

# **Crystal Field Theory- I**

**Coordination Chemistry-II**

**Inorganic Chemistry-4**

**Semester IV**

**CEMA-CC-4-10-TH**



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## **References:**

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3. Inorganic Chemistry by J. D. Lee (3<sup>rd</sup> Ed)
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## Crystal Field Theory

One of the most striking characteristics of transition-metal complexes is the wide range of colours they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition metal complexes, including their colours, magnetism, structures, stability, and reactivity. Crystal field theory was proposed by scientists Hans Bethe and van Vleck (1929). The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature and there is no orbital overlap. Even though this assumption is clearly not valid for many complexes, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and geometry of metal complexes.

### **Basic Assumptions**

In Crystal Field Theory, it is assumed that the ions are **simple point charges** (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law of interactions). Thus potential energy  $E$  is:

$$E \propto Q_1Q_2/r \quad (1)$$

With

- $E$  the bond energy between the charges
- $Q_1$  and  $Q_2$  are the charges of the interacting ions and
- $r$  is the distance separating them.

This approach leads to the correct prediction that large cations of low charge, such as  $K^+$  and  $Na^+$ , should form few coordination compounds. For transition metal cations that contain varying numbers of  $d$  electrons in orbitals that are NOT spherically symmetric, however, the situation is quite different. The shape and occupation of these  $d$ -orbitals then becomes important in an accurate description of the bond energy and properties of the transition metal compound.

### **Description of $d$ -Orbitals**

To understand CFT, one must understand the description of the lobes:

$d_{xy}$ : 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 doughnut shape ring that lies on the  $xy$  plane around the other two lobes.

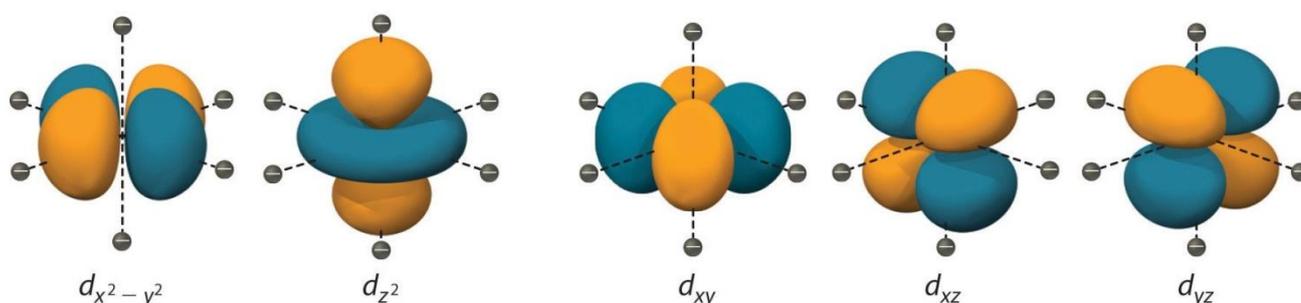


Figure 1: Spatial arrangement of ligands in an octahedral ligand field with respect to the five  $d$ -orbitals.

