Chem 309: Coordination Compounds (Part II)

I- The Valence Bond Theory (VBT):

In the thirties of the past century, Linus Pauling elaborated the valence bond theory, which has given important impetus to advances in coordination chemistry. Today, this theory is primarily of historical interest since it has been superceded by more advanced propositions. Yet the main advantage of Pauling's theory in its simplified version remains its high illustrative value, which makes it an ideal introduction to complex compounds.

According to the **VBT**, every ligand is a *donor of electrons*. Its electron pairs are transformed to the *vacant orbitals of the central metal ion*. When the ligand donate its pairs of electron to the vacant orbitals of the central metal ion (or atom), the vacant orbitals are *oriented to be equivalent* and to form symmetrical complex structure. For octahedral complex, the vacant orbitals are oriented toward the vertices of the octahedron, but for tetrahedral complex they are directed toward the vertices of the tetrahedron, and if the complex is a planner square, the vacant orbitals are oriented toward the corners of the square. The orientation of these vacant orbitals are occurred by means of the *hybridization of the orbitals* according to the following scheme:

Hybridization type $\left\{ \begin{array}{rl} d^2sp^3 \text{ or } sp^3d^2 & \text{---- octahedron} \\ sp^3 & \text{---- tetrahedron} \\ dsp^2 & \text{---- square} \end{array} \right\}$ symmetry of the coordination polyhedron

According to the concept of donor-acceptor bonding, VBT introduced the so-called ***inner-*** and ***outer-***complexes.

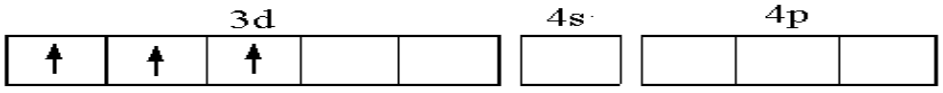
i- Inner-orbital complexes:

In the inner-orbital complexes, the electron pairs of the ligand occupy the *vacant inner orbitals* of the complexing ion; that are of the lower energy. Thus, inner-orbital complexes may be of the **spin– free** (*high spin*) or of the **spin–paired** (*low spin*), which they differ in the magnetic properties. The spin–free (high spin) complexes are *paramagnetic*, whereas the spin–paired (low spin) complexes are *diamagnetic*. ((The magnet attracts the paramagnetic substances, whereas it repels the diamagnetic ones)).

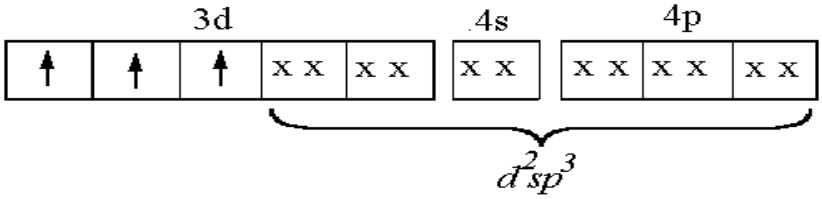
Examples:

(a) $\mathbf{[Cr(NH_3)_6]^{3+}}$ is a representative example of the inner-orbital complexes of the spin – free (high spin) type:

(At.N. of Cr = 24) and, the electron configuration of the Cr^{3+} ,(d^3) is:



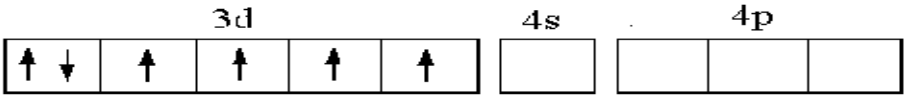
Indeed, the number of empty energy boxes at the electron sublevels *3d*, *4s*, and *4p* in the bond diagram corresponds exactly to what is needed to form an octahedral complex (*hybridization of the d^2sp^3 type*). Since the *number of lone-pair electrons does not change* in Cr^{3+} during complex formation, such a complex ($[Cr(NH_3)_6]^{3+}$) is referred to as spin-free or high-spin:



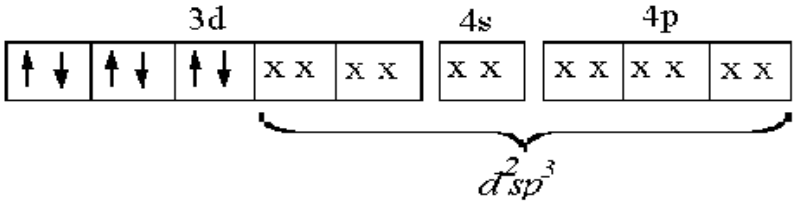
(Whereas the arrows in the energy boxes represent electrons of the central metal ion, the crosses represent the electrons of the donor atoms of nitrogen).

(b) **$[Co(NH_3)_6]^{3+}$** is a representative example of the outer-orbital complexes of the spin – paired (low spin) type:

(At.N. of Co = 27), and the electron configuration of the Co^{3+} ,(d^6) is:



For octahedral (d^2sp^3) distribution of six ligands (Co^{3+} coordinates with six nitrogen atoms of the ammonia molecules) to occur in the complex $[Co(NH_3)_6]^{3+}$, it is necessary to *empty* two energy boxes at the *3d* sublevel of the Co^{3+} ion. This can be achieved in two ways: (1) by "urging" two electrons from the 3*d* sublevel to move up to energetically higher-lying orbitals, such as 4*d* or 5*s*, or (2) by *pairing electrons* at the 3*d* sublevel. The second alternative is energetically more favorable.

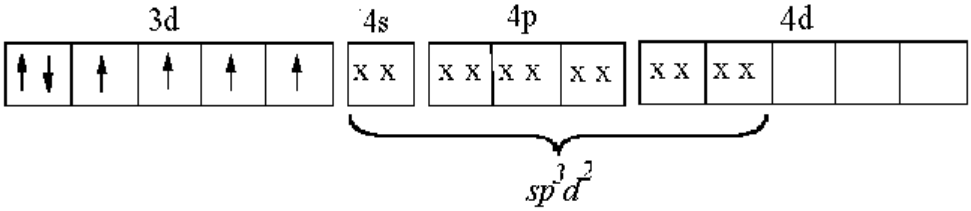


So the electrons coming from the donor will occupy the three vacant orbitals (of 4*s* and 4*p* sublevels) and two *vacated* orbitals of the 3*d* sublevel. Hence, the *number of lone-pair electrons changes* in Co^{3+} during complex formation, such a complex ($[Co(NH_3)_6]^{3+}$) is referred to as spin-paired or low-spin.

ii- Outer-orbital complexes:

In the outer-orbital complexes, the electron pairs of the ligand occupy the *vacant outer orbitals* of the complexing ion; that are of the lower energy. Thus, outer-orbital complexes are, *as a rule*, spin – free, high spin, that is no change of the lone pair electrons in the inner-orbitals of Co^{3+} beside no vacation of electrons are occurred, and in turn they are *paramagnetic*.

The outer-orbital complexes are simplified by **$[CoF_6]^{3-}$** complex. So according to the **VBT**, its structure may be represented schematically as follows:



Limitations of the VBT:

Even after the concepts of the outer- and inner-orbital complexes have been introduced, the VBT could not explain many of the aspects having to

do with their structures and properties. (1) The VBT fails to account for the absorption spectra of complex compounds because it does not take into account the possible occurrence of excited states, and (2) The VBT concerned only with the formation of σ–bonding complexes.

II- The Crystal Field Theory (CFT):

The crystal field theory (**CFT**) was formulated in 1929 by Hans Bethe, and since the fifties it has been used in coordination chemistry as one of the theories giving an insight into some structural features of complex compounds, more specifically the origin of their absorption spectra.

Unlike the VBT, the crystal field theory ignores the concepts of orbital hybridization and donor – acceptor bonding.

It deals with the spatial distribution of the ***d*** (or ***f***) orbitals of the central ion and takes into account the electrostatic repulsion of these electron-carrying orbitals from the ligands.

Ligands are treated as *negative point charges* or *dipoles* so distributed in space that the energy of mutual repulsion of these charges is *minimal*. This condition is met if the ligands are located at the *vertices* of the octahedron (when the coordination number of the central ion is 6) or at those of the tetrahedron (when the coordination number is 4).

