

CRYSTAL FIELD THEORY (CFT)

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Crystal Field Theory was proposed by the physicist Hans Bethe in 1929 to describe the bonding in coordination complexes and to rationalize and predict some important properties of coordination complexes (colours, magnetism etc.). This model was based on a purely interaction between the ligands and the metal ion in the complexes with various geometries like octahedral, tetrahedral, square planar etc. Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions.

This theory is based on the concept that when the negative charges of the incoming ligands (or the negative ends of dipolar molecules like NH_3 and H_2O) attract the positively charged metal ion, there is also repulsive interaction between d electrons present on the metal ion and the ligands. Certain assumptions are taken while dealing with CFT-

1. The ligands are treated as point charges. In fact, this is not practically true since sometimes the size of ligand particularly when it is sulfur or phosphorus donating ligands, is approximately similar to the size of metal ion.
2. The interactions between metal ion and ligand are treated as purely electrostatic, no covalent interactions are considered. This again is not true, some of the observations cannot be explained without invoking covalent interactions. In isolated gaseous metal ion, all of the five d-orbitals are degenerate.
3. When a hypothetical spherical field of ligand approaches the metal ion, d-orbitals still remain degenerate, but their energy level is raised a bit due to repulsion between the orbitals of metal & ligand. This energy level is called Barycenter. But in the transition metal complexes, the geometry about the metal ions are octahedral, tetrahedral or square planar etc., the field provided by the ligands is not at all spherically symmetrical therefore d-orbitals are unequally affected by the ligands and degeneracy of d-orbitals in metal removed and split into different energy levels (**e.g. t_{2g} or e_g**).

- To understand CFT, one must understand the description of the lobes of d-orbitals given in the figure:
- d_{xy} : lobes lie in-between the x and the y axes.
- d_{xz} : lobes lie in-between the x and the z axes.
- d_{yz} : lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z^2} : there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

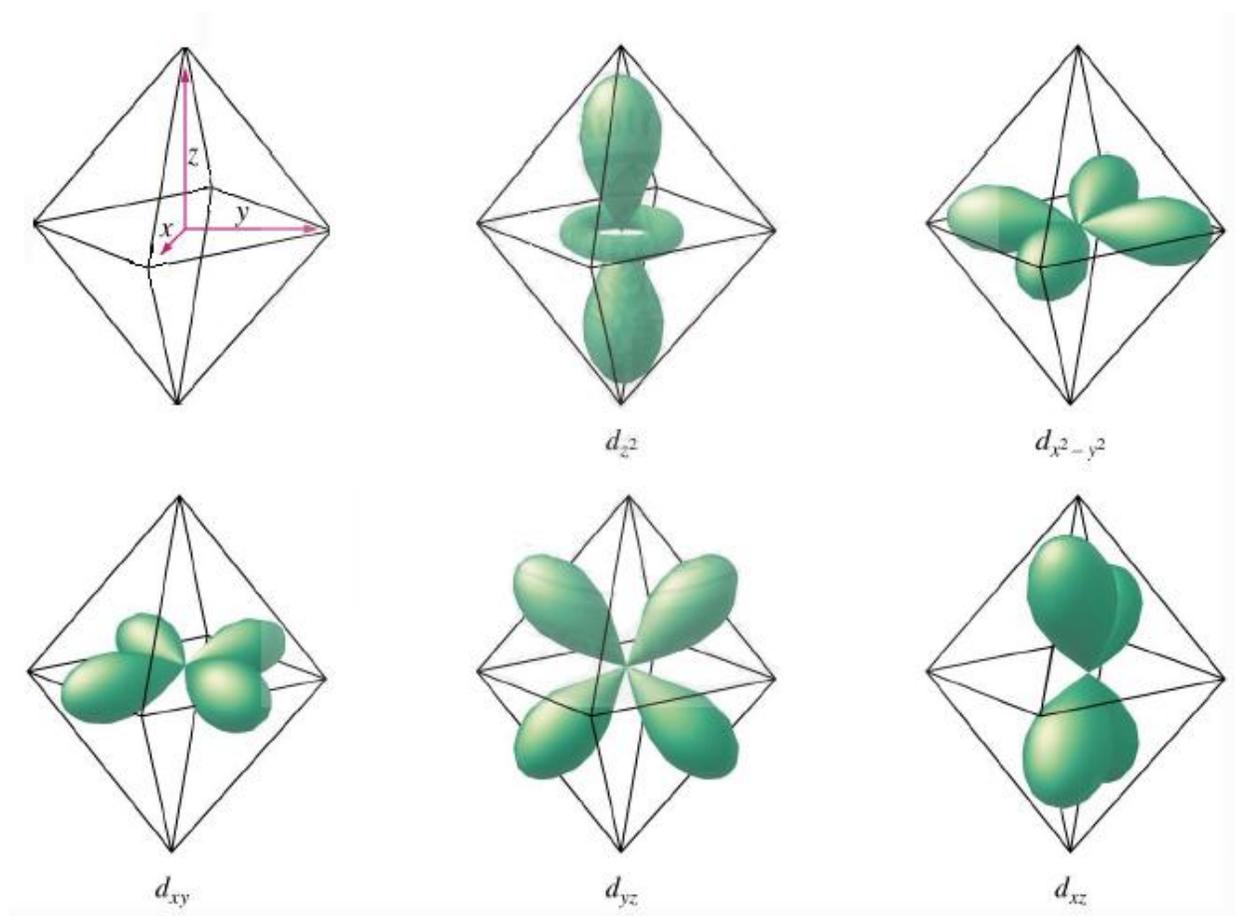
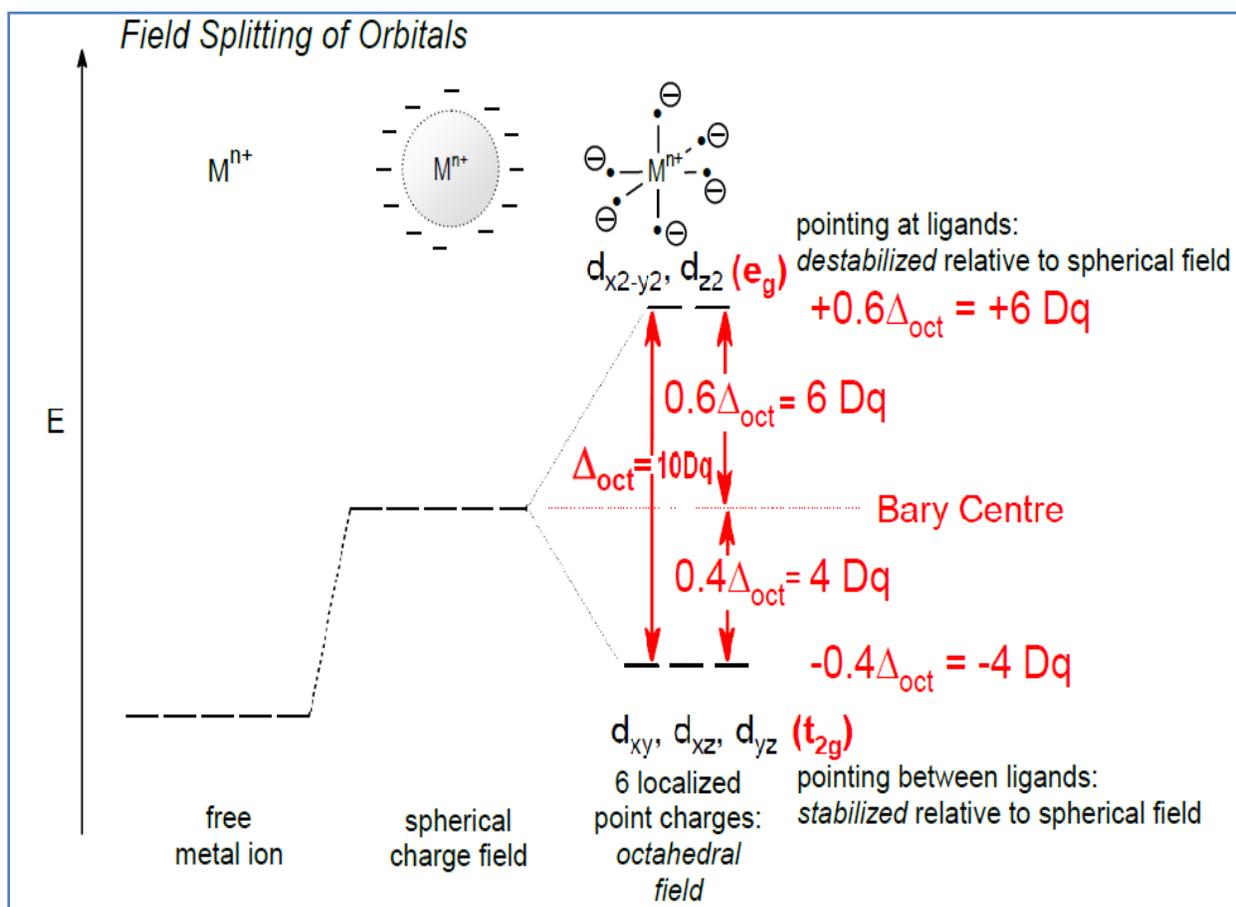


