**Distortions in Octahedral Geometry**

**Regular Octahedron:** Complexes with regular octahedral geometry are expected to form, when all of the ligands are of the same kind.

**Compressed**

**Elongated**

**Distorted Octahedron:** Complexes with distorted octahedral geometry are expected to form, when the ligands are of different kinds.
Distortions in Octahedral Geometry

If the ground electronic configuration of a non-linear complex is orbitally degenerate, the complex will distort so as to remove the degeneracy and achieve a lower energy. This is called the Jahn-Teller Effect.

Ni\(^{2+}\): Only one way of filling the orbitals; not degenerate and no Jahn-Teller Distortion

Cu\(^{2+}\): Two ways of filling the e\(_g\) orbitals; there is degeneracy and Jahn-Teller Distortion is observed
Jahn-Teller Distortion in Cu(II) Complexes

\[
d_{x^2-y^2} \quad d_{z^2} \quad d_{xy} \quad d_{xz} \quad d_{yz}
\]

Cu(II) in regular octahedral environment

Cu(II) after J-T distortion

energy

\[
e_g \quad t_{2g}
\]
Jahn-Teller Distortion in $d^9$ Complexes

\[ \Delta \gg \delta_1 \gg \delta_2. \]
Jahn-Teller Distortion in $d^1$ Complexes

d$^1$ in regular octahedral environment

d$^1$ after J-T distortion
Distortions are more pronounced if the degeneracy occurs in an $e_g$ orbital.
Distortions in Low-Spin Complexes

\[ \text{d}^{6} \times \text{d}^{7} \times \text{d}^{8} \times \text{d}^{9} \times \text{d}^{10} \]
Distortions in High-Spin Complexes

\[
\begin{array}{cccccc}
\uparrow \uparrow & \uparrow \uparrow & \uparrow \uparrow & \uparrow \downarrow \uparrow & \uparrow \downarrow \uparrow & \uparrow \downarrow \uparrow \\
\downarrow \uparrow \uparrow & \downarrow \uparrow \downarrow \uparrow & \downarrow \uparrow \downarrow \uparrow & \downarrow \uparrow \downarrow \uparrow & \downarrow \uparrow \downarrow \uparrow & \downarrow \uparrow \downarrow \uparrow \\
\text{d}^6 & \text{d}^7 & \times & \text{d}^8 & \text{d}^9 & \times \\
\hline
\hline
\_\_ & \_\_ & \_\_ & \_\_ & \_\_ & \_\_ \\
\_\_ & \_\_ & \_\_ & \_\_ & \_\_ & \_\_ \\
\downarrow \_ \_ \_ & \_\_ \_ \_ \_ & \_\_ \_ \_ \_ & \_\_ \_ \_ \_ & \_\_ \_ \_ \_ & \_\_ \_ \_ \_ \\
\text{d}^1 & \text{d}^2 & \times & \text{d}^3 & \text{d}^4 & \times \\
\end{array}
\]
Thermodynamic Aspects of CFSE

**Lattice Energy:** Estimated using Borne-Lande equation

Heats of hydration for M^{2+} ions
Site Preference in Spinels

Spinel – \( \text{Mg}^{\text{II}}\text{Al}^{\text{III}}_2\text{O}_4 \)

\( \text{A}^{\text{II}}\text{B}^{\text{III}}_2\text{O}_4 \)

The oxide ions form a close packed arrangement with octahedral and tetrahedral voids and the metal ions occupy the voids.

**Normal Spinels:** \( (\text{A}^{\text{II}})^{\text{tet}}(\text{B}^{\text{III}}_2)^{\text{oct}}\text{O}_4 \)

The divalent \( \text{A}^{\text{II}} \) ions occupy the tetrahedral voids, whereas the trivalent \( \text{B}^{\text{III}} \) ions occupy the octahedral voids in a close packed arrangement of oxide ions.