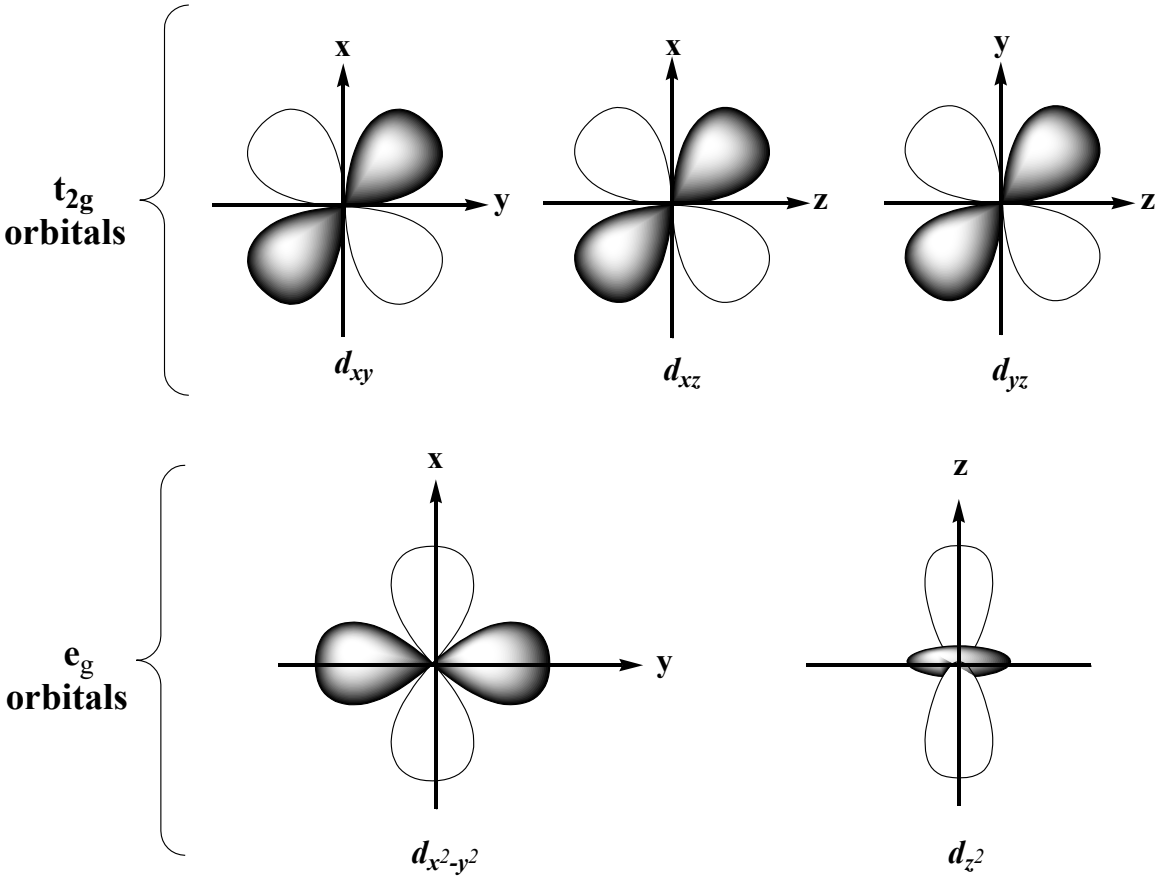
The CFT is based on the principle of taking into account the *electrostatic repulsion* of the electrons of the ligand and central ion. So that, it is assumed that the orbitals of the central ion in a complex are repulsed from the point charges of the ligand and, therefore, tend to occupy such a position in space that their interaction is minimal. This is quit opposite to the VBT which it implied that complexing takes place when the orbitals of the ligand and

central metal ion are directed toward each other and overlap forming σ–bonds. (N.B, Covalent forces are not taken into consideration).

According to the CFT, the "free" ion – that is, the ion in the ground state – of the transition metal, such as the first element of a long period, has its 3***d*** electrons arranged at random at the five available ***d*** orbitals (d_{xy} , d_{xz} , d_{yz} , d_{z^2} , $d_{x^2-y^2}$) (of course, Hund's rule and Pauli's principle are complied with). In this case, none of the *d* orbitals is preferable, all of them being equivalent from the energy standpoint. Such orbitals are known as ***degenerate***.

The electrons coming from the ligands are located, as posited by the CFT, at the vertices of the tetrahedron or octahedron (sometimes square) in accordance with the minimal electrostatic interaction principle. In this case, the electrons of the central metal ion tend to occupy those orbitals that are the farthest from the portions of the sphere where the charge of the ligands is concentrated. That is, not all of the ***d*** orbitals are equivalent: ***removal of degeneracy***.

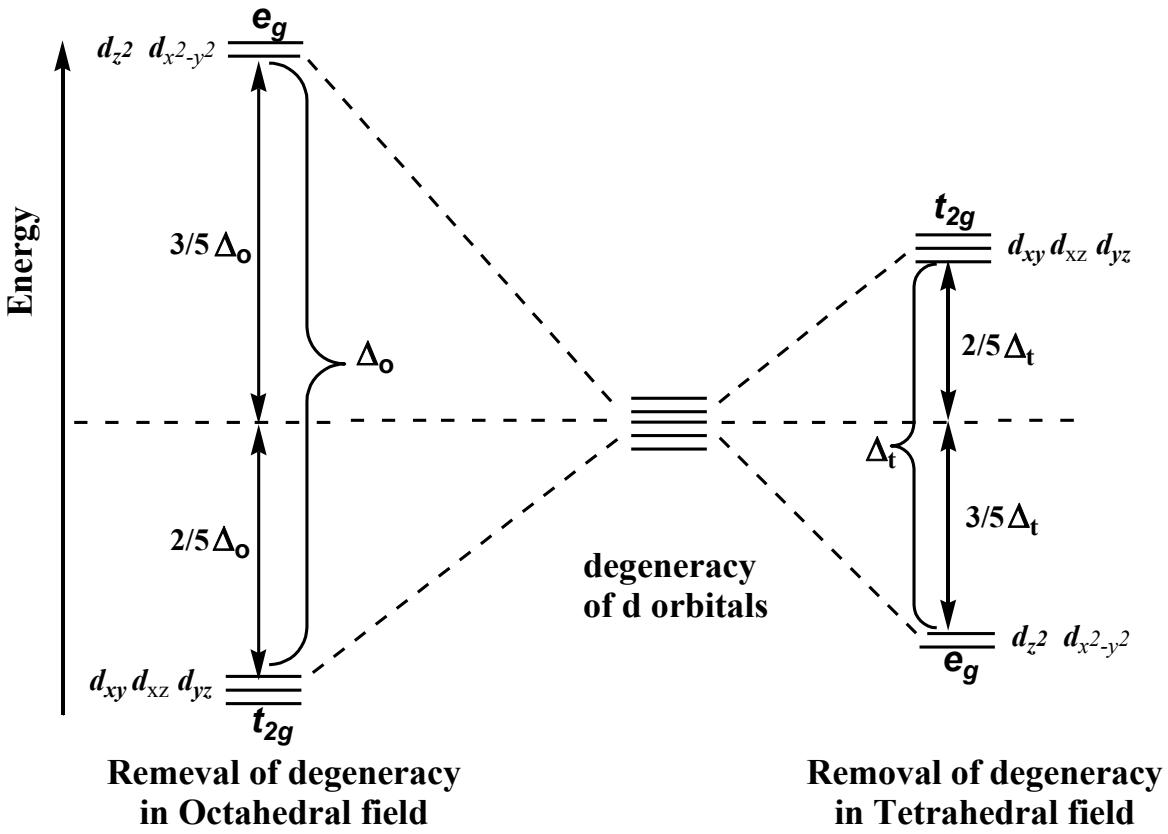
It is assumed that the $d_{x^2-y^2}$ and d_{z^2} orbitals of the metal ion coincide in direction with the axes of the octahedron whose vertices accommodate the ligands. It is then become evident that the electron clouds corresponding to the d_{xy} , d_{xz} ,and d_{yz} orbitals will find themselves between the axes of the octahedron and, therefore, their electrostatic repulsion from the ligands will be much weaker than that of the electron clouds at $d_{x^2-y^2}$ and d_{z^2} orbitals because the latter are directed straight toward the ligands.



_d_ Orbitals

The opposite is true as regards a tetrahedral complex. In this case, coinciding in direction toward the ligands are the axes of the d_{xy} , d_{xz} ,and d_{yz} orbitals, and in the weakest interaction with the ligands are the electrons that are at the $d_{x^2-y^2}$ and d_{z^2} orbitals. According to the CFT, it is these two orbitals that should preferably be occupied by electrons.

Thus, the *d* orbitals of the central metal ion in the octahedral and tetrahedral field of the ligands are *not equivalent energetically*. This means that degeneracy is removed from these orbitals, which can be shown schematically as follows:



(Δ_0 and Δ_t are the energy of splitting for octahedral and tetrahedral complexes respectively)

The three energetically favorable *d* orbitals of the metal ion in the octahedral complex are designated t_{2g}, and the two energetically unfavorable once are e_g orbitals. Quite the opposite, in the tetrahedral complex, energetically mare favorable are the two e_g orbitals, while the three t_{2g} orbitals have a higher energy and, consequently, are not favorable for filling with electrons.

The difference in the energies of the e_g and t_{2g} orbitals is denoted by Δ and is called splitting. In the octahedral complex (splitting Δ_0), the energy

level e_g for each electron is 3/5 Δ_0 higher, and the t_{2g} level is 2/5 Δ_0 lower, than the ground level of the degenerate unsplit orbitals.

In the tetrahedral complex the reverse is true: the t_{2g} level for each electron is 2/5 Δ_t higher, and the e_g level is 3/5 Δ_t lower, than the ground level of the degenerate unsplit orbitals.