Figure 1: Shapes of d-orbitals

CRYSTAL FIELD EFFECTS ON OCTAHEDRAL COMPLEXES

- In octahedral complexes, the ligands approach along the axes.
- The d-orbitals where electron density is oriented along the axes, $d_{x^2-y^2}$ and d_{z^2} are repelled much more by the ligands while the orbitals d_{xy} , d_{xz} , d_{yz} having electron density oriented in between the axes are repelled lesser by the ligands.
- Two sets of orbitals e_g (doubly degenerate set) and t_{2g} (doubly and triply degenerate) are formed due the repulsion between metals and ligands orbitals.



a, b = singly degenerate labels
 e = doubly degenerate
 t = triply degenerate

g = gerade (symmetrical about origin)
 u = ungerade (unsymmetrical about origin)

Figure2: Splitting of d-orbitals in Octahedral Field

- The energy gap between e_g and t_{2g} is called **crystal field splitting energy** and it is denoted by Δ_o or Δ_{oct} or $10Dq$, where Δ represent **Crystal field splitting energy**, "o" in Δ_o is for octahedral.
- Because the overall energy is maintained, the energy of the three t_{2g} orbitals are lowered or stabilised by $0.4 \Delta_o$ and the energy of the two e_g orbitals are raised or repelled by $0.6\Delta_o$ with respect to hypothetical the spherical crystal field or Bary Centre.

The Dq notation has mathematical origins in CFT but Δ_o is preferred because of its experimentally determined origin.

The size of Δ_o can be measured easily using UV-Vis spec.

Example: $[\text{Ti}(\text{OH}_2)_6]^{3+}$. hexaaquatitanium(III) ion ($\text{Ti}=d^1$).

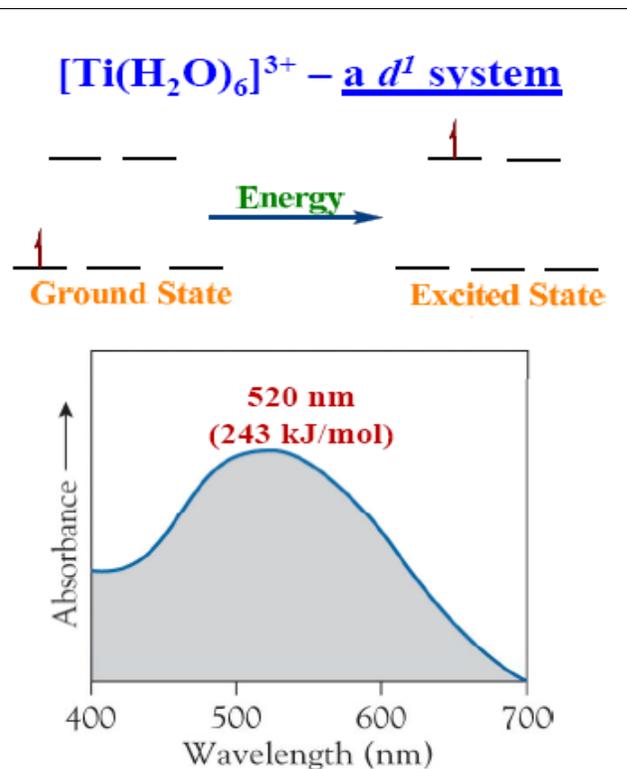
The complex absorbs light of the current wavelength (energy) to promote the electron from the t_{2g} level to the e_g level. ($20300\text{cm}^{-1} = 493/520 \text{ nm}$)

$$1\text{kJmol}^{-1} = 83.7\text{cm}^{-1}, \Delta_o = 20300/8.7 = 243\text{kJmol}^{-1}$$

The single d electron occupies an energy level $2/5 \Delta_o$ which is below the average energy of the d orbitals because of the CFSE of the d -orbitals.

$$\text{CFSE} = 2/5 \times 243 = 97\text{kJmol}^{-1}$$

As a result the complex is stable



CRYSTAL FIELD STABILIZATION ENERGY (CFSE)

- The energy difference between the distribution of electrons in a particular crystal field and that for all electrons in the hypothetical spherical or uniform field levels is called the **crystal field stabilization energy (CFSE)** [This is the measure of the net energy of occupation of the d orbitals relative to their mean energy, Bary Centre].
- As we have seen, the energy difference between t_{2g} and e_g orbitals is defined as Δ_o . The energy level of each of the two e_g orbitals would be $0.6 \Delta_o$ above the zero of energy (barycenter), whereas the energy level of each of the three t_{2g} orbitals would be $0.4 \Delta_o$ below the zero energy.
- Consider the example, the $Ti (H_2O)_6^{3+}$ ion. Ti^{3+} has a d^1 electron configuration with the electron occupying t_{2g} , the crystal field stabilization energy (CFSE) is $-0.4 \Delta_o$. For d^2 , the $CFSE = -0.8 \Delta_o$ and for d^3 , $CFSE = -1.2 \Delta_o$. Upon reaching the d^3 configuration, however, the t_{2g} level becomes half-filled and there are no further orbitals of this energy to accept electrons without pairing.

