**Jahn-Teller Effect**

The Jahn-Teller theorem essentially states that any nonlinear molecule system possessing electronic degeneracy will be unstable and will undergo distortion to form a system of lower symmetry as well as lower energy and thus the degeneracy will be removed.

This effect describes the geometrical distortion of molecules and ions that is associated with electronically degenerate configurations. A configuration is said to be electronically degenerate if more than one site are available for the filling of a single electron. The Jahn-Teller effect is generally encountered in octahedral transition metal complexes. The phenomenon is much more common in hexacoordinated complexes of bivalent copper. The $d^9$ configuration of Cu$^{2+}$ ion yields three electrons in the doubly degenerate $e_g$ orbitals set, leading to a doubly degenerate electronic state as well. Such complexes distort along one of the molecular four-fold axis (always labeled the $z$-axis), which has the effect of removing the orbital and electronic degeneracies and lowering the overall energy. The distortion usually occurs via the elongation the metal-ligand bonds along the $z$-axis, but sometimes also occurs as a shortening of the same bonds instead. Moreover, the Jahn-Teller theorem predicts the presence of an unstable geometry only and not the direction of the distortion. When distortion involving elongation occurs to decrease the electrostatic repulsion between the electron-pair on the ligand-attached and any extra electrons in metal orbitals with a $z$-component; and hence lowering the energy of the metal complex. Inversion center is retained after $z$-out as well as $z$-in the distortion. Symmetrical configurations possess electronic degeneracy while the unsymmetrical ones do not. Various symmetrical and unsymmetrical configurations are given below.

Table 10. Symmetrical and Unsymmetrical $t_{2g}$ and $e_g$ orbitals.

<table>
<thead>
<tr>
<th>Symmetrical configurations</th>
<th>Unsymmetrical configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{2g}^0, t_{2g}^3, t_{2g}^6$</td>
<td>$t_{2g}^1, t_{2g}^2, t_{2g}^4, t_{2g}^5$</td>
</tr>
<tr>
<td>$e_g^0, e_g^4, e_g^2$ (high-spin)</td>
<td>$e_g^1, e_g^3, e_g^2$ (low-spin)</td>
</tr>
</tbody>
</table>

Now, the conditions for different kinds of distortion can be summed up as:

Table 11. Conditions for Jahn-Teller distortion.

<table>
<thead>
<tr>
<th>Type of distortion</th>
<th>Configuration required</th>
</tr>
</thead>
<tbody>
<tr>
<td>No distortion</td>
<td>$t_{2g}$ (symmetrical) + $e_g$ (symmetrical)</td>
</tr>
<tr>
<td>Slight distortion</td>
<td>$t_{2g}$ (unsymmetrical)</td>
</tr>
<tr>
<td>Strong distortion</td>
<td>$e_g$ (unsymmetrical)</td>
</tr>
</tbody>
</table>
Let the case of the low-spin Co\(^{2+}\) octahedral complex. The corresponding electronic configuration is \(t_{2g}^6 e_g^1\). Owing to the electronically degenerate state, the Jahn-Teller distortion is expected. Now suppose that the single electron of \(e_g\) set is present in \(d_{z^2}\) orbital; the ligands approaching from \(z\)-axis will feel more repulsion than the ligands coming from \(x\) and \(y\)-axis. Therefore, the bonds along \(z\)-axis will be weaker in comparison to the bond along \(x\) and \(y\)-axis. This results in a tetragonal elongation about \(z\)-axis with two longer and four shorter bonds. This is formally called as \(z\)-out distortion. On the other hand, if the single electron of \(e_g\) set is present in \(d_{x^2-y^2}\) orbital; the ligands approaching from \(x\) and \(y\)-axis will feel more repulsion than the ligands coming from \(z\)-axis. Therefore, the bonds along \(x\) and \(y\)-axis will be weaker in comparison to the bond along \(z\)-axis. This results in a tetragonally flattened octahedral geometry about \(z\)-axis with two shorter and four longer bonds. This is formally called as \(z\)-in distortion.

Consider the following examples

1. \([\text{Co(CN)}_6]^{4-}\): It is a low-spin complex with \(t_{2g}^6 e_g^1\) electronic configuration and will undergo strong Jahn-Teller distortion.

2. \([\text{Cr(NH}_3)_6]^{3+}\): It is a high-spin complex with \(t_{2g}^3 e_g^6\) electronic configuration which is completely symmetrical; and therefore, will not show any Jahn-Teller distortion.

3. \([\text{FeF}_6]^{4-}\): It is a high-spin complex with \(t_{2g}^4 e_g^2\) electronic configuration and will undergo slight Jahn-Teller distortion.