Note that, when all the five ***d*** orbitals the octahedral or the tetrahedral complex are completely filled with electrons, the total energy of the system; either octahedral or tetrahedral complex, equals to *zero*. Also, the energy center of gravity of the system remains the same, when compared to that of the degenerate state, i.e.:

For octahedral:

10 electrons fill the *d* orbitals; **4** electrons in the e_g level and **6** electrons in the t_{2g} level. *So that*:

$$e_g^4 \Longrightarrow 3/5\ \Delta_0 \times 4 = 12/5\ \Delta_0$$

$$t_{2g}^6 \Longrightarrow 2/5\ \Delta_0 \times 6 = 12/5\ \Delta_0$$

$$\text{The energy of the system} = 12/5\ \Delta_0 + (-12/5\ \Delta_0) = 0$$

For tetrahedral:

10 electrons fill the *d* orbitals; **4** electrons in the e_g level and **6** electrons in the t_{2g} level. *So that*:

$$t_{2g}^6 \Longrightarrow 2/5\ \Delta_t \times 6 = 12/5\ \Delta_t$$

$$e_g^4 \Longrightarrow 3/5\ \Delta_t \times 4 = 12/5\ \Delta_t$$

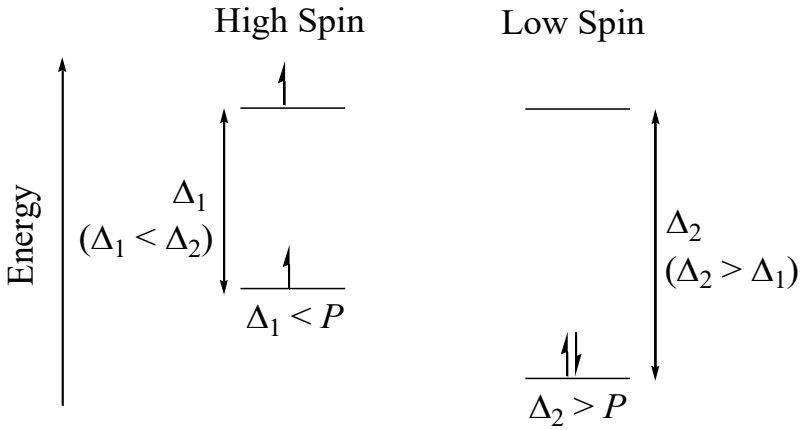
$$\text{The energy of the system} = 12/5\ \Delta_t + (-12/5\ \Delta_t) = 0$$

N.B, d^0 , d^5 , and d^{10} lead to zero result of the energy of splitting.

Two factors control pairing of the electrons or in general the electron distribution through the *d* orbitals. These two factors are (1) the energy of splitting, Δ, (Δ_0 for octahedral or Δ_t for tetrahedral), and (2) the energy expenditures (*P*) involved in (required for) pairing of electrons.

Whereas the energy of splitting is caused mainly by the ligand, the central metal has the main role in responsibility for the energy of expenditure (*P*). So that, the ratio between *P* and Δ depends both on the metal ion species and on the nature of the ligand.

The ratio between *P* and Δ determines the magnetic properties of the formed complexes whether they are of low – spin (spin paired) or of high – spin (spin free).



Dependence of high and low spin configurations on extent of orbital splitting (Δ_1) and electron pairing energy *P* for a simple two-orbital system.

Thus, when $P > \Delta$, the formed complex will be of high – spin (spin free), and when $P < \Delta$, the complex will be of low – spin (spin paired).

That is, the configurations with the maximum possible number of unpaired electrons (when $P > \Delta$) are called the high-spin (spin free) configuration, and those with the minimum number of unpaired spins (when $P < \Delta$) are called the low-spin (spin-paired) configurations.

With respect to the values of the pairing energy P, P is very high for the Mn^{2+} and Fe^{3+} ions with electron configuration d^5 (P = 25 000 to 30 000 cm^{-1}) (At. No. of Mn^{2+} and Fe^{3+} is 23). This is explained by especially high stability of the half-filled d sublevel at d^5 configuration. So that, ions of d^5 configuration form predominantly high-spin (spin free) complexes.

In the case of d^6 configuration (Fe^{2+} and Co^{3+}), P is much lower (17 000 cm^{-1}). (At. No. of Fe^{2+} and Co^{3+} is 24). So that, ions of electron configuration d^6 form predominantly low-spin (spin paired) complexes.

(Since the splitting energy is related with the positions of absorption bands, as it will be discussed later, it is convenient and common practice to use the same unit; the reciprocal centimeter or wave number, abbreviated cm^{-1}, for the unit of frequency in the spectra and the unit of the energy for the orbitals. N.B.: 1 KJ mol^{-1} = 83.7 cm^{-1}).

The amount of splitting Δ_o (the splitting energy in octahedral complexes is taken here for explanation) is greater for complexes of the triple-charged

ions of 3*d*-transition elements (usually 14 000 to 25 000 cm^{-1}), as opposed to the double-charged ions (7 500 to 12 500 cm^{-1}). This is due to the stronger electrostatic repulsion of the orbitals from the ligands in the case of triple-charged central ions than that in the case of the double-charged central ions.

In general, in the series of 3*d*-, 4*d*-, and 5*d*-transition metals, when all other conditions being equal, Δ_o increases from one period to another by 30 to 35 per cent. For example:

$[Co(NH_3)_6]^{3+}$, $\Delta_o = 23\ 000\ cm^{-1}$;
$[Rh(NH_3)_6]^{3+}$, $\Delta_o = 34\ 000\ cm^{-1}$;
$[Ir(NH_3)_6]^{3+}$, $\Delta_o = 41\ 000\ cm^{-1}$.

A possible explanation is that the *d* orbitals grow in special extent and their repulsion from the ligand becomes stronger with increasing atomic number of the element constituting the central ion.

It should be taken into account that in tetrahedral complexes splitting (repulsion of orbitals) is less pronounced in octahedral ones:

$$\Delta_t \approx 4/9\ \Delta_o .$$

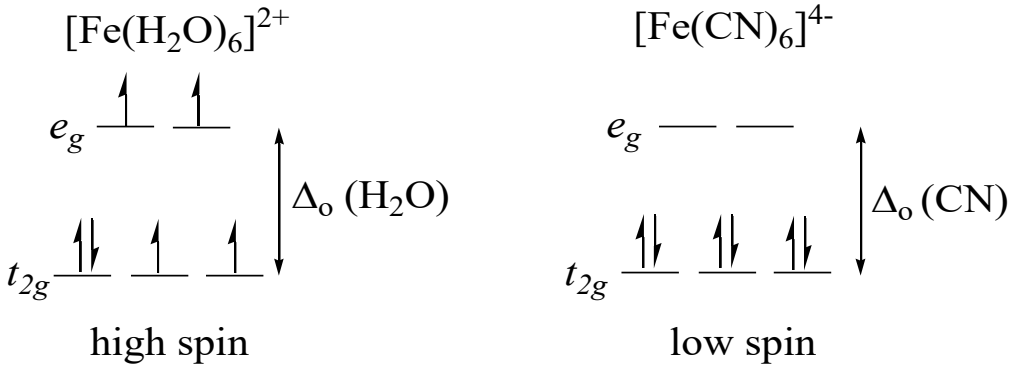
Therefore, the probability of $P < \Delta$ is lower in the tetrahedral complexes, and so tetrahedral complexes are more often of the high-spin (spin free) type, as opposed to the octahedral ones.

The effect of the ligand species on the ratio between P and Δ is also of great importance for a given metal ion.

For instance, in the case of Fe^{2+} (configuration d^6) with pairing energy P = 17 600 cm^{-1}, the splitting energy varies in the following two octahedral complexes:

$[Fe(H_2O)_6]^{2+}$ has Δ_o = 10 400 cm^{-1},
$[Fe(CN)_6]^{4-}$ has Δ_o = 33 000 cm^{-1}.

In the former case, aquo complex, $P > \Delta_o$, so that the complex is of high-spin (spin free). But in the second case, cyano complex, $P < \Delta_o$, so that the complex has the low-spin (spin paired) magnetic property.



Electron configuration for Fe^{2+} in an octahedral complex

In accordance with the amount of splitting in octahedral complexes, ligands form the following so-called ***spectrochemical*** series:

$I^- < Br^- < Cl^- < F^- < C_2O_4^{2-} \leq H_2O < NCS^- <$ *py* ~ $NH_3 <$ *en* < *dipy* < $NO_2^- < CN^- \approx CO$.

This order of increasing Δ_o is usually, but not always, observed for most central complexing ions.

Two groups are distinguished according to the amount of splitting in octahedral complexes: ***weak***- and ***strong***-field ligands.

In the above spectrochemical series, the ligands to the *left* of NH_3 usually form *weak field* (high-spin, or spin free, complexes), and those to *the right* form *strong field* (low-spin, or spin paired, complexes).

Depending on the electron *structure of the central ion* and *the position of the ligand in the spectrochemical series*, complexing results in a certain gain in energy, which is known as the **E**nergy of **S**tabilization by the **C**rystal **F**ield (**ESCF**).

Stabilization by the crystal field (of the ligand) is attained as a result of distribution of the central atom electrons primarily among the lower energy sublevels of a given level split under the effect of the ligand field of a particular symmetry.