## d-Orbital Splittings

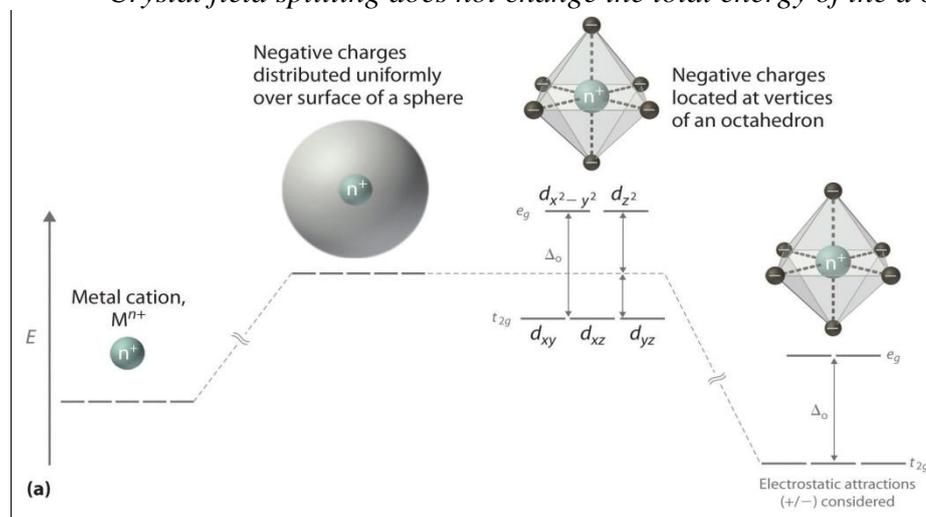
CFT focuses on the interaction of the five  $(n - 1)d$  orbitals with ligands (treated as point charges) arranged in a regular array around a transition metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the  $d$  orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five  $d$  orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the  $d$  orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the  $d$  orbitals (Figure 1). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the  $d$  orbitals, but it does remove their degeneracy: the five  $d$  orbitals split into two groups whose energies depend on their orientations. As shown in Figure 1, the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals point directly at the six negative charges located on the  $x$ ,  $y$ , and  $z$  axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the  $e_g$  orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three  $d$  orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  collectively called the  $t_{2g}$  orbitals) are all oriented at a  $45^\circ$  angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

The difference in energy between the two sets of  $d$  orbitals is called the crystal field splitting energy ( $\Delta$ ), where the subscript  $o$  stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes:  $\Delta$ ) It is important to note that the splitting of the  $d$  orbitals in a crystal field does not change the total energy of the five  $d$  orbitals: the two  $e$  orbitals increase in energy by  $0.6\Delta$ , whereas the three  $t$  orbitals decrease in energy by  $0.4\Delta$ . Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0 \quad (2)$$

*Crystal field splitting does not change the total energy of the  $d$  orbitals.*



**Figure 2:** An octahedral arrangement of six negative charges around a metal ion causes the five  $d$  orbitals to split into two sets with different energies. (a) Distributing a charge of  $-6$  uniformly over a spherical surface surrounding a metal ion causes the energy of all five  $d$  orbitals to increase due to electrostatic repulsions, but the five  $d$  orbitals remain degenerate. Placing a charge of  $-1$  at each vertex of an octahedron causes the  $d$  orbitals to split into two groups with different energies: the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals increase in energy, while the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals decrease in energy.

The average energy of the five  $d$  orbitals is the same as for a spherical distribution of a  $-6$  charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five  $d$  orbitals to decrease in energy but does not affect the splittings of the orbitals.

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 2).

### Tetrahedral Complexes

In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three ( $t_2$ ) consist of the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals. The bottom two (e) consists of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not.