\section*{Energetics of Jahn-Teller Distortion}

The Jahn-Teller distortion results in a system of lower symmetry and lower energy. This is actually the opposite of what is expected. Generally, symmetry leads to stability; but the Jahn-Teller effect is actually an exception to this statement. Therefore, it is necessary to discuss the driving force responsible for this behavior. The magnitude of Jahn-Teller effect is larger where the electron density associated with the
degenerate set orbitals is more concentrated. Hence, Jahn-Teller effect plays a significant role in determining the structure of transition metal complexes with active 3d-orbitals. The whole energetics of the Jahn-Teller can be understood by the case study of \( d^0 \) and \( d^1 \) complexes.

1. Cu\(^{2+} \) complexes: The electronic configuration of free Cu\(^{2+} \) ion is \( d^9 \); and in an octahedral environment, it is \( t_{2g}^6 \ e_g^3 \). Before we put any conclusive remark on the direction or nature of the distortion, we shall find the crystal field stabilization energy for \( z \)-out as well as for \( z \)-in case.

i) Crystal field stabilization energy for \( z \)-out distortion:

CFSE due to distortion = Energy of the distorted complex (\( E_2 \)) − Energy of the complex without distortion (\( E_1 \))

\[
E_1 = 6(-0.4\Delta_0) + 3(+0.6\Delta_0)
\]

\[
E_1 = -0.6\Delta_0
\]

\[
E_2 = 4(-0.4\Delta_0 - \delta_2/3) + 2(-0.4\Delta_0 + 2\delta_2/3) + 2(+0.6\Delta_0 - \delta_1/2) + 1(+0.6\Delta_0 + \delta_1/2)
\]

\[
E_2 = -0.6\Delta_0 - \delta_1/2
\]

\[
\text{CFSE due to distortion} = E_2 - E_1 = -\delta_1/2
\]

Hence, the crystal field stabilization due to \( z \)-out distortion is \(-\delta_1/2\).
ii) Crystal field stabilization energy for z-in distortion:

\[ E_1 = 6(-0.4\delta_o) + 3(+0.6\delta_o) \]

\[ E_2 = 4(-0.4\delta_o - 2\delta_i/3) + 2(-0.4\delta_o + \delta_i/3) + 2(+0.6\delta_o - \delta_i/2) + 1(+0.6\delta_o + \delta_i/2) \]

\[ E_{\text{CFSE}} = E_2 - E_1 = -\delta_i/2 \]

Hence, the magnitude of crystal field stabilization due to z-in distortion is \(-\delta_i/2\).

Hence, the magnitude of crystal field stabilization in z-out case is same as that is present in z-in complex. This implies that Jahn-Teller effect cannot predict the direction of the distortion. However, it has been observed that it is the z-out case that dominates in most of the cases. It may depend on the repulsive forces between the d-electrons and the ligands, so the odd electron will prefer \(d_{z^2}\)-orbital more than \(d_{x^2-y^2}\) due to the lesser number of ligands it will repel with. Moreover, when a z-in distortion occurs, one can also view it terms of equatorial elongation while z-out will mean the weakening of two axial metal-ligand bonds. In other words, it is easier to weaken two bonds rather stretching four metal-ligand bonds.
2. Ti$^{3+}$ complexes: The electronic configuration of free Ti$^{3+}$ ion is $d^1$; and in an octahedral environment, it is $t_{2g}^1 e_g^0$. Before we put any conclusive remark on the direction or nature of the distortion, we shall find the crystal field stabilization energy for $z$-out as well as for $z$-in case.

i) Crystal field stabilization energy for $z$-out distortion:

\[ E_1 = -0.4\Delta_o \]
\[ E_2 = -0.4\Delta_o - \delta_2/3 \]

\[ \text{CFSE due to distortion} = E_2 - E_1 = -\delta_2/3 \]

Hence, the crystal field stabilization due to $z$-out distortion is $-\delta_2/3$. Moreover, it is worthy to note that this type of Jahn-Teller distortion is unable to remove the electronic degeneracy completely (the single electron can still be filled in two degenerate orbitals namely $d_{z^2}$ and $d_{x^2-y^2}$). Therefore, homoleptic octahedral complexes of $d^1$-configuration undergoing $z$-in distortion are quite rare.
ii) Crystal field stabilization energy for z-in distortion:

\[ E_1 = 1(-0.4\Delta_o) \]

\[ E_2 = 1(-0.4\Delta_o - 2\delta_2/3) \]

CFSE due to distortion = \[ E_2 - E_1 = -2\delta_2/3 \]

Hence, the crystal field stabilization due to z-in distortion is \(-2\delta_2/3\).