The gain in energy (ESCF) is maximum if the t_{2g} sublevel is fully occupied by electrons (strong field, configuration $^6t_{2g}$), while the e_g sublevel remains vacant. (splitting energy = 6 x $2/5\Delta_o = 12/5\Delta_o$)

On the other hand, the ESCF is zero if both t_{2g} and e_g sublevels are filled completely, d^{10}, (for both strong and weak fields). When electrons occupy both t_{2g} and e_g levels, electron configuration $^6t_{2g}\ ^4e_g$ is achieved. So that a compensation of the energy between the two *d*-sublevels (t_{2g} and e_g) and the net result will be zero:

Energy of $^6t_{2g} = 6 \times 2/5\Delta_o = 12/5\Delta_o$

Energy of $^4e_g = 4 \times 3/5\Delta_o = 12/5\Delta_o$

The total energy (ESCF) = $12/5\Delta_o + (-12/5\Delta_o) = 0$

Also, ESCF equals zero for the high spin octahedral complexes (weak field) whose central atom has the electron configuration d^5 (or $^3t_{2g}\ ^2e_g$):

ESCF = $3 \times 2/5\Delta_o + (-2 \times 3/5\Delta_o) = 0$

Examples:

For high-spin (spin free) complexes

The highest value of the ESCF is attained for Cr^{3+}, that is of d^3 electron configuration. Electrons will occupy the t_{2g} sublevel only, i.e. $^3t_{2g}$. So that, ESCF being equals to $3 \times 2/5\Delta_o = 6/5\Delta_o$, which is a very high value.

If the number of electrons at the *d* level of the central ion is increased or decreased, for example in going to high-spin complex with configuration $d^4 = {}^3t_{2g}\ {}^1e_g$, the ESCF will be lowered:

ESCF of ${}^3t_{2g}\ {}^1e_g = 3 \times 2/5\Delta_o - 3/5\Delta_o = 3/5\Delta_o$

For low-spin (spin paired) octahedral complexes:

The ESCF is maximum for the Co^{3+}, that is d^6 electron configuration: ${}^6t_{2g}\ {}^0e_g$.

So, ESCF of ${}^6t_{2g}\ {}^0e_g = 6 \times 2/5\Delta_o = 12/5\Delta_o$.

Any increase or decrease in the number of electrons at the *d* sublevel leads to lower the ESCF;

ESCF of ${}^6t_{2g}\ {}^1e_g$ (Ni^{3+} and Co^{2+}) $= 6 \times 2/5\Delta_o - 3/5\Delta_o = 9/5\Delta_o$

ESCF of ${}^5t_{2g}\ {}^0e_g$ (Mn^{2+} and Fe^{3+}) $= 5 \times 2/5\Delta_o = 10/5\Delta_o$

The value of the ESCF reflects the kinetic inertness or lability of the complexes.

That is $[Fe(CN)_6]^{3-}$ complex; Fe(III) and d^5 electron configuration), has a low value of ESCF. It is a labile complex and so it is very toxic. $[Fe(CN)_6]^{4-}$ complex; Fe(II) and d^6 electron configuration, has a high value of ESCF. It is an inert complex and it is not toxic.

As mentioned earlier that in tetrahedral complexes splitting (repulsion of orbitals) is less than in octahedral ones by:

$$\Delta_t \approx 4/9\ \Delta_o\ .$$

Therefore, the probability of $P < \Delta$ is lower in the tetrahedral complexes, and so tetrahedral complexes are more often of the high-spin (spin free) type, as opposed to the octahedral ones.

Sometimes, both configurations (octahedral and tetrahedral) are equally probable in complex formation:

Consider Co(II*) of* d^7*;*

In a weak field, the octahedral configuration takes the form $^5t_{2g}\ ^2e_g$ and in a tetrahedral configuration, the form is $^4e_g\ ^3t_{2g}$, so that:

$ESCF_{oct.} = 5 \times 2/5\Delta_o - 2 \times 3/5\Delta_o = 4/5\Delta_o$

$ESCF_{tet.} = 4 \times 3/5\Delta_t - 3 \times 2/5\Delta_t = 6/5\Delta_t$

Since $\Delta_t \approx 4/9\ \Delta_o$

So $6/5\Delta_t \approx 6/5 \times 4/9\Delta_o = 8/15\Delta_o \approx 3/5\Delta_o$

i.e., $ESCF_{tet.} \approx ESCF_{oct.}$

For this reason, Co(II) complexes are characterized by equally probable occurrence of octahedral and tetrahedral forms:

$[Co(H_2O)_4]^{2+} \leftrightarrow [Co(H_2O)_6]^{2+}$ in an equilibrium.

Tetragonal Distortion of Octahedral Complexes:

(Jahn-Teller Effect)

The stereochemistry or shape of any complex is determined by the tendency of electron pairs to occupy positions as far away from each other as possible, and also is affected by the presence of non-bonding *d* electrons.

If the *d* electrons are symmetrically arranged with respect to an octahedral ligand field, they will repel all six ligands equally and a completely regular octahedral structure will be formed. The symmetrical arrangements are shown in the following table:

Table : Symmetrical Electronic Arrangements

Elect. Config.	t_{2g} d_{xy}	t_{2g} d_{xz}	t_{2g} d_{yz}	e_g $d_{x^2-y^2}$	e_g d_{z^2}	Nature of Ligand field	Examples
d^0						Strong or weak	$[Ti^{IV}F_6]^{2-}$
d^3	↑	↑	↑			Strong or weak	$[Cr^{III}(H_2O)_6]^{3+}$
d^5	↑	↑	↑	↑	↑	Weak	$[Mn^{II}F_6]^{4-}$
d^6	↑↓	↑↓	↑↓			Strong	$[Fe^{II}(CN)_6]^{4-}$
d^8	↑↓	↑↓	↑↓	↑	↑	Weak	$[Ni^{II}F_6]^{4-}$
d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	Strong or weak	$[Zn^{II}(NH_3)_6]^{2+}$

All other arrangements have an unsymmetrical arrangement of *d* electrons.

Asymmetric filling may arise either in the t_{2g} orbitals or in the e_g orbitals.

The asymmetric filling of the t_{2g} orbitals can be represented by the following table:

Table : Asymmetrical Electronic Arrangements of the t_{2g} Orbitals

Elect. Config.	t_{2g} d_{xy}	d_{xz}	d_{yz}	e_g $d_{x^2-y^2}$	d_{z^2}	Nature of Ligand field	Spin type
d^1	↑					Strong or weak	High spin
d^2	↑	↑				Strong or weak	High spin
d^4	↑↓	↑	↑			Strong	Low spin
d^5	↑↓	↑↓	↑			Strong	Low spin
d^6	↑↓	↑	↑	↑	↑	Weak	High spin
d^7	↑↓	↑↓	↑	↑	↑	Weak	High spin

Since the t_{2g} orbitals point in between the ligand directions, asymmetric filling of these orbitals has little effect on the stereochemistry; the shape of the formed complexes.

Asymmetric filling in the e_g orbitals can be represented by the following table:

Table : Unsymmetrical Electronic Arrangement in the e_g Orbitals

	t_{2g}	e_g	Field	Spin type	Examples
d^4	↑ ↑ ↑	↑	Weak	High spin	Cr^{2+},Mn^{3+}
d^7	↑↓ ↑↓ ↑↓	↑	Strong	Low spin	Co^{2+},Ni^{3+}
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	Strong or weak		Cu^{2+}

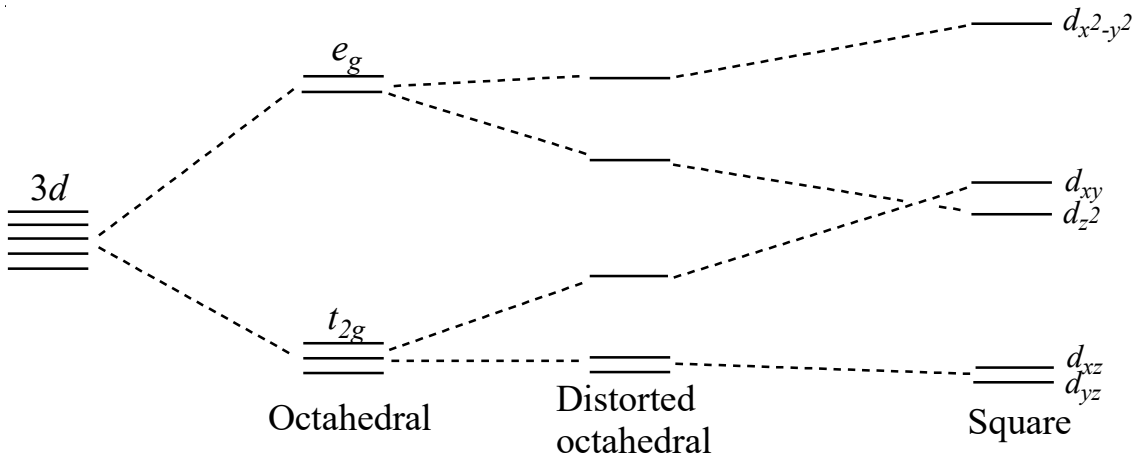
The e_g orbitals, in contrast to t_{2g} orbitals, point directly at the ligands, hence asymmetric filling of these orbitals causes some ligands to be repelled more than others. Accordingly, a significant distortion of the octahedral shape will be resulted.

