Crystal Field Splitting in an Octahedral Field

$e_g$ - The higher energy set of orbitals ($d_{z^2}$ and $d_{x^2-y^2}$)

$t_{2g}$ - The lower energy set of orbitals ($d_{xy}$, $d_{yz}$ and $d_{xz}$)

$\Delta_o$ or 10 $Dq$ - The energy separation between the two levels

The $e_g$ orbitals are repelled by an amount of $0.6 \Delta_o$.
The $t_{2g}$ orbitals to be stabilized to the extent of $0.4 \Delta_o$. 
The higher energy set of orbitals ($d_{xz}$, $d_{yz}$, $d_{xy}$) is labeled as $t_2$ and the lower energy set ($d_{z^2}$ and $d_{x^2-y^2}$) is labeled as $e$.

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 $\Delta_t = \frac{4}{9} \Delta_o$.
Octahedral Vs Tetrahedral

- $d_{xy}$, $d_{yz}$, $d_{xz}$
- $e$
- $d_{x^2-y^2}$, $d_{z^2}$
- $t_2$
- $t_{2g}$
- $e_g$
- $0.4 \Delta_t$
- $0.6 \Delta_t$
- $0.6 \Delta_o$
- $0.4 \Delta_o$
- $0.4 \Delta_t$
- $0.6 \Delta_o$
- Tetrahedral Field
- Spherical Field
- Octahedral Field
The single electron in the \( t_{2g} \) orbitals absorbs energy in the form of light and gets excited to the \( e_g \) orbitals. In case of \([\text{Ti(H}_2\text{O)}_6]^{3+}\), this corresponds to 520 nm (20,300 cm\(^{-1}\)).
Factors Affecting the Magnitude of $\Delta$

1. Higher oxidation states of the metal atom correspond to larger $\Delta$.
   $\Delta = 10,200 \text{ cm}^{-1}$ for $[\text{Co}^{II}(\text{NH}_3)_6]^{2+}$ and $22,870 \text{ cm}^{-1}$ for $[\text{Co}^{III}(\text{NH}_3)_6]^{3+}$
   $\Delta = 32,200 \text{ cm}^{-1}$ for $[\text{Fe}^{II}(\text{CN})_6]^{4-}$ and $35,000 \text{ cm}^{-1}$ for $[\text{Fe}^{III}(\text{CN})_6]^{3-}$

2. In groups, heavier analogues have larger $\Delta$.
   For hexaammine complexes $[\text{M}^{III}(\text{NH}_3)_6]^{3+}$:
   $\Delta = 22,870 \text{ cm}^{-1}$ (Co)
   $34,100 \text{ cm}^{-1}$ (Rh)
   $41,200 \text{ cm}^{-1}$ (Ir)

3. Geometry of the metal coordination unit affects $\Delta$ greatly.
   Tetrahedral complexes $\text{ML}_4$ have smaller $\Delta$ than octahedral ones $\text{ML}_6$:
   $\Delta = 10,200 \text{ cm}^{-1}$ for $[\text{Co}^{II}(\text{NH}_3)_6]^{2+}$
   $5,900 \text{ cm}^{-1}$ for $[\text{Co}^{II}(\text{NH}_3)_4]^{2+}$

   For $[\text{Co}^{III}\text{L}_6]$, $\Delta$ in cm$^{-1}$: 13,100 (F$^-$); 20,760 (H$_2$O); 22,870 (NH$_3$)
   For $[\text{Cr}^{III}\text{L}_6]$, $\Delta$ in cm$^{-1}$: 15,060 (F$^-$); 17,400 (H$_2$O); 26,600 (CN$^-$)
Spectrochemical Series

An arrangement of ligands according to their ability to increase $\Delta$ for a given metal center

Weak – I\textsuperscript{-}, Br\textsuperscript{-}, SCN\textsuperscript{-}, Cl\textsuperscript{-}, N\textsubscript{3}\textsuperscript{-}, F\textsuperscript{-}, H\textsubscript{2}NC(O)NH\textsubscript{2}, OH\textsuperscript{-}, ox\textsuperscript{2-}, O\textsuperscript{2-}, H\textsubscript{2}O, NCS\textsuperscript{-}, py, NH\textsubscript{3}, en, bpy, phen, NO\textsubscript{2}\textsuperscript{-}, CH\textsubscript{3}\textsuperscript{-}, C\textsubscript{6}H\textsubscript{5}\textsuperscript{-}, CN\textsuperscript{-}, CO – Strong
Distribution of Electrons in an Octahedral Complex

Net energy decrease is called crystal field stabilization energy (CFSE)

For $d^1$, $\text{CFSE} = 1 \times 0.4 = 0.4 \Delta_o$

For $d^2$, $\text{CFSE} = 2 \times 0.4 = 0.8 \Delta_o$

For $d^3$, $\text{CFSE} = 3 \times 0.4 = 1.2 \Delta_o$
**Distribution of Electrons in an Octahedral Complex**

There are two possibilities for metal ions having $d^4$-$d^7$ electronic configuration. Depending on the nature of the ligands and the metal they could be **high-spin** or **low-spin** complexes.