Hence, the magnitude of crystal field stabilization in z-out case is half of what is observed in z-in complex. This implies that Jahn-Teller effect can predict the direction of the distortion. However, it is the \(d^1\)-configuration that has been observed to show z-in distortion; otherwise, the z-out case dominates in most of the cases. It may be explained in terms of the repulsive forces between the \(d\)-electrons and the ligands, so the odd electron will prefer \(d_{zx}^2\)-orbital more than \(d_{xy}^2\) due to the lesser number of ligands it will repel with. Nevertheless, Ti\(^{3+}\) octahedral complexes prefer to undergo z-in due to the greater value of crystal field stabilization energy.
Effect of Jahn-Teller Distortion on Electronic Spectra

Jahn-Teller distortions affect the UV-visible spectra of many transition metal complexes in a significant manner and sometimes it is almost impossible to find out the values of the Racah parameter and crystal splitting energy if we do not take it into account. In UV-visible absorption spectroscopy, distortion causes the splitting of bands in the spectrum due to a reduction in symmetry (O\textsubscript{h} to D\textsubscript{4h}). The complexes undergoing Jahn-Teller distortion show an increased number of bands. Consider the following examples:

1. [Cr(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}: The Cr\textsuperscript{2+} ion in aqueous solutions is pale blue and its UV-visible absorption spectrum consists of a weak broad band with a maxima 14000 cm\textsuperscript{-1}. In normal conditions, this band is expected to provide the value of crystal field splitting value directly (from Orgel-diagram of d\textsuperscript{4}-configuration); however, the actual value of \(\Delta_o\) is considerably different. The electronic configuration for high-spin Cr\textsuperscript{2+} in the octahedral field is \(t_2\textsuperscript{2}e\textsuperscript{3}\); and therefore, this complex is bound to undergo strong Jahn-Teller distortion. The energy level diagram and main transitions are shown below.

The ground state term for a regular octahedral [Cr(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+} complex would be \(5\)\textsubscript{E\textsubscript{g}} but the ground as well as excited electronic state will undergo a Jahn-Teller distortion. It is worthy to note that the former state shows strong while splitting of later one is weak. Hence, the Tanabe-Sugano diagram cannot be used to describe the energy levels in the complex. The gaussian deconvolution of the overall spectrum has shown that the transition between the split components of the \(5\)\textsubscript{E\textsubscript{g}} level (\(2\)\textsubscript{B\textsubscript{1g}} → \(2\)\textsubscript{A\textsubscript{1g}}) occurs at around 10000 cm\textsuperscript{-1} and contributes to the low-energy tail of the broad band in aqueous solution.
Figure 63. UV-visible spectra of [Cr(H₂O)₆]²⁺.

The transitions from the ²B₁g ground state to the components of the ⁵T₂g state are unresolved and together give rise to the band at around 14000 cm⁻¹. Now, suppose that the Jahn-Teller effect produces a symmetrical splitting of the ²Eg state, we can obtain the d-orbital splitting of the parent octahedral complex from the energy of the ²B₁g → ⁵T₂g transition minus half the energy of the ²B₁g → ²A₁g transition. This gives the estimated value of crystal field splitting as follows:

\[ \Delta_o = \frac{\nu_2 (²B₁g → ⁵T₂g) - \nu_1 (²B₁g → ²A₁g)}{2} \]

\[ \Delta_o = 14000 - 10000/2 = 9000 \text{ cm}^{-1} \]

Similar results have been observed in the low-temperature spectra of other hydrate complexes with Jahn-Teller distortion.

2. [Fe(H₂O)₆]²⁺: The Fe²⁺ ion in aqueous solutions is pale green and its UV-visible absorption spectrum is consisted of a weak broad band with a maxima 10000 cm⁻¹. The electronic configuration for high-spin Fe²⁺ in octahedral field is ³t₂g⁴ ⁴e₂g; and therefore, this complex is bound to undergo slight Jahn-Teller distortion. The ground state term for a regular octahedral [Fe(H₂O)₆]²⁺ complex would be ⁵T₂g but the ground as well as excited electronic state will undergo a Jahn-Teller distortion. It is worthy to note that the former state shows strong while splitting of later one is weak.

Hence, the Orgel-diagram can be used to describe the energy levels in the complex. Moreover, as the band is obviously a doublet, we don’t need gaussian deconvolution the overall spectrum. The transition from ⁵T₂g to the split components of the ⁵Eg level (³B₁g and ³A₁g) are split by an energy difference of around 2000 cm⁻¹. This contributes to the broadening of the band in aqueous solution. The energy level diagram and main transitions are shown below.
Figure 64. The schematic energy level diagram and prominent transitions in [Fe(H₂O)₆]²⁺.

The corresponding spectrum is given below.