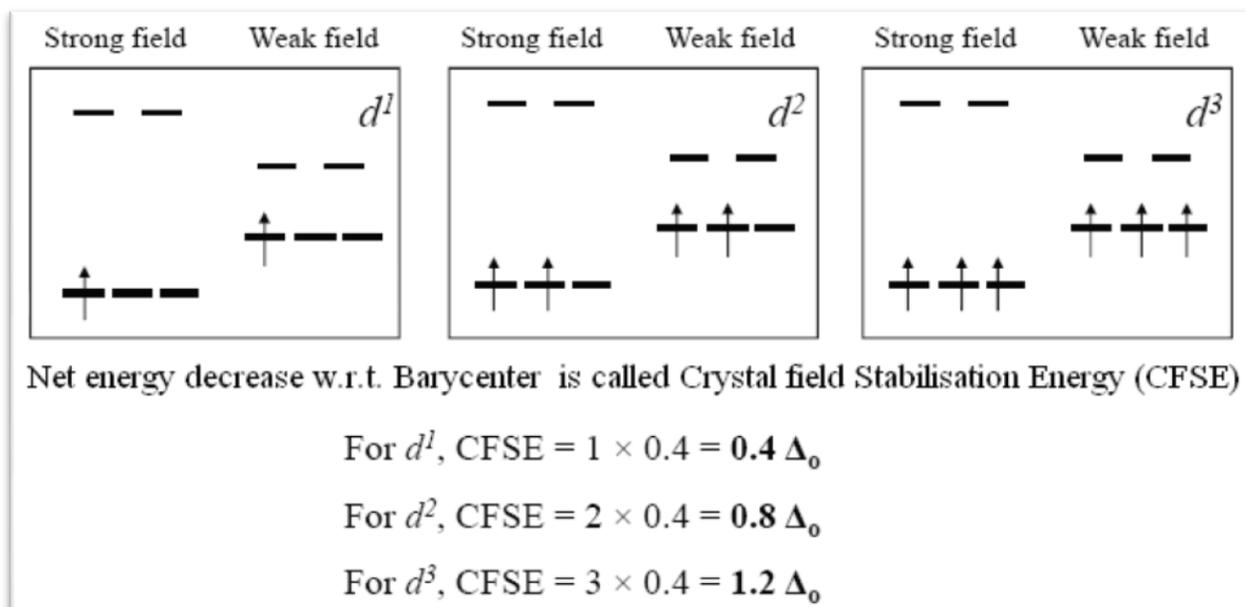


Figure3: Distribution of electrons and CFSE for d^1 - d^3 configurations

- For configurations d^4 , d^5 , d^6 and d^7 two possibilities arise. The determining factor whether high-spin or low-spin complexes arise is the ligand-field splitting parameter. When Δ_o is larger than the pairing energy P for the electrons, the electron pair in the t_{2g} orbitals as far as possible. If the energy required for pairing up the electrons (electrostatic repulsion) is greater than Δ_o , the electrons will be distributed between t_{2g} and e_g levels. In the former case we have the strong-field ($\Delta_o > P$) arrangement with low-spin complexes, while in the latter we have the weak-field ($\Delta_o < P$) arrangement with high-spin complexes.

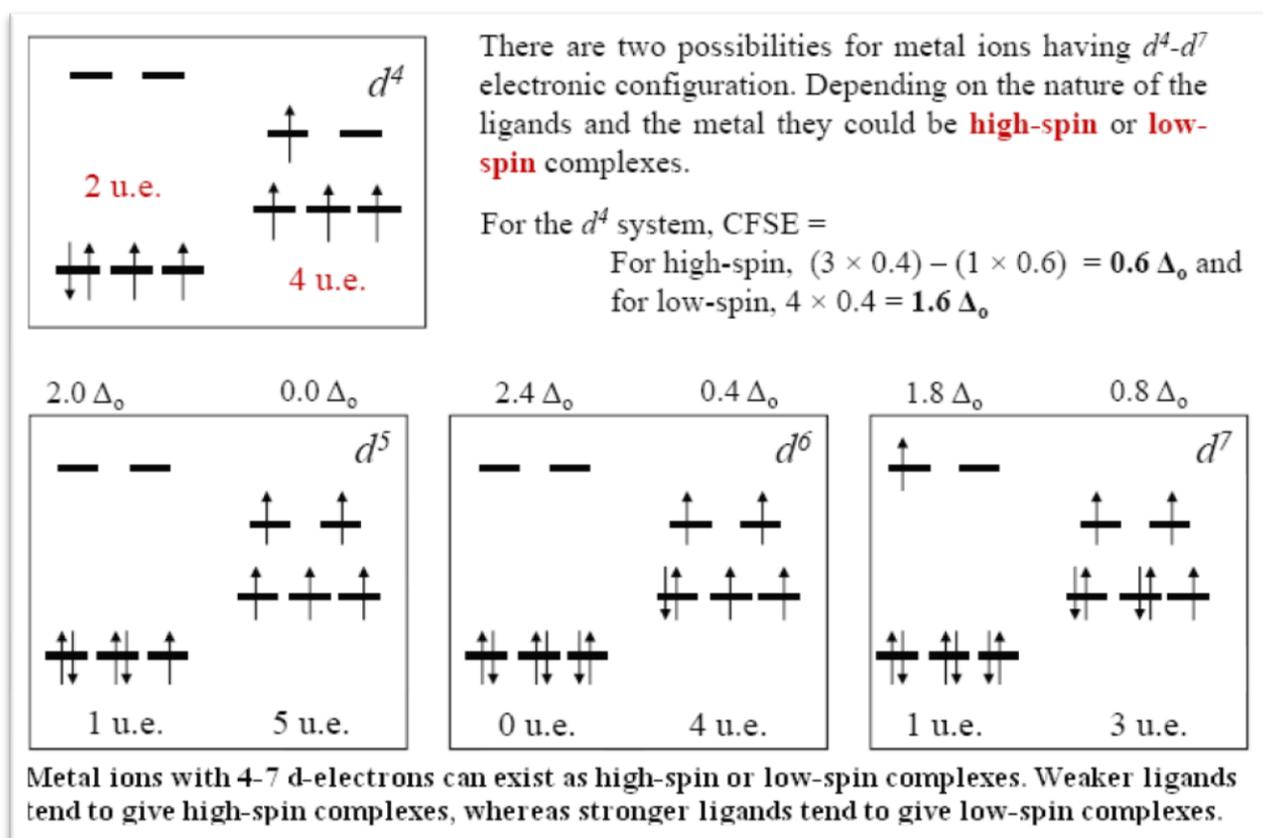


Figure4: Distribution of electrons and CFSE for d^4 - d^7 configurations

- With d8 , d9 and d10 configurations there is only one possible way for distributing the electrons between the t_{2g} and e_g orbitals. The arrangement of electrons in the d-orbitals of ions in octahedral complexes is illustrated in figure 3. Also, for d1 to d10 the resultant CFSE are listed in Table 3.1 , together with the number of unpaired electrons expected for each configuration .