The two e_g orbitals; $d_{x^2-y^2}$ and d_{z^2}, are normally degenerate, but if the e_g level is asymmetrically filled in an octahedral environment, this degeneracy is destroyed, and the two orbitals are no longer equal in energy.

The $d_{x^2-y^2}$ orbital has four lobes whilst the d_{z^2} orbital has only two lobes pointing at the ligands. To minimize the repulsion with the ligands, the single e_g electron will occupy the d_{z^2} orbital. This is equivalent to splitting the degeneracy of the e_g level so that d_{z^2} is more stable (of relative lower energy), whereas $d_{x^2-y^2}$ is the less stable (of relative higher energy).

Thus the two ligands approaching along the +z and –z directions are subjected to greater repulsion than the four ligands along +x, –x, +y and –y.

The net result of the asymmetrical electronic arrangements in the e_g orbitals is an additional removing of degeneracy from ***d*** orbitals as shown in the following scheme:



Examples:

Ni^{2+} (with configuration d^8) should provide the splitting ${}^6t_{2g}{}^2e_g$ for both the strong and weak fields. However, the formed complexes of strong fields have the square shape, not the octahedral ones. This means that an additional removal of degeneracy from the *d* orbitals must be occurred.

Thus, if the Ni^{2+} ion finds itself in a field formed by a "*strong*" ligand responsible for splitting sufficient to compensate for the energy spent on pairing of the e_g level electrons, the square configuration of the field will be the most favorable. In a square complex (e.g., $[Ni(CN)_4]^{2-}$), the vacant orbital in the Ni^{2+} ion is the $d_{x^2-y^2}$, which is characterized by the strongest electrostatic repulsion from the ligands. All *d* electrons of Ni^{2+} occupy low energy levels to ensure maximum **ESCF**.

Cu^{2+} of d^9 ($^6t_{2g}{}^3e_g$) forms octahedral complexes with the weak fields, e.g. with H_2O it forms the complex $[Cu(H_2O)_6]^{2+}$. With strong ligands Cu^{2+} forms square complexes, e.g. $[Cu(CN)_4]^{2-}$.

The further (additional) removal of degeneracy; i.e. splitting, which is caused as a result of the strong field (ligands) depends mainly on the number of non-bonding electrons of the central metals.

This behavior is called **Jahn-Teller Effect.**

Jahn-Teller effect states that: any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some kind of distortion that will lower its symmetry and splits the degenerate state.

The Jahn-Teller effect is pronounced if the state of degeneracy occurs at the e_g orbitals (rather than t_{2g}) of an octahedral complexes.

In general, the complexes formed by the central metals of 1, 2 or 3 electrons in the e_g state are undergoing affected by the Jahn-Teller effect.

The following scheme shows the first raw transition elements with their ability of the additional splitting (Jahn-Teller effect):

Table : Jahn-Teller effect on the first raw transition elements.

	t_{2g}	e_g	**Spin type**	**Jahn-Teller effect**	**Metals**
d^1	1	0	High or low	No	Ti^{3+}
d^2	2	0	High or low	No	Ti^{2+}, V^{3+}
d^3	3	0	High or low	No	Cr^{3+}
d^4	3	1	High spin	Yes	Mn^{3+}
	4	0	Low spin	No	
d^5	3	2	High spin	Yes	Mn^{2+}, Fe^{3+}
	5	0	Low spin	No	
d^6	4	2	High spin	Yes	Fe^{2+}, Co^{3+}
	6	0	Low spin	No	
d^7	5	2	High spin	Yes	Co^{2+}, Ni^{3+}
	6	1	Low spin	Yes	
d^8	6	2	High or low	Yes	Ni^{2+}
d^9	6	3	High or low	Yes	Cu^{2+}
d^{10}	6	4	High or low	No	Zn^{2+}

Electronic Absorption Spectra

One of the main corollaries of the CFT has to do with the absorption spectra of complex compounds, whose origin finds adequate explanation in this theory.

Consider, by way of example, the origin of the absorption spectrum of the titanium (III) aquo-ion of composition $[Ti(H_2O)_6]^{3+}$.

The electron configuration of the Ti^{3+} ion is $\boldsymbol{d^1}$. According to the CFT, the $\boldsymbol{d^1}$ electron occupies, in the octahedral field, the lowest-energy level ${}^1t_{2g}{}^0e_g$.

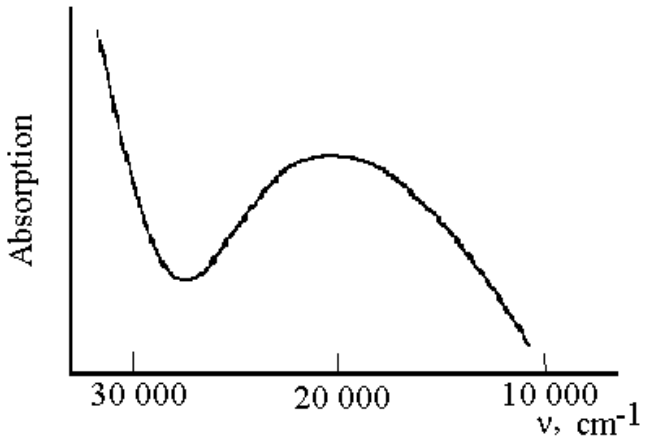
When the aquo-ion $[Ti(H_2O)_6]^{3+}$ is exposed to light, it absorbs energy quanta at a frequency $\boldsymbol{\nu = \Delta_o/h}$ (h is Planck constant).

The absorbed energy is expended in excitation of the electron in the t_{2g} orbital and, as a result, this electron will be transferred to the e_g orbital.

The absorption spectrum reveals a region in which the intensity of the transmitted light is lower than that of the incident one. This spectral region is known as the absorption band.

In the case of $[Ti(H_2O)_6]^{3+}$ the absorption band (as shown in the Fig.) is in the visible region of the spectrum and accounts for the red-violet coloration of the solutions and solid compounds containing the hexaaquo-ion

of Ti(III). The maximum of the absorption band for $[Ti(H_2O)_6]^{3+}$ is at 5000 Å (or 20 000 cm^{-1}).



The visible absorption spectrum of $[Ti(H_2O)_6]$
(d-d transition)

According to Planck's equation, $\boldsymbol{E = hc/\lambda}$, where $\boldsymbol{E}$ is the energy of electron transfer from the ground to excited level; that is, in this case of $[Ti(H_2O)_6]^{3+}$, $\boldsymbol{E = \Delta_o}$.

Knowing the wavelength corresponding to the maximum of the absorption band in the electron spectrum, one can calculate the splitting energy.

The maximum of the absorption band for $[Ti(H_2O)_6]^{3+}$ is 20 000 cm^{-1} , and since there are 83.7 cm^{-1} per kJ, so that the splitting energy (Δ_o) is ~ 240 kJ mol^{-1} (or 57 kcal mol^{-1}),

For $[Ti(H_2O)_6]^{3+}$, this task is rather simple because only one electron (d^1) is excited. In more complex systems where exposure to light causes redistribution of two and more electrons among the energy sublevels, several transitions are possible giving rise to a number of absorption bands, which complicates the spectrum and its interpretation.

In general, it was indicated that by means of the CFT, the energy separations between various states of ***d*** electrons could be calculated from the frequencies of the absorption bands in the visible spectra.

It has been found that by experimental study of the spectra of a large number of complexes containing various metal ions and various ligands, that ligands may be arranged in a series according to their capacity to cause d orbital splittings. That is the so-called ***Spectrochemical Series***.

$I^- < Br^- < Cl^- < F^- < C_2O_4^{2-} \leq H_2O < NCS^- <$ *py* ~ $NH_3 <$ *en* < *dipy* < $NO_2^- < CN^- \approx CO$.

The idea of this series is that the *d* orbital splittings and hence the relative frequencies of visible absorption bands for two complexes containing the same metal ion but different ligands can be predicted from the above series whatever the particular metal ion may be.

Naturally, one cannot expect such a simple and useful rule to be universally applicable. The following qualifications must be remembered in applying it:

1. The series is based upon data for metal ions in common oxidation states. Because the nature of the metal–ligand interaction in an unusually high or unusually low oxidation state of the metal may be in certain respects qualitatively different from that for the metal in a normal oxidation state. This means that ligands may not follow the order of the spectrochemical series when they interact with metal of unusual oxidation states.

2. Even for metal ions in their normal oxidation states inversions of the order of adjacent or nearly adjacent members of the series are sometimes found.

The colors of coordination compounds

One of the most interesting properties of the transition elements is that their complexes are usually colored. With an understanding of *d* orbital splitting, the origin of the color can be explained.

Knowing that, white light covers a range of different colors, from red light of low energy and long wavelength to violet light of high energy and short wavelength.

We perceive the color of transition metal complexes in solution by the color of the transmitted or nonabsorbed light. A solution of the compound absorbs light of one or more colors, and the color or colors not absorbed are perceived by our eyes.