Figure 65. UV-visible spectra of [Fe(H₂O)₆]²⁺.

Now, suppose that the Jahn-Teller effect produces a symmetrical splitting of the ⁵E₉ state, we can obtain the d-orbital splitting of the parent octahedral complex from the energy of the ⁵T₂g → ⁵E₉ transition, and that value, in this case, is 10000 cm⁻¹. These results are rather similar to what we have observed in [Ti(H₂O)₆]³⁺. Both complexes possess Jahn-Teller distortion associated with the electronic degeneracy of t₂g orbital.
Static and Dynamic Jahn-Teller Distortion

On the basis of the observed geometry, the Jahn-Teller distortion can be classified in two types as given below.

1. Static Jahn-Teller distortion: Some molecules show tetragonal shape under all conditions i.e., in solid state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Teller distortion. Hence the distortion is strong and permanent. For example, in CuF$_2$ lattice

![Figure 66. Static Jahn-Teller distortion in CuF$_2$ lattice.](image)

2. Dynamic Jahn-Teller distortion: If the energy gap between z-out and z-in is smaller than the available thermal energy, the complex ions tend to attain both states, i.e., compressed and elongated. This is known as the "Dynamic Jahn Teller Effect". For example, consider K$_2$Pb[Cu(NO$_2$)$_6$] complex:

![Figure 67. Dynamic Jahn-Teller distortion in K$_2$Pb[Cu(NO$_2$)$_6$].](image)
**Consequences of Jahn-Teller Distortion**

Some of the main consequences of the Jahn-Teller effect in the field of chemical science are given below.

1. **Irving-William series:** Stability of metal complexes with a given ligand follows the order $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$. The increase in the stability of the complexes from $\text{Mn}^{2+}$ to $\text{Zn}^{2+}$ is the increase in the effective nuclear charge. However, the exceptionally greater stability of $\text{Cu}^{2+}$ complexes is due to the Jahn-Teller distortion.

![Figure 68. Variation of log $K_1$ for the addition of first ethylenediamine.](image)

The sequence is generally quoted only for Mn(II) to Zn(II) as there is little or no data available for the other $3d$ series transition metal ions as their M(II) oxidation states are not very much stable. Crystal field theory is based on the idea that the interactions between the metal centre and the ligands attached are purely ionic in nature; this suggests that the stability of the complexes should be related to the charge to radius ratio (ionic potential).

2. **Disproportionation of $\text{Au}^{2+}$ salts:** Bivalent gold is less stable and undergoes disproportionation to form $\text{Au}^{1+}$ and $\text{Au}^{3+}$. On the other hand, bivalent salts of Cu and Ag ions are quite common and relatively more stable. However, as far as the electronic configuration is concerned, all of the three belong to the same group and are $d^9$ systems.

Thus, a strong Jahn-Teller distortion is expected. The disproportion of $\text{Au}^{2+}$ can be explained in terms of increasing $\Delta$ value down the group. Therefore, bivalent salts of gold would have the maximum magnitude of crystal field splitting, which results in high destabilization associated with the filling of last electron in $d_{x^2-y^2}$. This makes $\text{Au}^{2+}$ to undergo either to form $\text{Au}^{3+}$, a $d^8$ system; or reduction to $\text{Au}^{1+}$, a $d^{10}$ system. The $d^8$ system ($\text{Au}^{3+}$) is usually square-planar in geometry and quite stable as the electron from the $d_{x^2-y^2}$ is removed. The $d^{10}$ system ($\text{Au}^{1+}$) is of linear geometry and stable due to fully filled configuration.
3. Stability order of ethylenediamine complexes of Cu\(^{2+}\): Jahn-Teller distortion is responsible for the stability order of \([\text{Cu(en)}_3]^{2+}\), cis-\([\text{Cu(en)}_2(\text{H}_2\text{O})_2]^{2+}\), trans-\([\text{Cu(en)}_2(\text{H}_2\text{O})_2]^{2+}\).

![Figure 69](image)

![Figure 70](image)

[Bivalent copper cannot form \([\text{Cu(en)}_3]^{2+}\) because the Jahn-Teller distortion induces strain into the ethylenediamine molecule that is added along z-axis. Therefore, the only complex that exists is \([\text{Cu(en)}_2(\text{H}_2\text{O})_2]^{2+}\). Similarly, cis-\([\text{Cu(en)}_2(\text{H}_2\text{O})_2]^{2+}\) is less stable in comparison than trans-\([\text{Cu(en)}_2(\text{H}_2\text{O})_2]^{2+}\). The extra stability of trans-\([\text{Cu(en)}_2(\text{H}_2\text{O})_2]^{2+}\) is because of the non-involvement of longer bonds in chelation.](image)
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