\( \text{MgAl}_2\text{O}_4, \text{Mn}_3\text{O}_4, \text{ZnFe}_2\text{O}_4, \text{FeCr}_2\text{O}_4 \)

**Inverse Spinels:** \( (\text{B}^{\text{III}})^{\text{tet}}(\text{A}^{\text{II}}\text{B}^{\text{III}})^{\text{oct}}\text{O}_4 \)

The \( \text{A}^{\text{II}} \) ions occupy the octahedral voids, whereas half of \( \text{B}^{\text{III}} \) ions occupy the tetrahedral voids.

\( \text{Fe}_3\text{O}_4, \text{CoFe}_2\text{O}_4, \text{NiFe}_2\text{O}_4 \)
Site Preference in Spinels

NiFe$_2$O$_4$

Ni is in +2 oxidation state and has 8 electrons in the $d$ orbitals

In a tetrahedral void,
\[ \text{Configuration} = e^4t_2^4; \text{CFSE} = 0.8 \Delta_t (0.4 \Delta_o) \]

In an octahedral void,
\[ \text{Configuration} = t_{2g}^6e_g^2; \text{CFSE} = 1.2 \Delta_o \]

Fe is in +3 oxidation state and has 5 electrons in the $d$ orbitals

In a tetrahedral void,
\[ \text{Configuration} = e^2t_2^3; \text{CFSE} = 0 \]

In an octahedral void,
\[ \text{Configuration} = t_{2g}^3e_g^2; \text{CFSE} = 0 \]

Hence, it is advantageous to have Ni$^{2+}$ ion in the octahedral voids. This results in an inverse spinel structure for the compound.

Fe$^{III}$[Ni$^{II}$Fe$^{III}$]O$_4$
Site Preference in Spinels

\( \text{Mn}_3\text{O}_4 \)

When Mn is in +2 oxidation state, it has 5 electrons in the \( d \) orbitals
- In a tetrahedral void,
  \( \text{Configuration} - e^2t^3; \text{CFSE} - 0 \)
- In an octahedral void,
  \( \text{Configuration} - t^3e^2; \text{CFSE} - 0 \)

When Mn is in +3 oxidation state, it has 4 electrons in the \( d \) orbitals
- In a tetrahedral void,
  \( \text{Configuration} - e^2t^2; \text{CFSE} - 0.4 \Delta_t (0.2 \Delta_o) \)
- In an octahedral void,
  \( \text{Configuration} - t^3e^1; \text{CFSE} - 0.6 \Delta_o \)

Hence, it is advantageous to have Mn\(^{3+}\) ions in the octahedral voids. This results in a normal spinel structure for the compound.

\( \text{Mn}^{II}[\text{Mn}^{III}]_2\text{O}_4 \)
The Beer-Lambert Law

\[ A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon cl \]

where \(\varepsilon\) is the molar extinction coefficient (in L cm\(^{-1}\) mole\(^{-1}\)), \(c\) is concentration in mole L\(^{-1}\) and \(l\) is the path length in cm. \(A\) is known as ‘Absorbance’ and it is dimensionless.

Origin of Color

<table>
<thead>
<tr>
<th>Absorbed Color</th>
<th>(\lambda) (nm)</th>
<th>Observed Color</th>
<th>(\lambda) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>400</td>
<td>Green-yellow</td>
<td>560</td>
</tr>
<tr>
<td>Blue</td>
<td>450</td>
<td>Yellow</td>
<td>600</td>
</tr>
<tr>
<td>Blue-green</td>
<td>490</td>
<td>Red</td>
<td>620</td>
</tr>
<tr>
<td>Yellow-green</td>
<td>570</td>
<td>Violet</td>
<td>410</td>
</tr>
<tr>
<td>Yellow</td>
<td>580</td>
<td>Dark blue</td>
<td>430</td>
</tr>
<tr>
<td>Orange</td>
<td>600</td>
<td>Blue</td>
<td>450</td>
</tr>
<tr>
<td>Red</td>
<td>650</td>
<td>Green</td>
<td>520</td>
</tr>
</tbody>
</table>
Color of $[\text{Ti(H}_2\text{O)}_6]^{3+}$

Absorption at 520 nm gives the complex its purple color.