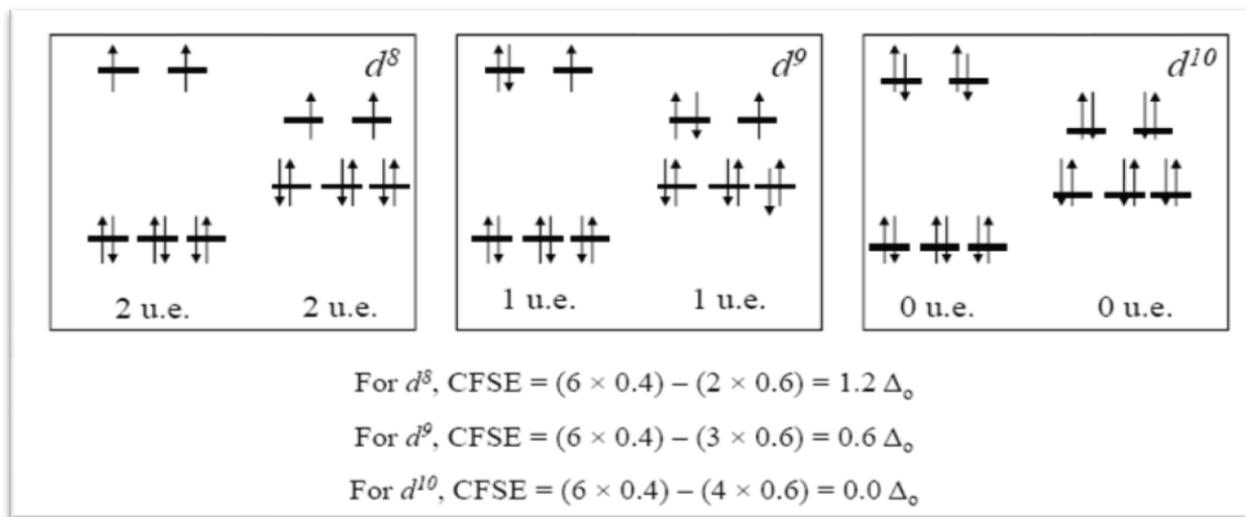


Figure4: Distribution of electrons and CFSE for d⁴-d⁷ configurations

Note: In all the cases the electronic configuration involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons

Table1: Octahedral crystal field stabilization energies (CFSE) for dⁿ configurations.

Table: Distribution of d-electrons in t_{2g} and e_g sets of orbitals of central metal ion surrounded by ligands in octahedral complexes.

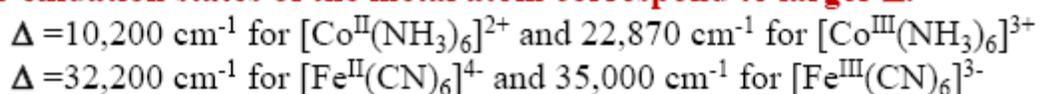
No of electrons	Weak field ligand					CFSE	n	s = $\frac{n}{2}$	Strong field ligand					CFSE	n	s = $\frac{n}{2}$
	t _{2g} orbitals			e _g orbitals					t _{2g} orbitals			e _g orbitals				
d ¹ (Ti ³⁺)	↑					-4Dq or -0.4Δ _o	1	$\frac{1}{2}$	↑					-4Dq or -0.4Δ _o	1	$\frac{1}{2}$
d ² (Ti ²⁺)	↑	↑				-8Dq or -0.8Δ _o	2	1	↑	↑				-8Dq or -0.8Δ _o	2	1
d ³ (V ²⁺)	↑	↑	↑			-12Dq or -1.2Δ _o	3	$\frac{3}{2}$	↑	↑	↑			-12Dq or -1.2Δ _o	3	$\frac{3}{2}$
d ⁴ (Cr ²⁺)	↑	↑	↑	↑		-6Dq or -0.6Δ _o	4	2	↑↓	↑	↑			-6Dq or -0.6Δ _o	2	1
d ⁵ (Fe ³⁺)	↑	↑	↑	↑	↑	0	5	$\frac{5}{2}$	↑↓	↑↓	↑			0	1	$\frac{1}{2}$
d ⁶ (Co ²⁺)	↑↓	↑	↑	↑	↑	-4Dq + P or -0.4Δ _o + P	4	2	↑↓	↑↓	↑↓			-4Dq + P or -0.4Δ _o + P	0	0
d ⁷ (Co ³⁺)	↑↓	↑↓	↑	↑	↑	-8Dq + 2P or -0.8Δ _o + 2P	3	$\frac{3}{2}$	↑↓	↑↓	↑↓	↑		-8Dq + 2P or -0.8Δ _o + 2P	1	$\frac{1}{2}$
d ⁸ (Co ²⁺)	↑↓	↑↓	↑↓	↑	↑	-12Dq + 3P or -1.2Δ _o + 3P	2	1	↑↓	↑↓	↑↓	↑	↑	-12Dq + 3P or -1.2Δ _o + 3P	2	1
d ⁹ (Cu ²⁺)	↑↓	↑↓	↑↓	↑↓	↑	-6Dq + 4P or -0.6Δ _o + 4P	1	$\frac{1}{2}$	↑↓	↑↓	↑↓	↑↓	↑	-6Dq + 4P or -0.6Δ _o + 4P	1	$\frac{1}{2}$
d ¹⁰ (Zn ²⁺)	↑↓	↑↓	↑↓	↑↓	↑↓	0Dq + 5P	0	0	↑↓	↑↓	↑↓	↑↓	↑↓	0Dq + 5P	0	0

THE FACTORS AFFECTING CRYSTAL FIELD SPLITTING ENERGY, Δ OR $10Dq$

There are several factors that affect the extent of splitting of the d-orbitals by ligands.

(I) **Oxidation state of the metal** . For a given metal, the change of the oxidation state from +2 to +3 would result in a corresponding increase in Δ by 50% . The increased charge of the metal ion will draw the ligands in more closely, hence they will have a greater effect in perturbing the metal d-orbitals.

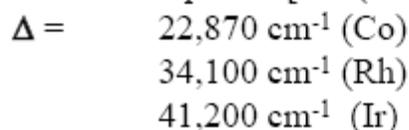
Higher oxidation states of the metal atom correspond to larger Δ .



