then d^4, d^5, d^6 and d^7 configuration have sa CFSE values for both spin states.

ii) When Δ_0 > p the CFSE values of low spin states becomes smaller th that of high spin state. Therefore the low spin state becomes the prefer state of the ion. In other words, when Δ_0>p electrons tend to pair up a hence low spin complexes result.

iii) When Δ_0<p the CFSE values of high spin becomes smaller than that low spin state. Therefore the high spin state becomes the prefer state of he ion. In other words, when Δ_0<p electrons fond to pair up a hence high spin complexes result.

Thus we see that the spin state of an ion in a complex depends on whethe the crystal field splitting (Δ_0) is more or less than the pairing energy (p).

Strong and weak ligands :

Ligands which cause only a small degree of splitting of *d*-orbitals a called weak ligands and those high cause a large splitting have highe values of Δ_0. The CF splitting ability of the ligands decreases in the order

$$CN^- > NO_2^- > en > NH_3 > H_2O > F^- > OH^- > Cl^- > Br^- > I^-$$

This order is known as **spectrochemical series.**

Distributions of electrons in *d*-orbitals:

The two factors, which determine the distruption of electrons, are

i) The electrons tend to occupy the lower energy *d*-orbitals in preference to dγ d - orbitals of higher energy.

ii) The electrons tend to occupy the dξ or dγ orbitals singly with thier spin parallel in accordance with Hund's rule

The strong ligands force the electrons to pair up in the lower energy t_2g set. Thus they reduce the number of unpaired electrons and the resultant spin(S). The complexes formed by strong ligands have minimum number of unpaired electrons. Such complexes are called low spin (LS) or spin-paired complexes.

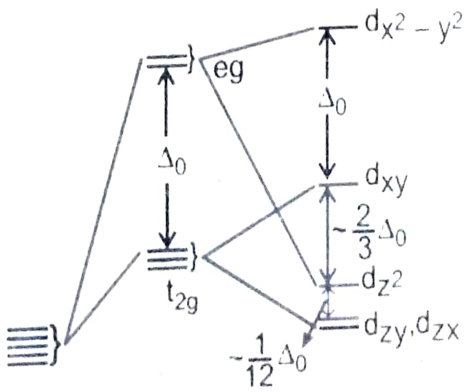
The weak ligands first make the electrons to occupy all the five *d* -orbitals singly and then pairing occurs. Thus weak ligands give higher number of unpaired electrons (or higher value of S). The complexes given by weak ligands are called high spin (HS) or spin-free complexes.

E.g.,$[Fe(H_2O)_6]^{2+}$ is high spin complexes since H_2O is a weak field ligands $[Fe(CN)_6]^{4}$ is a low spin complex since CN is a strong ligand.

Crystal field splitting in square planner complexes:

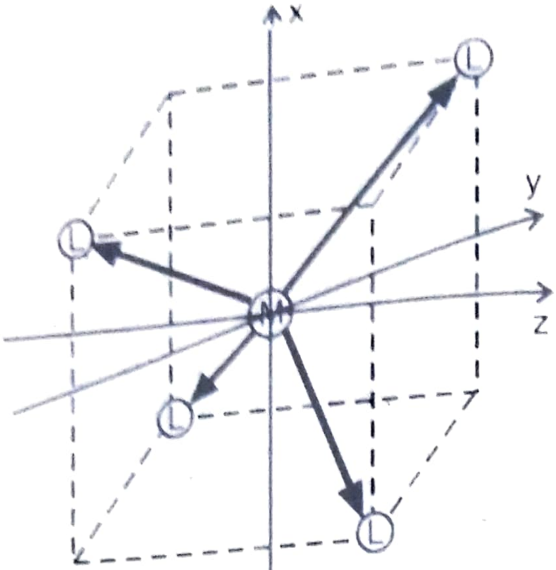
In the square planar complexes due to the absence of ligands along the Z-axis the dz^2 orbital drops far below d_{xy} so at it is nearly as stable as d_{yz} and d_{zx} orbitals and d_{xy} rises more in comparison with d_{yz} and d_{xz}