For the $d^4$ system, $\text{CFSE} =$

For high-spin, $(3 \times 0.4) - (1 \times 0.6) = 0.6 \Delta_o$ and

for low-spin, $4 \times 0.4 = 1.6 \Delta_o$
Distribution of Electrons in an Octahedral Complex

For $d^8$, CFSE = $(6 \times 0.4) - (2 \times 0.6) = 1.2 \Delta_o$

For $d^9$, CFSE = $(6 \times 0.4) - (3 \times 0.6) = 0.6 \Delta_o$

For $d^{10}$, CFSE = $(6 \times 0.4) - (4 \times 0.6) = 0.0 \Delta_o$

In all electronic configurations involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons.

Metal ions with 4 – 7 electrons in the $d$ orbital can exist as high-spin or low-spin complexes. Weaker ligands tend to give high-spin complexes, whereas stronger ligands tend to give low-spin complexes.
## Distribution of Electrons in an Octahedral Complex

<table>
<thead>
<tr>
<th></th>
<th>High-spin</th>
<th>Low-spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1$</td>
<td>$t_{2g}^1e_g^0$</td>
<td>$0.4 \Delta_o$</td>
</tr>
<tr>
<td>$d^2$</td>
<td>$t_{2g}^2e_g^0$</td>
<td>$0.8 \Delta_o$</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$t_{2g}^3e_g^0$</td>
<td>$1.2 \Delta_o$</td>
</tr>
<tr>
<td>$d^4$</td>
<td>$t_{2g}^3e_g^1$</td>
<td>$0.6 \Delta_o$</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$t_{2g}^3e_g^2$</td>
<td>$0.0 \Delta_o$</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$t_{2g}^4e_g^2$</td>
<td>$0.4 \Delta_o$</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$t_{2g}^5e_g^2$</td>
<td>$0.8 \Delta_o$</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$t_{2g}^6e_g^2$</td>
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<td>$t_{2g}^6e_g^3$</td>
<td>$0.6 \Delta_o$</td>
</tr>
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<td>$d^{10}$</td>
<td>$t_{2g}^6e_g^4$</td>
<td>$0.0 \Delta_o$</td>
</tr>
</tbody>
</table>
**Distribution of Electrons in a Tetrahedral Complex**

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 \( \text{Cr}[\text{N(SiMe}_3\text{)}_2]_3[\text{NO}] \)

\[
\begin{align*}
  d^1 & \quad e^1 t^0_2 & 0.6 \Delta_t \\
  d^2 & \quad e^2 t^0_2 & 1.2 \Delta_t \\
  d^3 & \quad e^2 t^1_2 & 0.8 \Delta_t \\
  d^4 & \quad e^2 t^2_2 & 0.4 \Delta_t \\
  d^5 & \quad e^2 t^3_2 & 0.0 \Delta_t \\
  d^6 & \quad e^3 t^3_2 & 0.6 \Delta_t \\
  d^7 & \quad e^4 t^3_2 & 1.2 \Delta_t \\
  d^8 & \quad e^4 t^4_2 & 0.8 \Delta_t \\
  d^9 & \quad e^4 t^5_2 & 0.4 \Delta_t \\
  d^{10} & \quad e^4 t^6_2 & 0.0 \Delta_t 
\end{align*}
\]
**When to Expect Tetrahedral Geometry**

If ligands are large; so as to avoid ligand-ligand repulsion

In case of metal ions with zero CFSE ($d^0$, $d^5$ and $d^{10}$) or
$\text{MnO}_4^-$ ($d^0$), $\text{FeCl}_4^-$ ($d^5$, h.s.), $\text{ZnCl}_4^{2-}$ ($d^{10}$)

In case of metal ions with small CFSE ($d^2$ and $d^7$)
$\text{CoCl}_4^{2-}$ ($d^7$, h.s.) – $0.8 \Delta_0$ vs $1.2 \Delta_t$
Ligands along the Z axis are removed from an octahedral complex to get a square planar complex.
When to Expect Square Planar Geometry

In the case of $d^8$ metals and strong ligands: Ni$^{2+}$, in the presence of strong field ligands such as CN$^-$ forms a square planar complex.

$2^{\text{nd}}$ and $3^{\text{rd}}$ row $d^8$ metals form square planar geometry irrespective of the nature of the ligand:
With Pd$^{2+}$ (which already generates a strong field) even a weak field ligand such as Cl$^-$ leads to the formation of a square planar complex, for example, [PdCl$_4$]$^{2-}$.