(II) **Nature of the metal ion involved** . For a given transition series the difference are not great, but within a given group in progressing from 3d \rightarrow 4d \rightarrow 5d the value of Δ increases by 25 - 50%.

In groups, heavier analogues have larger Δ .

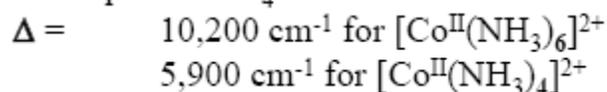
For hexaammine complexes $[\text{M}^{\text{III}}(\text{NH}_3)_6]^{3+}$:



(III) **Geometry of the complex** . The splitting in an octahedral field is about twice as strong as for a tetrahedral field for the same metal ion and the same ligands . In tetrahedral complex the ligands are directed much less efficiently than in octahedral complex

Geometry of the metal coordination unit affects Δ greatly.

Tetrahedral complexes ML_4 have smaller Δ than octahedral ones ML_6 :



(IV) **Nature and Number of the ligands** . Different ligands cause different degree of splitting.

Nature of the ligands.

For $[\text{Co}^{\text{III}}\text{L}_6]$, Δ in cm^{-1} : 13,100 (F^-); 20,760 (H_2O); 22,870 (NH_3)

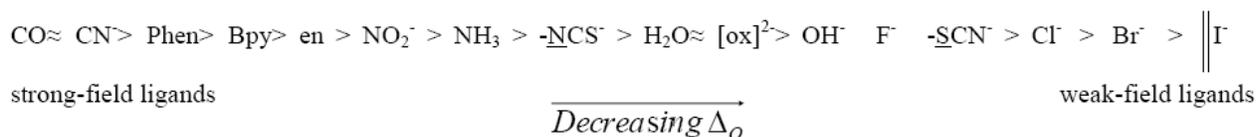
For $[\text{Cr}^{\text{III}}\text{L}_6]$, Δ in cm^{-1} : 15,060 (F^-); 17,400 (H_2O); 26,600 (CN^-)

- Depending on the charge (or oxidation state) and nature of metal ion (or metal) and ligand, the strength of the crystal field may be varied from strong to weak.

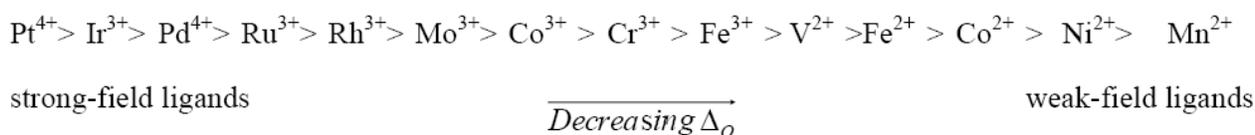
Δ (strong field) > Δ (weak field)

- It is possible to list ligands or metal ions in order of increasing field strength in a " spectrochemical series " .

i) Spectrochemical series for ligands



ii) Spectrochemical series for metal ions



The value of Δ_o increases with increasing oxidation number of the central metal ion. The variation of oxidation number reflects the smaller size of more highly charged ions and consequently shorter metal-ligand distances and stronger interaction energies. The value of Δ_o increases down the group. This reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interaction of the ligands.

Problems

1. Calculate CFSE for the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

Chromium in ground state is $[\text{Ar}]3d^5 4s^1$, in +2 state, will be a d^4 system with $t_{2g}^3 e_g^1$ configuration of electrons because H_2O is a weak field ligand. CFSE will be therefore

3 1

$$-0.4 \Delta_0 \times 3 + 0.6 \Delta_0 = -0.6 \Delta_0$$

2. Calculate CFSE for $[\text{Fe}(\text{CN})_6]^{4-}$

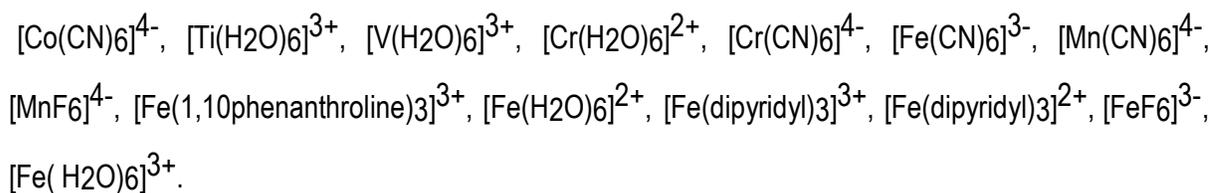
Iron in ground state is $[\text{Ar}]3d^6 4s^2$, in +2 state it will be a d^6 system with $t_{2g}^6 e_g^0$ configuration of electrons because CN^- is a strong field ligand. Therefore, CFSE be

$$-0.4 \Delta_0 \times 6 + 2P = -2.4 \Delta_0 + 2P$$

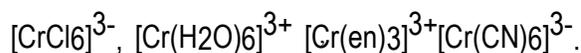
Exercise for Practice

1. An aqueous solution of titanium chloride shows zero magnetic moment. Write down its formula assuming it to be an octahedral complex in aqueous solution.

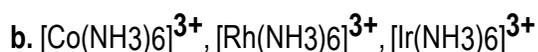
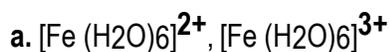
2. Calculate CFSE for the following complexes-



3. Give correct order for the energy gap between two sets of d orbitals in the following complexes-

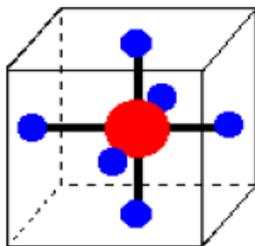


4. Give correct order for energy gap between two sets of d levels in the following complexes –

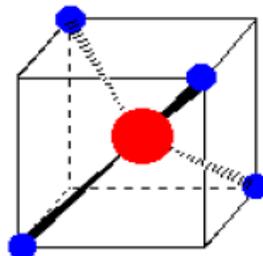


Tetrahedral Complexes

d-Orbital splitting for tetrahedral coordination. A cube, an octahedron, and a tetrahedron are related geometrically. Octahedral coordination results when ligands are placed in the centers of cube faces. Tetrahedral coordination results when ligands are placed on alternate corners of a cube.