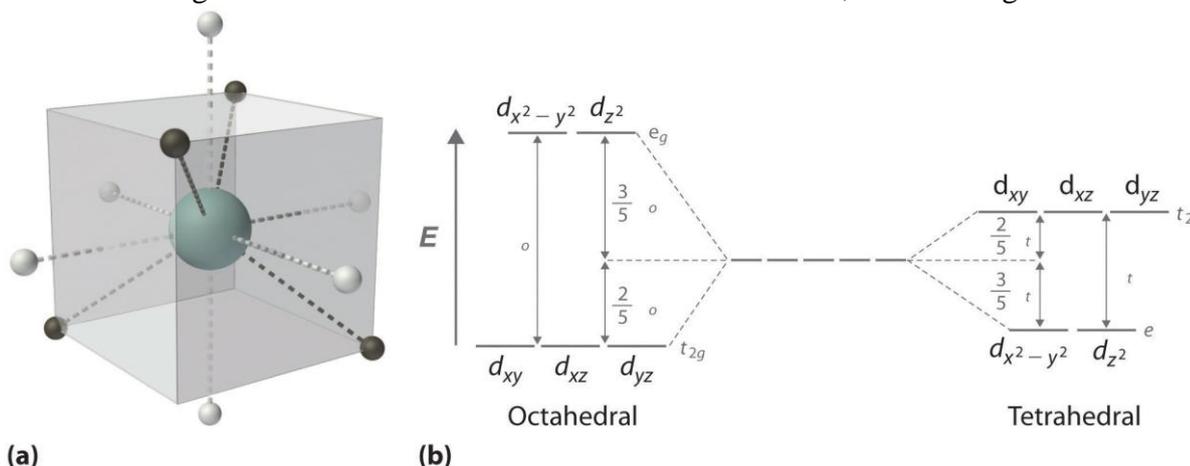


Figure 3: (a) Tetrahedral ligand field surrounding a central transition metal (blue sphere). (b) Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field (left diagram) and the tetrahedral field (right diagram). The difference in the splitting energy is tetrahedral splitting constant ( $\Delta_t$ ), which less than ( $\Delta_o$ ) for the same ligands:

$$\Delta_t = 0.44\Delta_o \quad (3)$$

Consequently, is typically smaller than the spin pairing energy, so tetrahedral complexes are usually **high spin**.

### Square Planar Complexes

In a square planar, there are four ligands as well. However, the difference is that the electrons of the ligands are only attracted to the plane. Any orbital in the xy plane has a higher energy level. There are four different energy levels for the square planar (from the highest energy level to the lowest energy level):  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  and both  $d_{z^2}$  and  $d_{x^2-y^2}$ .

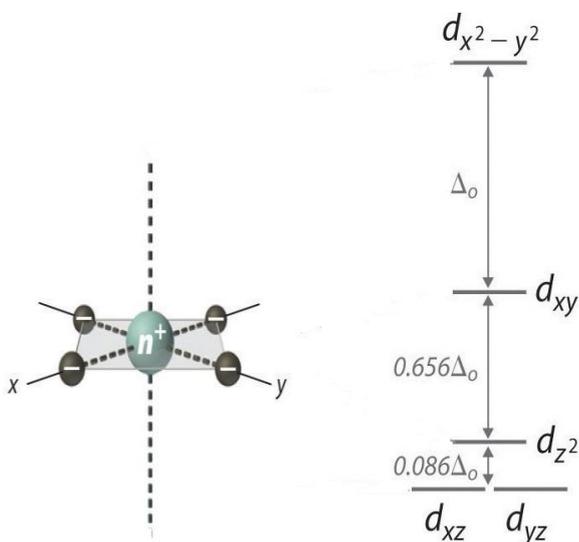


Figure 4: Splitting of the degenerate d-orbitals (without a ligand field) due to a square planar ligand field.

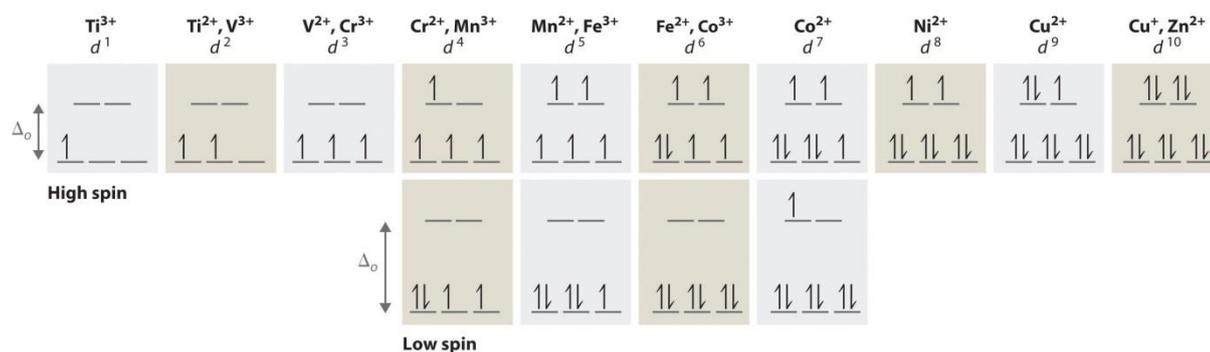
The splitting energy (from highest orbital to lowest orbital) is  $\Delta_{sp}$  and tends to be larger than  $\Delta_o$

$$\Delta_{sp} = 1.74\Delta_o \quad (4)$$

Moreover, is also larger than the pairing energy, so the square planar complexes are usually **low spin** complexes.

## Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 2 to predict electronic structures and some of the properties of transition-metal complexes. We start with the  $\text{Ti}^{3+}$  ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 2, for  $d^1$ – $d^3$  systems—such as  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ , and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , respectively—the electrons successively occupy the three degenerate  $t_{2g}$  orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , for example, by saying that the chromium ion has a  $d^3$  electron configuration or, more concisely,  $\text{Cr}^{3+}$  is a  $d^3$  ion.



**Figure 5:** The possible electron configurations for octahedral  $d^n$  transition-metal complexes ( $n = 1$ – $10$ ). Two different configurations are possible for octahedral complexes of metals with  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  configurations; the magnitude of  $\Delta$  determines which configuration is observed.

When we reach the  $d^4$  configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty  $e_g$  orbitals or one of the singly occupied  $t_{2g}$  orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy ( $P$ ). If  $\Delta$  is less than  $P$ , then the lowest-energy arrangement has the fourth electron in one of the empty  $e_g$  orbitals. Because this arrangement results in four unpaired electrons, it is called a *high-spin configuration*, and a complex with this electron configuration, such as the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion, is called a high-spin complex. Conversely, if  $\Delta$  is greater than  $P$ , then the lowest-energy arrangement has the fourth electron in one of the occupied  $t_{2g}$  orbitals. Because this arrangement results in only two unpaired electrons, it is called a *low-spin configuration*, and a complex with this electron configuration, such as the  $[\text{Mn}(\text{CN})_6]^{3-}$  ion, is called a low-spin complex. Similarly, metal ions with the  $d^5$ ,  $d^6$ , or  $d^7$  electron configurations can be either high spin or low spin, depending on the magnitude of  $\Delta$ . In contrast, only one arrangement of d electrons is possible for metal ions with  $d^8$ – $d^{10}$  electron configurations. For example, the  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion is  $d^8$  with two unpaired electrons, the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion is  $d^9$  with one unpaired electron, and the  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  ion is  $d^{10}$  with no unpaired electrons.

*If  $\Delta$  is less than the spin-pairing energy, a high-spin configuration results. Conversely, if  $\Delta$  is greater, a low-spin configuration forms.*

### Factors That Affect the Magnitude of $\Delta$

The magnitude of  $\Delta$  dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of  $\Delta$  (i.e.,  $\Delta > P$ ) yield a low-spin complex, whereas small values of  $\Delta$  (i.e.,  $\Delta < P$ ) produce a high-spin complex. As we noted, the magnitude of  $\Delta$  depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Here it should be kept in mind that:

$$\Delta \propto \text{wave number}$$

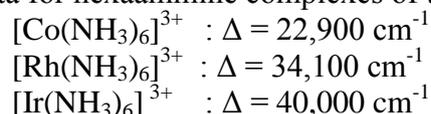
#### Factor 1: Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand

distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of  $\Delta$  increases as the charge on the metal ion increases. Typically,  $\Delta$  for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,  $\Delta = 11,800 \text{ cm}^{-1}$ ; for  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ ,  $\Delta = 17,850 \text{ cm}^{-1}$ .

### Factor 2: Principal Quantum Number of the Metal

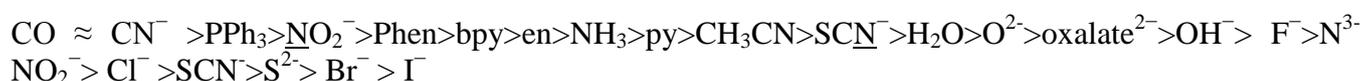
For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of  $\Delta$  increases with increasing principal quantum number:  $\Delta(3d) < \Delta(4d) < \Delta(5d)$ . The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:



The increase in  $\Delta$  with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