The energy level diagram in square planer compounds is as follows:



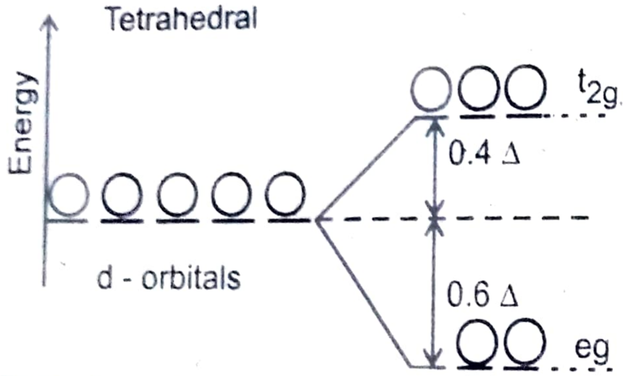
Crystal field splitting in tetrahedral complex:

The tetrahedral arrangement of a central metal ion surrounded by four ligands is shown in figure 16.



We find that in a tetrahedral arrangement no *d*-orbital points exactly towards the ligand, d_{xy} d_{yz} and d_{xz} are pointing approximately by in the directions of the approaching ligands. $d_{x^2-y^2}$ and d_{z^2} are lying in between approaching ligands. So the energies of d_{xy}, d_{yz} and d_{xz} *increase more than those of* $d_{x^2-y^2}$ and d_{z^2}.

Thus we find that the *p* orbital splitting is just the reverse of what happened in octahedral complexes.



The CFSE of tetrahedral complexes $\Delta_t \approx 0.45\ \Delta_0$. Thus the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex. Hence crystal field effects favor the formation of octahedral complexes over that of tetrahedral complexes.

CFSE gives us an idea about the stability of the molecules. Complexes with more CFSE will be more stable.

APPLICATIONS OF CRYSTAL FIELD THEORY:

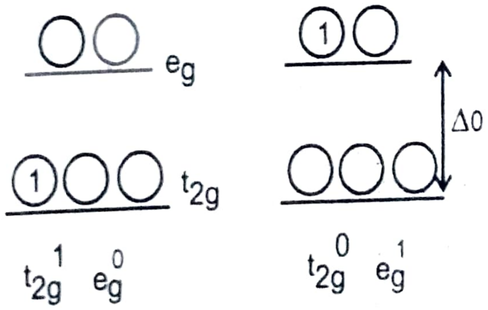
1. *Colour of transition metal complexes:*

One of the notable successes of CFT is that it is able to provide a satisfactory explanation for the colour of transition metal complexes. These give absorption bands in the visible region of the spectrum of light.

We find that the solution of transition metal complexes formed by metal cations having no unpaired electrons their orbitals (i.e., having completely filled or vacant *d*-orbitals) are colourless while the solution of transition metal complexes given by transition metal cations having one or more unpaired electrons in *d*-orbitals are coloured.

For example $[Ti(H_2O)_6]^{3+}$ ion is octahedral and is purple coloured. When white light falls on the solution, the ions in the solution absorb radiation from white light (i.e., Visible region). The λ_{max} is about 5000Å. The colour of this absorbed radiation is green. The transmitted light corresponding to this absorbed light is purple. So the colour of $[Ti(H_2O)_6]^{3+}$ solution is purple.

The cause of colour may be explained on the basis of CFT as follows. We know Ti^{3+} ion has got one electron in the *d*-orbital H_2O is weak field ligand. So $[Ti(H_2O)_6]^{3+}$ is high spin complex. It will have its one *d*-electron in the t_{2g} level. Now when white light falls on $[Ti(H_2O)_6]^{3+}$ ion the unpaired electron present in t_{2g} level moves from lower energy t_{2g} level to higher energy e_g level. For this transitions the molecules absorbs sufficient energy from the white light which is about 5000Å.[Figure - 18]



Grand state of
$[Ti(H_2O)_6]^{3+}$

Excited state of
$[Ti(H_2O)_6]^{3+}$

Δ_0 = 57 k cals / mole = 5000Å = λ_{max}

Figure - 18.