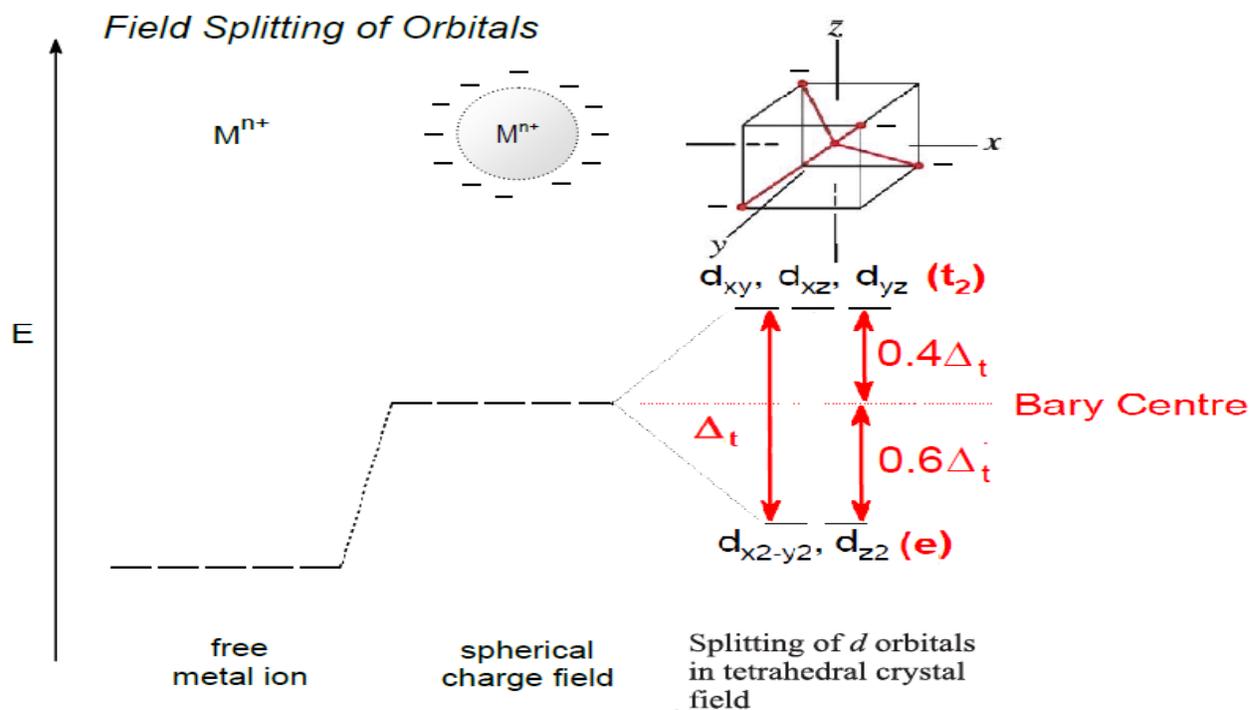
Octahedral complex in a cube.
Ligands are on the centers of the cube faces.



Tetrahedral complex in a cube.
Ligands are on alternate corners of the cube.

In a tetrahedral complex, there are four ligands attached to the central metal. These ligands do not point directly any of the d-orbitals of the metal but more closer to t_{2g} (d_{xy} , d_{yz} , d_{zx}) than e_g orbitals and therefore get repelled more than e_g orbitals. It can simply be stated that the d orbital splitting diagram in tetrahedral complexes is just inverse of octahedral complexes.

The splitting of energy levels in a tetrahedral field is less compare to an octahedral field of ligands due to the poor orbital overlap between the metal and the ligand orbitals. Tetrahedral complexes are high spin complexes as the energy gap between two sets of orbitals is roughly half of octahedral complexes



(Note that the orbitals are labelled t_2 and e , not t_{2g} and e_g ; g refers to a geometry, such as octahedral, that has a center of symmetry. The tetrahedral geometry has no center of symmetry)

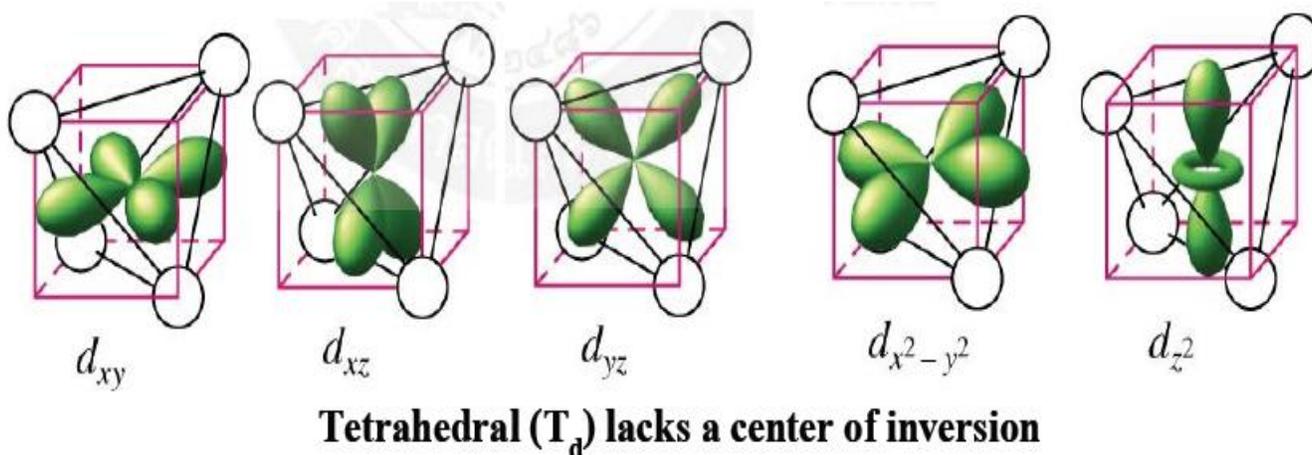


Figure 3. Splitting of *d*-orbitals in Tetrahedral Field

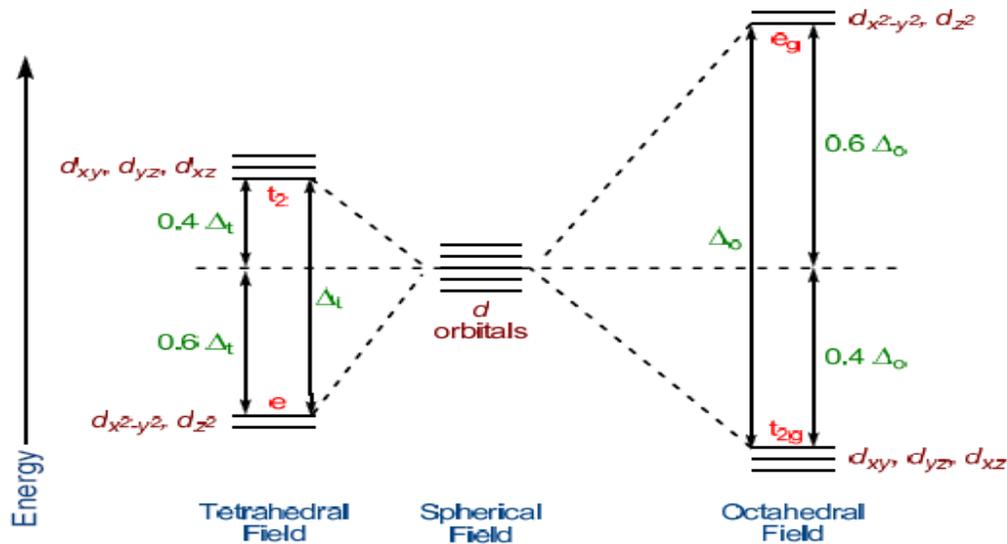
Table1: Tetrahedral crystal field stabilization energies (CFSE) for dⁿ configurations;