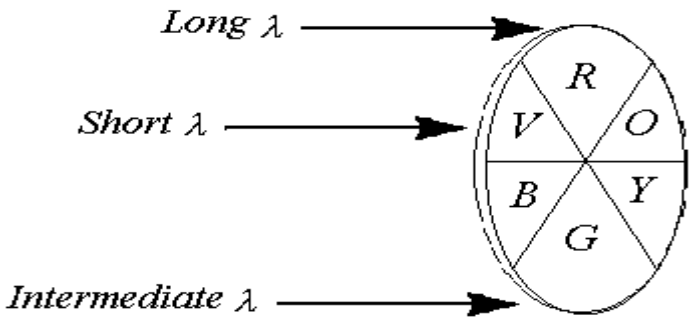
The six components of white light consist of three primary colors (red, yellow, and blue) and three secondary colors (orange, green, and violet) which can be made by mixing the primary colors in pairs as follows:

Red + Yellow $\rightarrow$ Orange

Yellow + Blue $\rightarrow$ Green

Blue + Red $\rightarrow$ Violet

A convenient way to remember this is to arrange the colors circularly on an “artist’s wheel”.



Artist's Wheel

Colors on opposite sides of the wheel are complementary; they add together to give white light.

If a solution absorbs light of one or more colors on one side of the wheel, the remaining colors will be seen. Thus, if the green color is seen, this means one of two things happened. If all but green light is absorbed, only green light is transmitted. Alternatively, if violet, red, and orange were absorbed, then blue, green, and yellow are transmitted, and we will see the middle of color of the three; that is the green color.

Spectrophotometers select photons (which consist white light) of each different frequencies to pass through a solution of the compound to be studied.

If photons of a given frequency are not absorbed, that light is unchanged in its intensity when it emerges from the sample. On the other hand, if photons of some frequency are absorbed, light of that frequency emerges from the sample with a decreased intensity.

By making a plot of the frequency or wavelength of the light against the intensity of the light absorbed at that frequency or wavelength, we obtain an ***absorption spectrum*** of the sample. When there is an absorption of light in a certain frequency range, the plot shows an ***absorption band***, and the variation in intensity of light absorbed with frequency is called a ***spectrum***.

Transition metal complexes can absorb light because photons of the appropriate energy can excite the complex from its ground state to a higher energy or excited state: in the octahedral complexes, as a result of excitation, an electron (or electrons) is transferred from the t_{eg} orbitals to the e_g ones.

The fact that high energy light is transmitted means that low energy light was absorbed.

Referring to the Spectrochemical series; predicting the possible color of a complex based on the nature of the ligands is risky, since the details of the spectroscopy of such complexes are complicated.

However, it is clear that weak field ligands lead to a small splitting, so the complex will absorb relatively low energy photons. Like $[Cu(H_2O)_6]^{2+}$ ion or $[CoF_6]^{3-}$, such complexes ***tend to*** have colors at the blue end of the spectrum.

Conversely, strong field ligands cause a large splitting, and their complexes, like $[Co(CN)_6]^{3-}$, ***tend to*** have colors at the red end of the spectrum.

The following table represents the spectral properties of some cobalt (III) complexes.

Co^{3+} complex	Wavelength of Light absorbed (nm)	Color of light absorbed	Color seen
$[CoF_6]^{3-}$	700	Red	Green
$[Co(H_2O)_6]^{3+}$	600	Orange	Blue
$[Co(NH_3)_5Cl]^{2+}$	535	Yellow	Purple
$[Co(NH_3)_5H_2O]^{3+}$	500	Blue-green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow-orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Tail of absorption band in visible gives pale yellow

The Ligand Field Theory (LFT):

The ligand field theory (LFT) was elaborated by J. H. Van Velck in the thirties and forties of the 20th century.

It incorporates the concepts of the molecular orbital and crystal field theories.

The basic principles of the LFT are as follows:

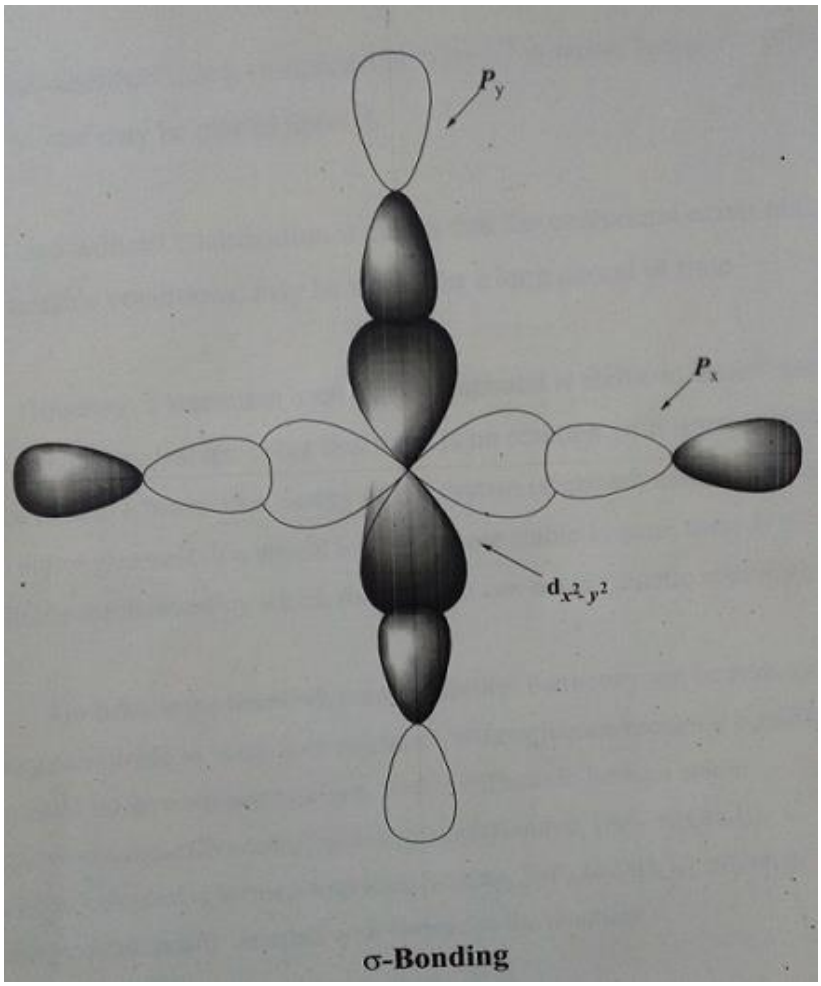
1. Unlike the CFT, the LFT posits that the formation of complex compounds, accompanied by removal of degeneracy from the *d* orbitals of the central ion, involves not only electrostatic forces but, also, primarily, overlapping of the orbitals of the central ion and ligand – that is, covalent interaction.

2. The interaction of two atomic orbitals, those of the central atom and ligand, results in formation of two molecular orbitals. One of them (***bonding***) lies below the interacting atomic orbital with the lower energy. The other (***antibonding***) lies above the other, higher-energy atomic orbital.

3. According to the LFT, only atomic orbitals of *similar symmetry* may interact. For example, the orbital of σ–symmetry belonging to the central ion and ligand may overlap. Those of π–symmetry, also belonging to the central ion and ligand, may overlap, too. If the

atomic orbitals of the central ion lack a partner of appropriate symmetry among those of the ligand, they remain ***nonbonding*** without changing their energy characteristics and becoming involved in bonding.

4. In the LFT, Pauli's principle and Hund's rule remain valid.



Consider now the structure of high- and low-spin complexes of Co(III) in the light of the LFT:

(i) The complex **$[CoF_6]^{3-}$** represents high-spin complexes:

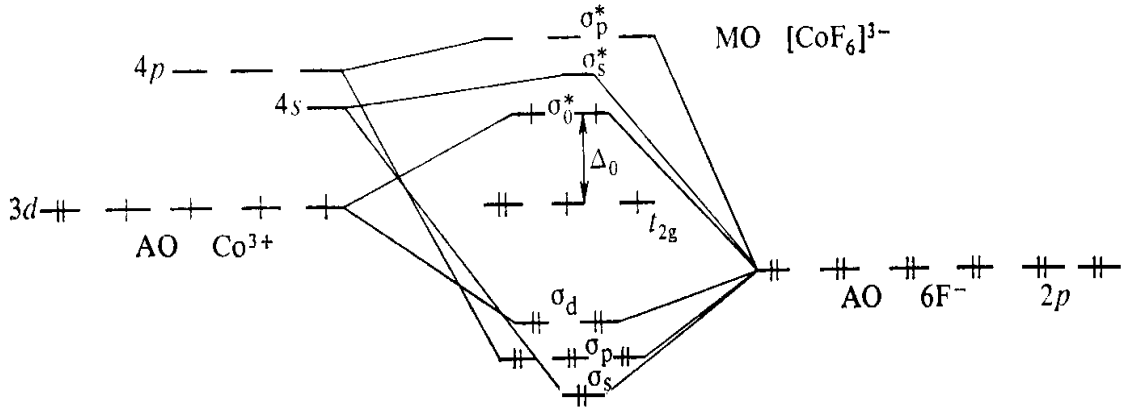
The complex $[CoF_6]^{3-}$ was already discussed in the contexts of the VBT and CFT.