This type of electronic transition form t_{2g} to e_g level is called *d-d* or ligand-field transition, which is cause of the colour of $[Ti(H_2O)_6]^{3+}$ ion. In similar fashion we can explain the colour of any other complex.

Depending upon Δ values the complex exhibits colour. For $[Co(NH_3)_6]^{2+}$ Δ_0 is very large. So it absorbs in the blue region and so appears red. Tetrahedral Co(II) complexes like $[CoX_4]^{2-}$ needs lesser excitation energy. So it absorbs near red portion of the spectrum. Thus it appears blue.

Hydrated copper sulphate is coloured while anhydrous $CuSO_4$ is whi This is because hydrated copper sulphate is in aqua complex of Cu^{2+} where *d-d* transitions are possible. It absorbs near the red portion of th spectrum. So it appears blue. Anhydrous $CuSO_4$ is not a complex. S transition of electrons between various electronic levels is not possible hence it does not absorb in the visible region. So it is colourless i.e. while man other amine complexes of Cu(II) are known all are much more intense blue than the aqua ion. This is because the amine produces a stronger ligand field.

This causes absorption in the middle red region than in far-red region. So the amine complexes are intensely blue when compared with their aqua counterparts.

A solution containing $[Ni(H_2O)_6]^{2+}$ is green. On adding cyanide $[Ni(CN)_4]$ is formed. The colour disappears. This is because H_2O is a weak ligand CN^- is a strong ligand. The aqua complex is octahedral while the cyano complex is tetrahedral. Thus Δ_0 of the aqua complex is less than Δ_t of the cynao complex. So *d-d* transitions are possible in aqua complex. So it is coloured. The same is difficult in cyano complex. So it colourless.

Further it must be noted that transition metal ions with completely filled d^{10} configuration and employ d^0 configuration are colourless E.g. $Cu^+(d^{10})$, $Zn^{2+}(d^{10})$, $Ag^+(d^{10})$, $Ti^{+4}(d^0)$, etc.

2. Magnetic properties of complexes:

The magnetic properties of co-ordination compounds can be interpreted successfully by Crystal Field Theory. Transition metals consist of one or more partially filled d-orbitals. The distribution of electrons on two factors

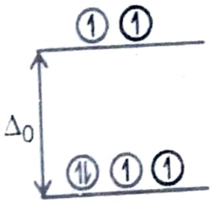
i) The electrons tend to occupy the lower energy t_{2g} orbitals in preference to e_g orbitals of higher energy.

ii) If Hund's rule is obeyed the electrons tend to occupy t_{2g} and e_g orbitals singly with thier spins parallel.

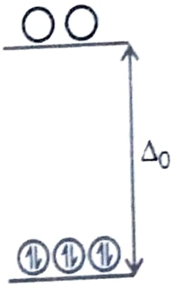
Consider a metal having three *d*-electrons. The distribution of electrons according to Hund's rule is as shown. Thus the metal ion has three unpaired electrons and is paramagnetic. The magnetic moment will be close to 3.87 BM.

With 4-7 *d*-electrons, two different *d*-orbital arrangements are possible depending upon the magnitude of crystal field splitting energy Δ_0 and pairing energy P of electrons (the energy required for the electrons to get paired).

If the crystal field is strong Δ_0 is greater than P and if it is weak Δ_0 is less than P. the strong ligands force the electrons to pair up in the lower energy (t_{2g}) orbitals and thus reduce the number of unpaired electrons (n) and therefore the resultant μ. Thus the complexes formed by strong ligands have the minimum number of unpaired electrons. Such complexes are called low spin (LS) of spin-paired complexes. In the presence of weak ligands, first the electrons occupy all the five d-orbitals singly and then pairing occurs. Thus complexes formed by weak ligands have higher number of unpaired electrons resulting in the higher value of μ. Such complexes are called high spin (HS) or spin free complexes. The relation between Δ_0 and arrangement of electrons in d-orbitals of octahedral complexes can be diagrammatically represented as follows:



$[CoF_6]^{3-}$
High spin



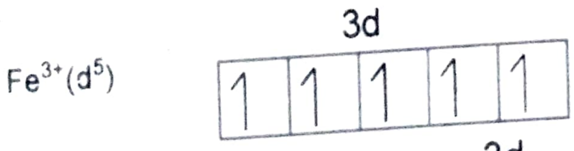
$[Co(NH_3)_6]^{3+}$
Low spin

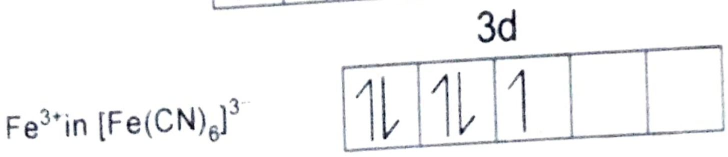
Magnetic properties of octahedral complexes:

Example: The magnetic moment of $[FeF_6]^{2-}$ ion is 5.9 BM while that of $[Fe(CN)_6]^{3-}$ ion is 1.8 BM. This property can be explained as follows:

Fe^{3+} is the central metal ion in both $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ ions.

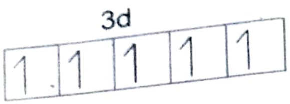
The electronic configuration of Fe^{3+} is as follows :





Low Spin complex

Fe^{3+} in$[FeF_6]^{3-}$



High Spin comple

CN^- being a strong ligand forces the electrons to pair up again Hund's rule. Hence a single unpaired electron is present in $[Fe(CN_6)]^{3-}$ io This is in agreement with the magnetic moment value of 1.8BM (μ for single unpaired electrons is 1.73 BM)

In the presence of a weak ligand such as F^- no pairing occurs in Fe ion. Hence five unpaired electrons are present in $[FeF_6]^{3-}$ ion. This is agreement with the magnetic moment value of 5.9 BM.

Other examples:

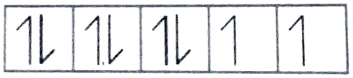
1. $[Co(NH_3)_6]^{3+}$ Diamagnetic
   $[CoF_6]^{3-}$ Paramagnetic corresponding to four unpaired electron
2. $[Fe(CN)_6]^{4-}$ Diamagnetic,
   $[Fe(H_2O)_6]^{3+}$ Paramagnetic corresponding to four unpaired electrons

Magnetic properties of tetrahedral complexes:

In tetrahedral complexes only outer 's' and 'p' electrons will be involved leaving d electrons unaffected. Such complexes are known as outer orbital complexes. They are generally paramagnetic. Example : $[Ni(NH_3)_4]^{3+}$

The electronic configuration of Ni is $3d^8\ 4s^2\ 4p^2$ and that of Ni^{2+} is $3d^8\ 4s^0$ $4p^0$

Ni^{2+} (d^8)



There are two unpaired electrons. Hence it is paramagnetic moment as the free central ion.

Other example : $[NiCl_4]^{2-}$ paramagnetic corresponding to two electrons.

$[Cu(NH_3)_4]^{2}$ paramagnetic corresponding to one electron.

Nickel carbonyl $[Ni(CO)_4]$ is tetrahedral but diamagnetic. Here the four carbonyl groups are co-ordinated to the nickel atom and Ni in this complex has an electronic configuration $3d^{10}\ 4s^0\ 4p^0$. There is no unpaired electron. Hence it is diamagnetic.

Magnetic properties of square planar complexes: complexes, the inner d electrons are also involved Su known as inner orbital complexes They are generally d

Example : $[Ni(CN)_4]^{2}$

The electronic structure of Ni^{2+} in $[Ni(CN)_4]^{2}$ is $3d^8\ 4s^2$

Ni^{2+} in $[Ni(CN)_4]^{2+}$

Since there is no unpaired electron in the ion it

Geometry:

Since according to CFT metal ligand bond is pu provide room for the existance of covalent bonds eith this theory by itself does not provide any idea ab molecule. However all that we have studied abo crystals in crystallography (solid state) can be app no covalence is envisaged in CFT hybridisation a molecules do not find a place in CFT. That w tetrahedral or square planar geometries in C knowledge about ionic crystals and their geom extent of saying that CFT fails in establishing molecules.