Tetrahedral splitting is seldom large enough to result in pairing of the electrons.
As a result, low-spin tetrahedral complexes are not common.
A rare example is $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3[\text{NO}]$

d^1	$e^1 t_2^0$	$0.6 \Delta_t$
d^2	$e^2 t_2^0$	$1.2 \Delta_t$
d^3	$e^2 t_2^1$	$0.8 \Delta_t$
d^4	$e^2 t_2^2$	$0.4 \Delta_t$
d^5	$e^2 t_2^3$	$0.0 \Delta_t$
d^6	$e^3 t_2^3$	$0.6 \Delta_t$
d^7	$e^4 t_2^3$	$1.2 \Delta_t$
d^8	$e^4 t_2^4$	$0.8 \Delta_t$
d^9	$e^4 t_2^5$	$0.4 \Delta_t$
d^{10}	$e^4 t_2^6$	$0.0 \Delta_t$

Octahedral vs Tetrahedral

The crystal field splitting in the tetrahedral field is intrinsically smaller than in the octahedral field. For most purposes the relationship may be represented as $\Delta_t = 4/9 \Delta_o$


Figure 4. Comparison of Splitting of d-orbitals in Octahedral and Tetrahedral Field

Problem

1. Should tetrahedral geometry be favored in $[\text{MnO}_4]^-$ and $[\text{MnO}_4]^{3-}$?

It will be favored because their electronic configurations are $e^0t_2^0$ and $e^2t_2^0$ respectively. There is no asymmetrical filling of electrons in these configurations.

Exercise

1. Out of the following configurations, which configurations are regular for tetrahedral geometry?

$e^2 t_2^3$, $e^2 t_2^2$, $e^4 t_2^4$, $e^2 t_2^1$ and $e^4 t_2^5$

2. Calculate CFSE for the following complexes-

$[\text{FeCl}_4]^-$, $[\text{FeO}_4]^{2-}$, $[\text{NiCl}_4]^{2-}$, $[\text{MnO}_4]^-$, $[\text{CrO}_4]^{2-}$, $[\text{MnO}_4]^{2-}$, $[\text{CrO}_4]^{3-}$, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$,

$[\text{MnO}_4]^{3-}$, $[\text{VCl}_4]^-$, $[\text{MnCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$, $[\text{ZnCl}_4]^{2-}$.

Tetragonal distortion of Octahedral Complexes (Jahn Teller Distortion)

The removal of degeneracy of the d-orbitals in a crystal field offers greater stability through crystal field stabilization energy. Sometimes further removal of degeneracy of the d-orbitals can also provide additional stability. Certain electron configurations with asymmetrical filling of degenerate d-orbitals of a metal ion result in unequal repulsion with incoming ligands. This facilitates such distortion in perfectly symmetric geometries. Practically, distortion in the regular octahedral geometry is observed when e_g orbitals which point directly at ligands, are asymmetrically filled. The t_{2g} orbitals do not point directly at ligands, asymmetrical filling of electrons in them does not give any observable distortion. Thus high spin $d^4(t_{2g}^3 e_g^1)$, low spin $d^7(t_{2g}^6 e_g^1)$ and $d^9(t_{2g}^6 e_g^3)$ configurations result in Jahn Teller distortion as e_g orbitals are asymmetrically filled. Among e_g orbitals, the electron in d_{z^2} experiences repulsion from two ligands but that in $d_{x^2-y^2}$ experiences repulsion from four ligands. Therefore, the electron tends to be present in d_{z^2} . Since the electron lies in d_{z^2} orbital the ligand approaching towards it, will be more repelled as compared to vacant $d_{x^2-y^2}$ orbital. Consequently, two of the bond lengths along Z-axis will be longer than the rest four. This is known as **tetragonal elongation or Z-out distortion**. On the other hand, if the electron is placed in $d_{x^2-y^2}$ orbital, reverse would occur and bond lengths along z axis are shorter than the rest four. This would result in **tetragonal compression or Z-in type of distortion**.