### Factor 3: The Nature of the Ligands

Experimentally, it is found that the  $\Delta_o$  observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of  $\Delta_o$  decreases as the size of the donor atom increases. For example,  $\Delta_o$  values for halide complexes generally decrease in the order  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$  because smaller, more localized charges, such as we see for  $\text{F}^-$ , interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as  $\text{NH}_3$ , results in significantly larger  $\Delta_o$  values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as  $\text{F}^-$ . The experimentally observed order of the crystal field splitting energies produced by different ligands is called the *spectrochemical series*, shown here in order of decreasing  $\Delta_o$ :



The values of  $\Delta$  illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

*The largest  $\Delta$  splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Therefore

- i. Number of d-electrons  $\propto 1/\Delta$
- ii. Oxidation State  $\propto \Delta$
- iii. Principle quantum no.  $\propto \Delta$

### Crystal Field Stabilization Energy (Newer concept)

A consequence of Crystal Field Theory is that the distribution of electrons in the d orbitals may lead to net stabilization (decrease in energy) of some complexes depending on the specific ligand field geometry and metal d-electron configurations. It is a simple matter to calculate this stabilization since all that is needed is the electron configuration and knowledge of the splitting patterns.

### Definition: Crystal Field Stabilization Energy

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

$$\text{CFSE} = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}} \quad (5)$$

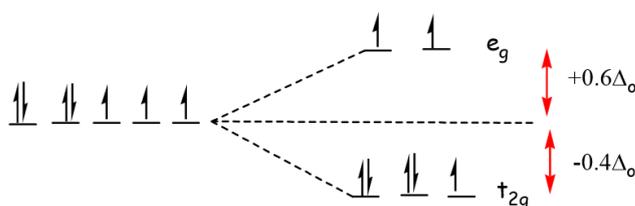
The CSFE will depend on multiple factors including:

- Geometry (which changes the d-orbital splitting patterns)
- Number of d-electrons
- Spin Pairing Energy
- Ligand character (via Spectrochemical Series)

For an octahedral complex, an electron in the more stable  $t_{2g}$  subset is treated as contributing  $-2/5\Delta_o$  whereas an electron in the higher energy  $e_g$  subset contributes to a destabilization of  $+3/5\Delta_o$ . The final answer is then expressed as a multiple of the crystal field splitting parameter  $\Delta_o$ . If any electrons are paired within a single orbital, then the term  $P$  is used to represent the spin pairing energy.

Example 1: CFSE for a high Spin  $d^7$  complex

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field is  $= E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$

The energy of the octahedral ligand field is  $= E_{\text{ligand field}} = (5 \times -2/5\Delta_o) + (2 \times 3/5\Delta_o) + 2P = -4/5\Delta_o + 2P$

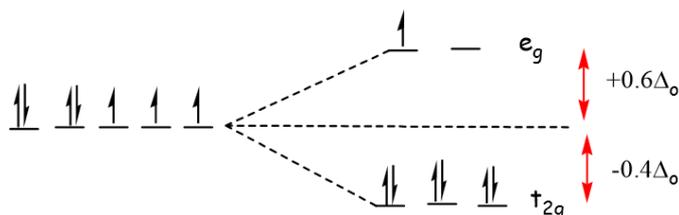
So via Equation 5, the CFSE is

$$CFSE = E_{\text{ligand field}} - E_{\text{isotropic field}} = (-4/5\Delta_o + 2P) - 2P = -4/5\Delta_o$$

Notice that the Spin pairing Energy falls out in this case (and will when calculating the CFSE of high spin complexes) since the number of paired electrons in the ligand field is the same as that in isotropic field of the free metal ion.

Example 2: CFSE for a Low Spin complex

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field is the same as calculated for the high spin configuration in Example 1:

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field is  $E_{\text{ligand field}} = (6 \times -2/5\Delta_o) + (1 \times 3/5\Delta_o) + 3P = -9/5\Delta_o + 3P$

So via Equation 1, the CFSE is

$$CFSE = E_{\text{ligand field}} - E_{\text{isotropic field}} = (-9/5\Delta_o + 3P) - 2P = -9/5\Delta_o + P$$

Adding in the pairing energy since it will require extra energy to pair up one extra group of electrons. This appears more and more stable configuration than the high spin  $d^7$  configuration in Example, but we have then to take into consideration the Pairing energy  $P$  to know definitely, which varies between  $200\text{--}400 \text{ kJ mol}^{-1}$  depending on the metal.