Merits of CFT / Evidences for CFT :

1. CFT provides satisfactory explanation for complexes.
2. It predicts a gradual change in the magn

Defects / Failures of CFT :

i) According to CFT metal ligand bonding has been shown to be partly covalent C
ii) CFT considers only d- orbitals of met other s,p etc orbitals and ligand p -orb
iii) Complexes have been shown to have for by CFT.
iv) CFT considers only metal orbital. It t interaction between the two is totally

Magnetic properties of square planar complexes: In square planar complexes, the inner d electrons are also involved. Such complexes are known as inner orbital complexes. They are generally **diamagnetic**.

Example : $[Ni(CN)_4]^{2}$

The electronic structure of Ni^{2+} in $[Ni(CN)_4]^{2}$ is $3d^8\ 4s^0$ **$4p^0$)**

Ni^{2+} in $[Ni(CN)_4]^{2+}$	↑↓	↑↓	↑↓	↑↓	

Since there is no unpaired electron in the ion it is diamagnetic.

Geometry:

Since according to CFT metal ligand bond is purely ionic. This does not provide room for the existance of covalent bonds either pure or partial. Hence this theory by itself does not provide any idea about the geometry of the molecule. However all that we have studied about the geometry of ionic crystals in crystallography (solid state) can be applied to these also. Since no covalence is envisaged in CFT hybridisation and consequent shapes of molecules do not find a place in CFT. That we talk about octahedral, tetrahedral or square planar geometries in CFT also is based on our knowledge about ionic crystals and their geometries. We can go to the extent of saying that CFT falls in establishing the geometry of complex molecules.

Merits of CFT / Evidences for CFT :

1. CFT provides satisfactory explanation for the colour of transition metal complexes.
2. It predicts a gradual change in the magnetic properties of complexes.

Defects / Failures of CFT :

i) According to CFT metal ligand bonding is purely is ionic. The bonding has been shown to be partly covalent. CFT has no explanation for this.

ii) CFT considers only d- orbitals of metals ions. It does not consider other s,p etc orbitals and ligand p -orbitals.

iii) Complexes have been shown to have p- bonds. This is not accounted for by CFT.

iv) CFT considers only metal orbital. It totally ignores ligand orbitals. The interaction between the two is totally ignored by CFT.

v) It does not explain properly the relative strengths of ligands to split the d-orbital.

vi) It furnishes little information regarding excited states in which there is electron or charge transfer.

vii) It does not recognize the existence of orbital overlap and hence the existence of specific bonding interactions between the ligands and metal orbital

Because of these reasons CFT is inadequate to describe completely bonding in complexes. These may also be taken as evidences against CFT.

Comparison between VBT and CFT:

Similarity:

The inner orbital octahedral complexes of VBT are the same as the spin paired or low spin octahedral complexes of CFT. Similarly outer orbital complexes of VBT are same as the spin free or high spin octahedral complexes of CFT.

Difference:

1. In the formation of some inner orbital octahedral complexes of VBT, the promotion of an electron from *d*-orbital to *s*-orbital is required, while in the formation of spin paired octahedral complexes of CFT no such promotion is required.
2. According to VBT, the metal ligand bonding in complexes is only covalent, since VBT assumes that ligand electrons are donated to the vacant *d*-orbitals on the central cation. On the other hand CFT considers the bonding to be entirely electro-static. Thus CFT does not allow the ligand electrons to enter the metal *d*-orbitals.

Reasons to show that crystal field theory is superior to Paulig's Valence bond theory:

1. The concept of outer orbital complex presumed in VBT is unsupported by evidences. In CFT there is no such unsupported assumption.
2. VBT is qualitative: CFT is qualitative and also quantitative. CFT accounts for the energy aspect of the complexes.
3. VBT offers no possibility of predicting or explaining magnetic behavior beyond the level of specifying numbers of unpaired electrons. CFT offers such a possibility.
4. VBT is unable to account for the colour of the complexes CFT provides explanation for colour of complexes