It will be recalled that the F^- ions are on the left-hand side of the spectrochemical series and, as a rule, form a weak field in which high-spin complexes are stable.

Co^{3+} has a d^6 configuration, and, in the weak field of an octahedtral complex, electrons are distributed in accordance with Hund's rule applicable to all of the five 3*d* orbitals of Co^{3+}: $^4t_{2g}{}^2e_g$.

The ligands, or six F^- ions, have unshared electron pairs at an atomic orbital (2*p*) below that of the valence electrons of Co^{3+} (3*d*). In addition to the 3*d* orbital of Co^{3+}, we shall also take into account its vacant 4*s* and 4*p* orbitals. Thus, the interaction involves six *p* orbitals of F^-, accommodating 12 electrons, and nine orbitals of Co^{3+} (3*d*, 4*s*, 4*p*), accommodating a total of six electrons.

The interaction of 15 atomic orbitals must yield 15 *molecular orbitals*, including equal numbers of *bonding* and *antibonding* plus *nonbondging* orbitals.



The bonding molecular orbitals in the complex $[CoF_6]^{3-}$ are formed from the atomic orbitals of the ligand, but along the energy axis they lie below the atomic orbitals of the six F^- ions.

Since the atomic orbitals of the F^- ions have a σ-symmetry, the bonding molecular orbitals based on them result from the overlapping of the atomic σ–orbitals of the F^- ions with those of the Co^{3+} ions. These are $3d_{z2}$, $3d_{x2\text{-}y2}$, and also $4s$, $4p_x$, $4p_y$, and $4p_z$ orbitals.

The resulting six bonding molecular orbitals (one σ_s, three σ_p, and two σ_d) are occupied by the electron pairs of the ligand (six F^- ions).

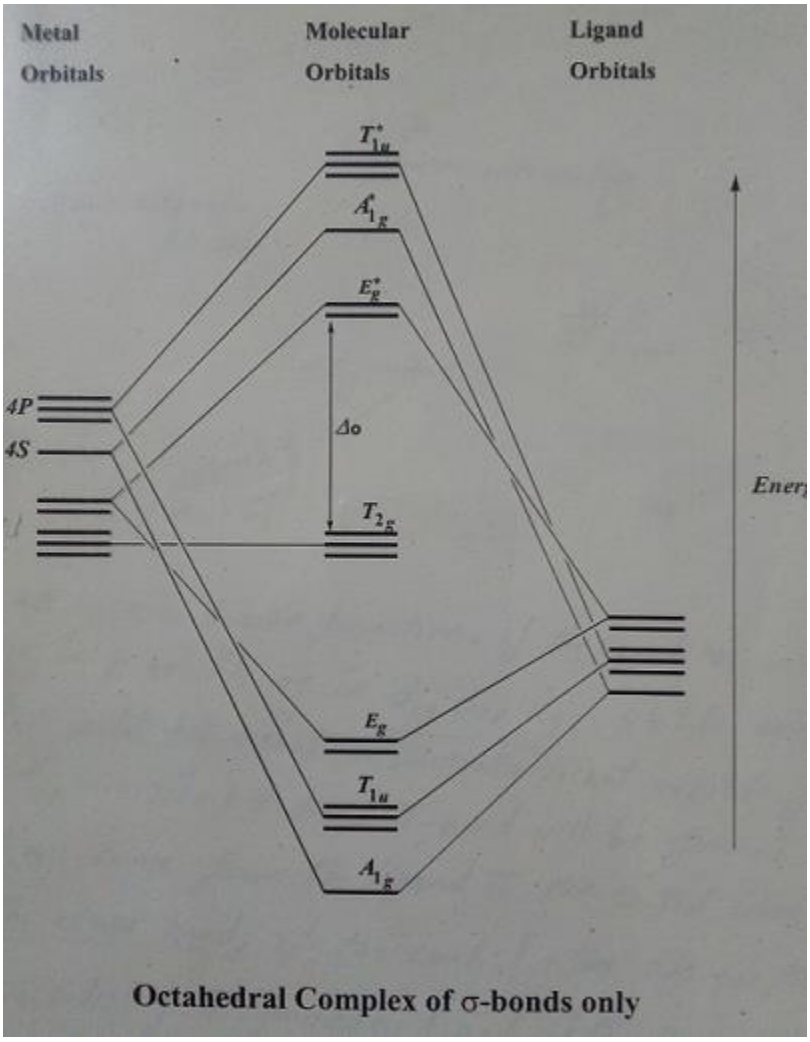
At the same time, six antibonding molecular orbitals, also of σ–symmetry, are formed. They (two lowest-energy degenerate σ^*_d orbitals) accommodate two lone-pair electrons of Co^{3+}.

Four electrons from the atomic 3*d* orbitals of Co^{3+} remain at the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals and are nonbonding. These atomic orbitals are of π–symmetry and do not overlap with those of the ligand.

Note that, the bonding orbitals (there are six of them) lie at an energy level below the atomic orbitals, whereas the antibonding ones (also six) lie above the 3*d* (e_g), 4*s*, and 4*p* orbitals of the Co^{3+} ion, on which they are based.

Just as the CFT, the LFT also takes into account the amount of splitting, for example Δ_o, in an octahedral field, which is essentially the difference between the energies of the e_g and t_{2g} orbitals. Here, the nonbonding molecular orbitals are taken as the t_{2g} level, and the antibonding ones, as the e_g level.

Although the electrons of Co^{3+} have not changed their energy as a result of complexing, the system as a whole has gained energy since the ligand electrons are now at a lower energy level than before the interaction with Co^{3+}.

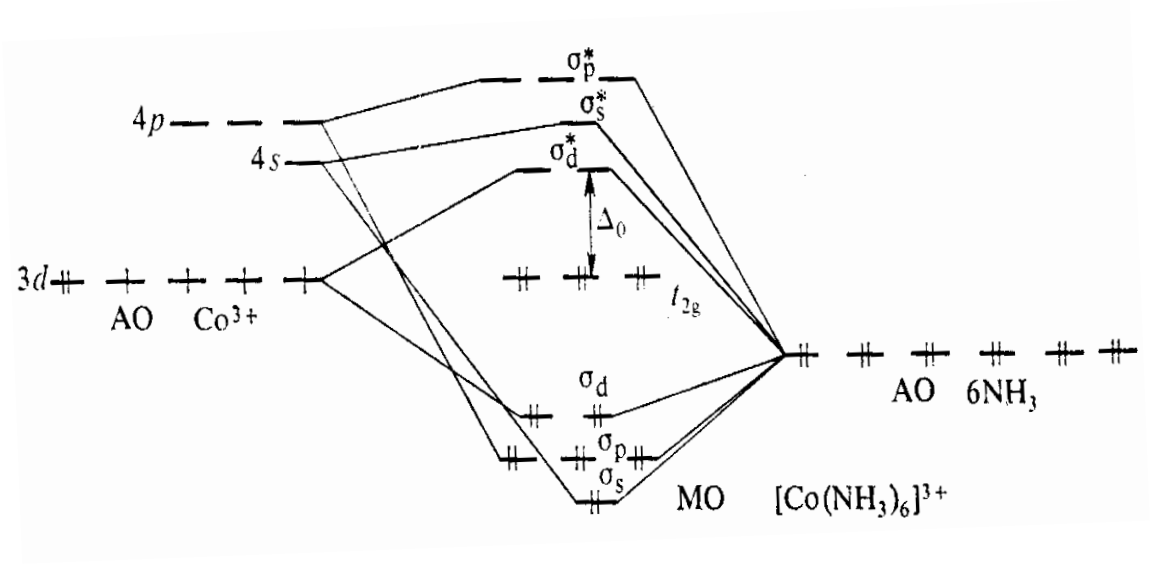


Octahedral Complex of σ-bonds only

(ii) **$[Co(NH_3)_6]^{3+}$** complex may represents the low-spin complexes:

In the low-spin complex $[Co(NH_3)_6]^{3+}$, the gain in energy is greater because all electrons of Co^{3+} are paired and occupy the nonbonding t_{2g} orbitals of π–symmetry, whereas the antibonding orbitals are vacant.

At the same time, all of the 12 electrons of the ligand, involved in complexing, have their energy lower and occupy the bonding σ–orbitals, which ensures a gain in energy for the entire system.



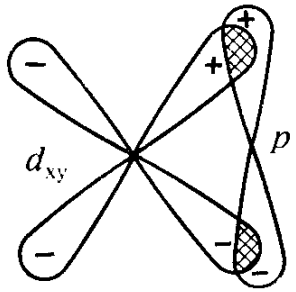
The above structure of Co^{3+} interpreted in terms of the LFT is oversimplified.

If the value of Δ_o had depended on the electrostatic interaction in the complex or only on the strength of the σ–bonds, it would have been possible

to consider the strength of the bond in the complex as being proportional to Δ_o.