### Octahedral Stabilization/Preference

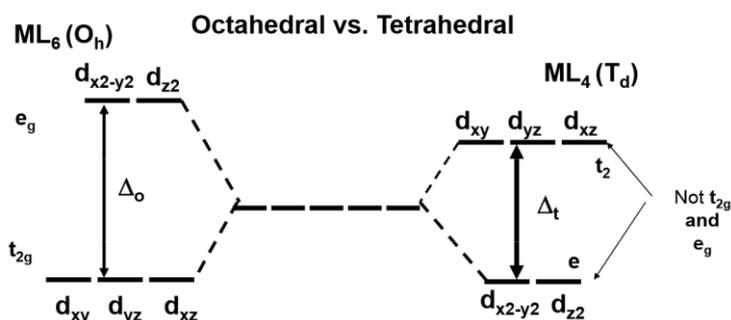
Similar CFSE values can be constructed for non-octahedral ligand field geometries once the knowledge of the d-orbital splitting is known and the electron configuration within those orbitals known. These energies can then be contrasted to the octahedral CFSE to calculate a thermodynamic preference (Enthalpy-wise) for a metal-ligand combination to favour the octahedral geometry. This is quantified via a Octahedral Site Stabilization/Preference Energy defined below.

#### Definition: Octahedral Site Stabilization/Preference Energies

The Octahedral Site Stabilization/ Preference Energy (OSSE/OSPE) is defined as the difference of CFSE energies for a non-octahedral (mainly Tetrahedral) complex and the octahedral complex. For comparing the preference of forming an octahedral ligand field vs. a tetrahedral ligand field, the OSSE/OSPE is thus:

$$OSSE/OSPE = CFSE(oct) - CFSE(tet) \quad (6)$$

The OSPE quantifies the preference of a complex to exhibit an octahedral geometry vs. a tetrahedral geometry.



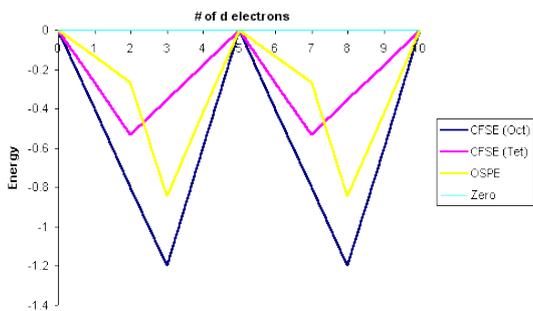
Note: the conversion between and used for these calculations is:

$$\Delta_t \approx 4/9 \Delta_o \quad (7)$$

which is applicable for comparing octahedral and tetrahedral complexes that involve same ligands only.

For example,

Total d-electrons	CFSE(Octahedral)	CFSE(Tetrahedral)	OSSE (for high spin complexes)
$d^1$	$-2/5 \Delta_o$	$-3/5 \Delta_t$	$-6/45 \Delta_o$
$d^2$	$-4/5 \Delta_o$	$-6/5 \Delta_t$	$-12/45 \Delta_o$
$d^3$	$-6/5 \Delta_o$	$-4/5 \Delta_t$	$-38/45 \Delta_o$



**Figure 6:** Crystal Field Stabilization Energies for both octahedral fields (CFSEoct) and tetrahedral fields (CFSEtet). Octahedral Site Preference Energies (OSPE) are in yellow. This is for high spin complexes.

From a simple inspection of Figure 6, the following observations can be made:

- The OSSE is small in  $d^1$ ,  $d^2$ ,  $d^5$ ,  $d^6$ , and  $d^7$  complexes and other factors influence the stability of the complexes including steric factors
- The OSSE is large in  $d^3$  and  $d^8$  complexes which strongly favour octahedral geometries