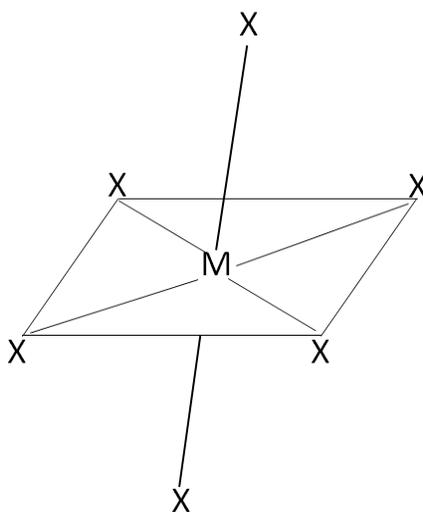


Figure 4. Tetragonal elongation or Z-out distortion

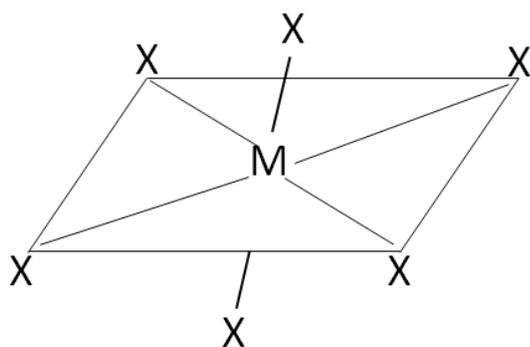


Figure 5. Tetragonal compression or Z-in distortion

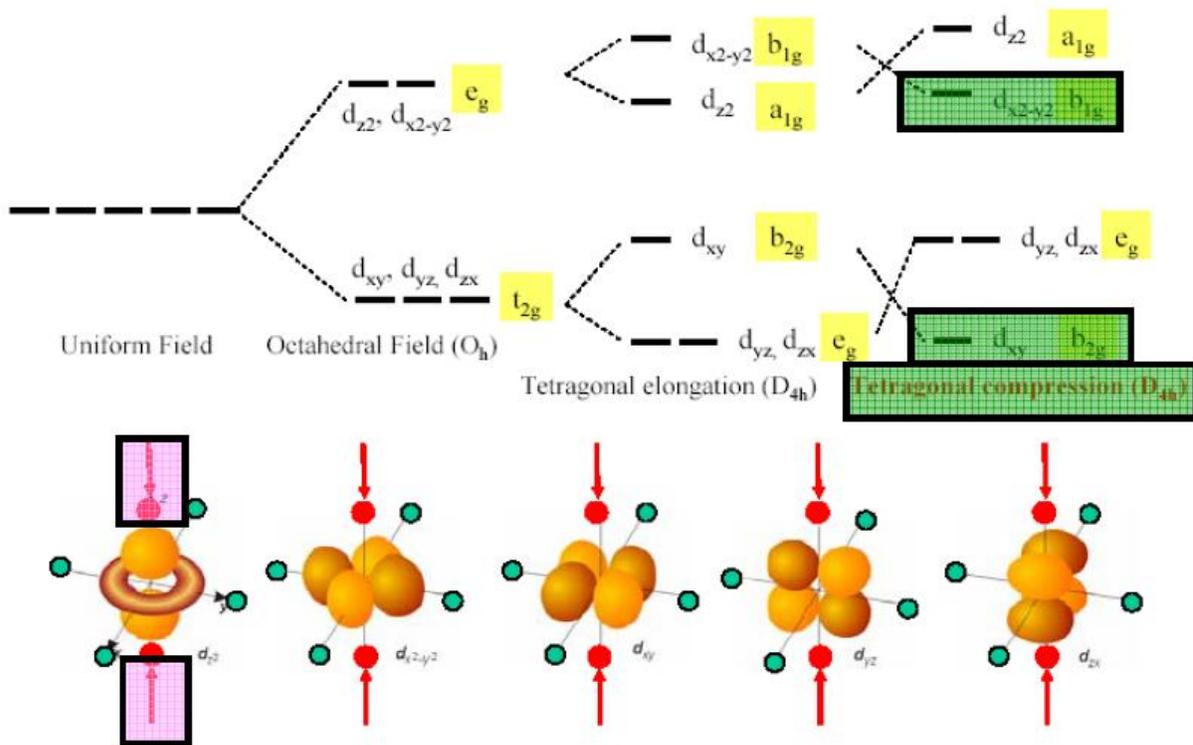


Figure 5. Tetragonal distortion

Square Planar Complexes

d-Orbital Splitting in Square Planar Coordination.

Square planar coordination can be imagined to be formed 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.

Thus, 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 d_{z^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 $d_{x^2-y^2}$ 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.

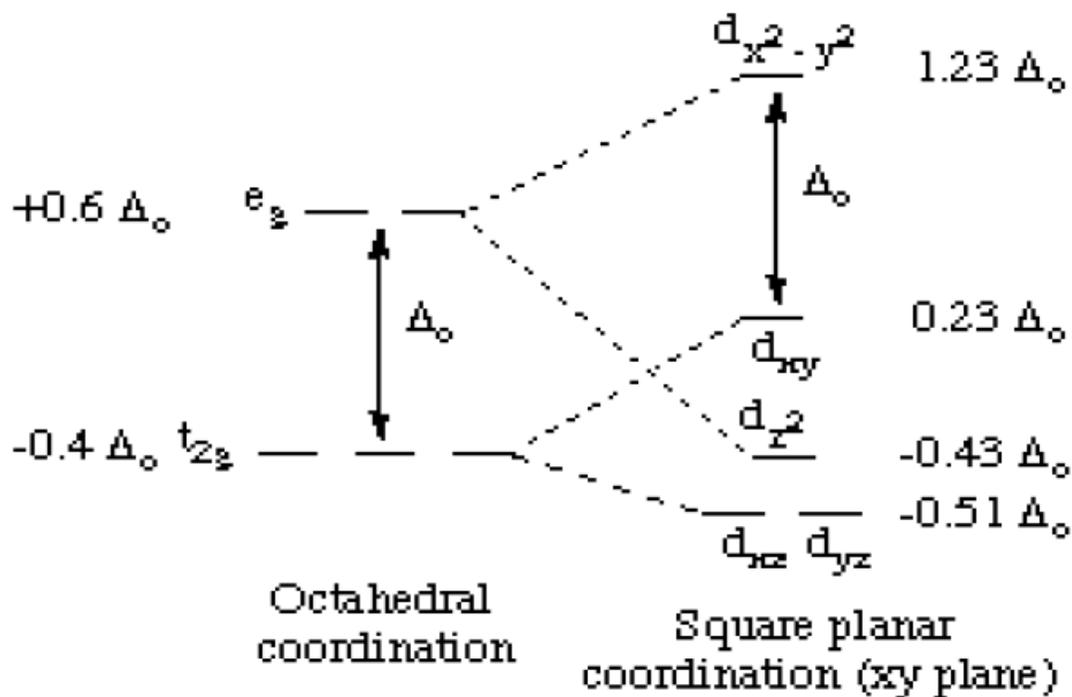


Figure 3. *Splitting of d-orbitals in Square Planar field.*

Problems

1. Predict the possibility of Jahn Teller distortion of Fe^{2+} ion in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

$\text{Fe}(\text{II})$ ion with electronic distribution as $t_{2g}^4 e_g^2$ showing asymmetrical filling of t_{2g} but symmetrical filling of electrons in e_g orbitals will not show any distortion in the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

2. The complex $[\text{Fe}(\text{CN})_6]^{4-}$ is easily formed but $[\text{Ni}(\text{CN})_6]^{4-}$ is not formed, instead $[\text{Ni}(\text{CN})_4]^{2-}$ is formed.

The complex $[\text{Fe}(\text{CN})_6]^{4-}$ with CN^- as strong field ligand, will have $t_{2g}^6 e_g^0$ electronic distribution. Ligand can approach easily along z direction as there will be no repulsion in z direction due to vacant e_g orbitals. However, in case of Ni (II) ion with $t_{2g}^6 e_g^2$ configuration, CN^- being strong field ligand causes pairing of electrons in d_{z^2} orbital and $d_{x^2-y^2}$ orbital becomes vacant. This happens because the electrons would feel repulsion from four ligands if these are in $d_{x^2-y^2}$ orbital and would feel repulsion from two ligands if these are in d_{z^2} orbital. Therefore, electrons prefer to be in the d_{z^2} orbital and ligand entry along this direction is not favored. As a result, **$[\text{Ni}(\text{CN})_4]^{2-}$ is formed instead of $[\text{Ni}(\text{CN})_6]^{2-}$.**

Exercise

1. Draw d-orbitals splitting patterns with filling of electrons in the appropriate d orbitals in the following complexes
 - (a). d^7 , octahedral low spin and high spin
 - (b). d^7 , tetrahedral
 - (c). d^8 , square planar
 - (d). d^9 , octahedral with tetragonal distortion
2. Calculate in units of Δ_0 , the difference in CFSE between complexes (a) and (b).
3. Which of the following complexes would undergo Jahn Teller distortion-
 - (a). $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{CN})_6]^{4-}$
 - (b). $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - (c). $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

4. With Cl^- as weak field ligand, Ni(II) forms tetrahedral complex $[\text{NiCl}_4]^{2-}$ but Pd(II) and Pt(II) belonging to the same group form square planar complexes $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ respectively, explain.