A more resolved absorption spectrum of the complex has a shoulder.
Color and CFT

\[ [\text{V(H}_2\text{O)}_6]^{3+} \]
\[ V(\text{III}) = d^2 \text{ ion} \]

\[ [\text{V(H}_2\text{O)}_6]^{2+} \]
\[ V(\text{II}) = d^3 \text{ ion} \]

violet light absorbed complex appears yellow

yellow light absorbed complex appears violet

\[ e_g \]
\[ \Delta_{\text{oct}} \]
\[ t_{2g} \]
\[ \Delta \text{ large} \]

\[ e_g \]
\[ \Delta_{\text{oct}} \]
\[ t_{2g} \]
\[ \Delta \text{ small} \]
**Color and CFT**

\[
\text{[Cr(NH}_3\text{)}_6\text{]}^{3+} \quad \text{[Cr(NH}_3\text{)}_5\text{Cl}]^{2+}
\]

Strong ligands, leading to high \(\Delta_0\). Absorbs violet and appears yellow.

Relatively weak set of ligands, leading to reduced \(\Delta_0\). Absorbs yellow and appears magenta.
**Laporte Rule**

In a molecule or ion possessing center of symmetry, transitions are not allowed between orbitals of same parity. Transitions are only possible between orbitals that differ by $\Delta l = \pm 1$; ‘l’ is the orbital quantum number.

Examples of forbidden transitions are: $s$ to $s$, $d$ to $d$, $p$ to $f$ etc.

Tetrahedral geometry is not affected by this rule as it does not have a center of symmetry. As a consequence, $\varepsilon$ for tetrahedral complexes are 100 times more than the $\varepsilon$ for octahedral complexes.

Even octahedral complexes lose their center of symmetry transiently due to unsymmetrical vibrations. This leads to color in octahedral and square planar complexes.
**Spin-forbidden and Spin-allowed Transitions**

Any transition for which $\Delta S^i \neq 0$ is strongly forbidden; that is, in order to be allowed, a transition must involve no change in spin state.

[Diagram showing allowed and forbidden transitions]

$[\text{Mn(H}_2\text{O)}_6]^{2+}$ has a $d^5$ metal ion and is a high-spin complex. Electronic transitions are not only Laporte-forbidden, but also spin-forbidden. The dilute solutions of Mn$^{2+}$ complexes are therefore colorless.

However, certain complexes such as MnO$_4^-$, CrO$_4^{2-}$ etc are intensely colored even though they have metal ions without electrons in the d orbitals. The color of these complexes are not from d-d transitions, but from charge-transfer from ligand to metal orbitals.
**$d^0$ and $d^{10}$ ions have no d-d transitions**

<table>
<thead>
<tr>
<th>Ion</th>
<th>$d^0$ ion</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$</td>
<td>$d^{10}$ ion</td>
<td>white</td>
</tr>
<tr>
<td>TiF$_4$</td>
<td>$d^0$ ion</td>
<td>white</td>
</tr>
<tr>
<td>TiCl$_4$</td>
<td>$d^0$ ion</td>
<td>white</td>
</tr>
<tr>
<td>TiBr$_4$</td>
<td>$d^0$ ion</td>
<td>orange</td>
</tr>
<tr>
<td>TiI$_4$</td>
<td>$d^0$ ion</td>
<td>dark brown</td>
</tr>
<tr>
<td>[MnO$_4$]⁻ Mn(VII)</td>
<td>$d^0$ ion</td>
<td>extremely purple</td>
</tr>
<tr>
<td>[Cr$_2$O$_7$]⁻ Cr(VI)</td>
<td>$d^0$ ion</td>
<td>bright orange</td>
</tr>
<tr>
<td>[Cu(MeCN)$_4$]$^+$  Cu(I)</td>
<td>$d^{10}$ ion</td>
<td>colourless</td>
</tr>
<tr>
<td>[Cu(phen)$_2$]$^+$  Cu(I)</td>
<td>$d^{10}$ ion</td>
<td>dark orange</td>
</tr>
</tbody>
</table>