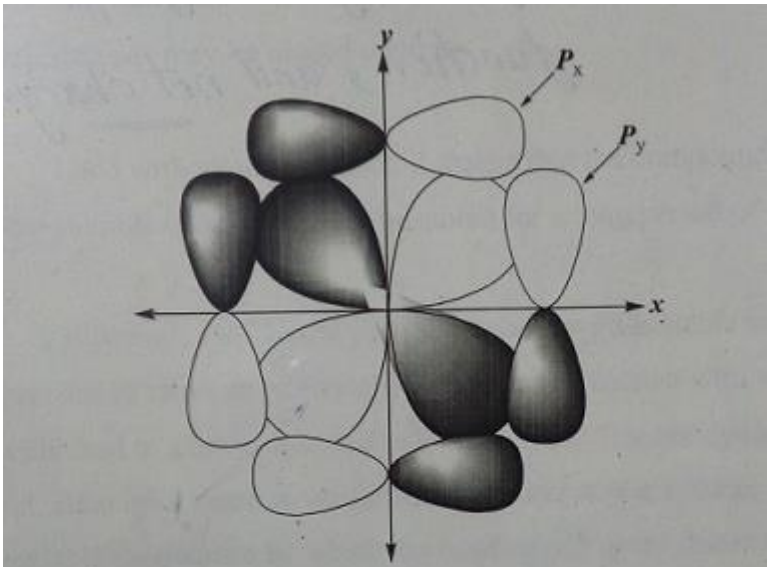
In reality, however, π-interactions almost always go hand in hand with σ–bonding. Note that, in the CFT the π–bonding could not be taken into account, whereas in the LFT this can be done.

For example, let a *p* orbital lie in the *xy* plane at the donor atom. It will then be capable of interacting with the d_{xy} orbital of the central ion, resulting in a π-bond; hence if the *p* orbital of the ligand has unshared electron pair and the d_{xy} orbital of the central ion is vacant or partially occupied by electrons, donor-acceptor π–bonding occurs.



Since ligands are usually more electronegative than the central atom, the lower-lying molecular orbital resulting during such interaction resembles the atomic orbital of the ligand (bonding t_{2g} orbital), while the higher-lying molecular orbital is similar to the atomic orbital of the central ion (antibonding t_{2g} orbital). Electrons tend to occupy the former because filling a low-lying orbital is energetically more productive. The latter molecular

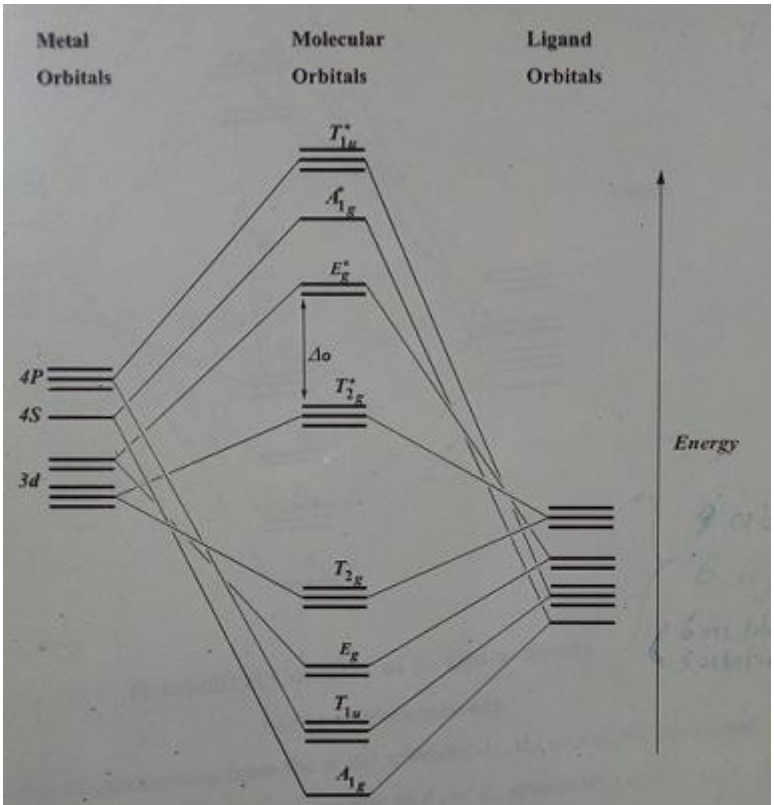
orbital (of the central atom) remains vacant or partially occupied, although, it becomes an antibonding t_{2g} orbital.



π-Bonding

Interaction of a d_{xy} orbital with ligand $P\pi$ orbitals

Such π–bonding ("**donor**" or "**direct**" π–bonding) leads to an increase in the energy of the t_{2g} orbitals of the metal and a decrease in Δ_o. In this case, the t_{2g} orbitals of the central ion cease (stop) to be nonbonding as in complexes having only σ–bonds. Such π–interaction occurs if the ligands are halogen ions, H_2O, alcohols, sulphide ions and so on.



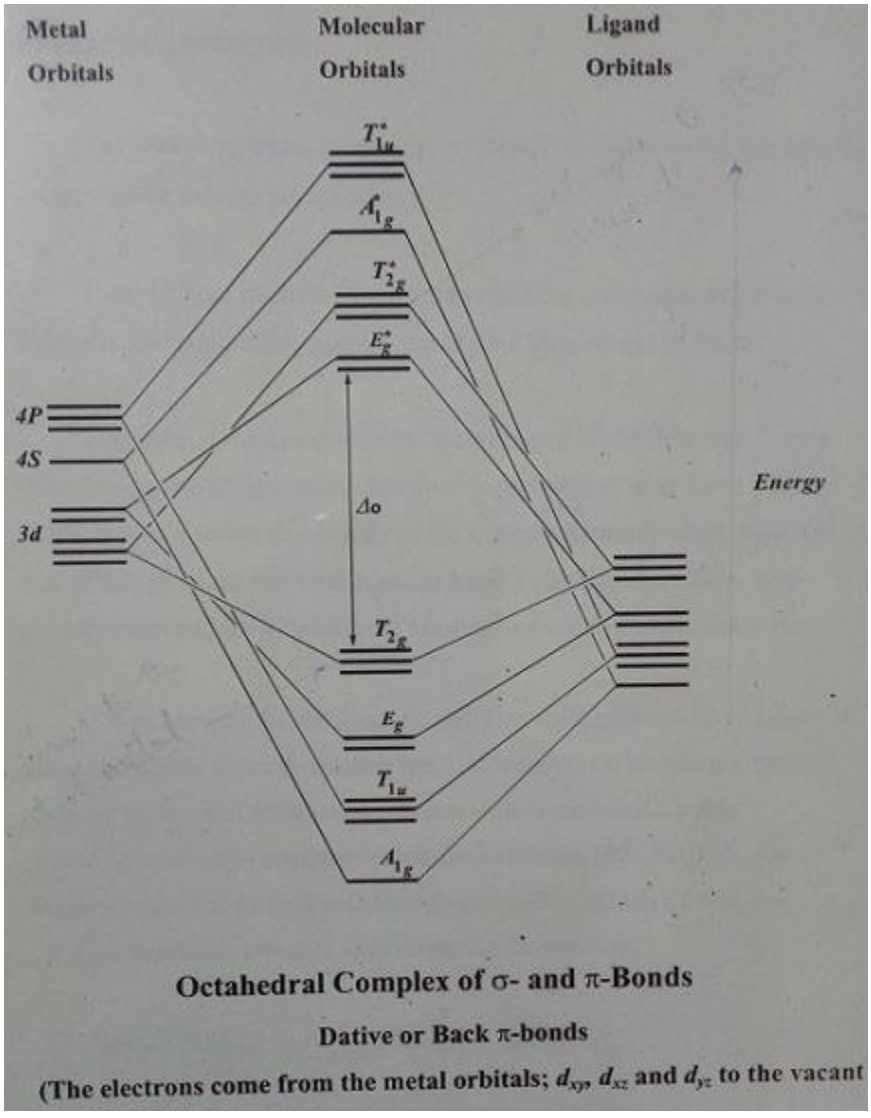
Octahedral Complex of σ- and π-Bonds

Direct π-bonds

(The electrons come from the ligand orbitals of P_π or d_π symmetry to the vacant metal orbitals of similar symmetry; d_{xy}, d_{xz} and d_{yz})

If the vacant orbitals involved in the π–bonding belonging to the ligand while the donor electrons belong to the atomic t_{2g} orbital, the π–bond is referred to as "**backward**" or "**dative**". In this case, the bonding molecular orbital results from the atomic orbital of the metal ion.

The antibonding molecular orbital resembles more closely the atomic orbital of the ligand.



Octahedral Complex of σ- and π-Bonds

Dative or Back π-bonds

(The electrons come from the metal orbitals; d_{xy}, d_{xz} and d_{yz} to the vacant

Dative bonding increases Δ_o because the t_{2g} orbitals of the central ion become involved in bonding and their energy level goes down, as compared to the atomic orbitals or complexes having only σ–bonds.

Dative bonding also increases the positive charge at the central ion, which enhances the contribution of electrostatic forces to complexing as well as strengthens the covalent coordinate bond: the t_{2g} and e_g orbitals become spaced wider apart.

The CO and CN^- ligands are capable of forming dative bonds owing to the vacant antibonding *p* orbitals at the carbon, while the halide anions (Cl^-, Br^-, I^-) can do the same through vacant and rather low-lying *d* orbitals.

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