Other Crystal Fields

• We can deduce the CFT splitting of $d$ orbitals in virtually any ligand field by

  ○ Noting the direct product listings in the appropriate character table to determine the ways in which the $d$ orbital degeneracies are lifted

  ○ Carrying out an analysis of the metal-ligand interelectronic repulsions produced by the complex’s geometry.

• Sometimes useful to begin with either the octahedral or tetrahedral results and consider the effects brought about by distorting the perfect geometry to bring about the new configuration.

  ○ The results for the perfect and distorted geometries can be correlated through descent in symmetry, using the appropriate correlation tables.

  ○ Can take this approach with distortions produced by ligand substitution or by intermolecular associations, if descent in symmetry involves a group-subgroup relationship.
Jahn-Teller Theorem
A Fundamental Cause of Distortion

• The Jahn-Teller theorem requires that for any nonlinear molecular system in a degenerate electronic state a distortion will occur so as to lower the symmetry and remove the degeneracy.
  ○ The theorem does not predict the exact nature of the distortion.
  ○ However, if the system is centrosymmetric, inversion symmetry will be preserved.

• A Jahn-Teller distortion results in partial or complete lifting of the degeneracies among some orbitals.
  ○ In so doing, electrons may occupy lower-energy orbitals, resulting in a lower overall energy state for the system.
  ○ The “perfect” geometries really cannot exist as stable species for certain electronic configurations, because the distorted molecule is the energetically preferred structure.

⚠️ Describing certain complexes as octahedral, tetrahedral, or square planar is often really an approximation of their true structure.
Degenerate Ground States of ML\textsubscript{6} \emph{O}_h Complexes

- We can identify octahedral ground state configurations subject to the Jahn-Teller effect by considering the degeneracy of possible \(d^n\) electronic configurations.

  - A degenerate electronic state results whenever the electrons in either the \(t_{2g}\) or \(e_g\) levels can be distributed in two or more ways among degenerate orbitals.

  Example: The \(d^1\) ground-state configuration can have the single electron in any one of the three \(t_{2g}\) orbitals, so the electronic state is triply degenerate.

    \[
    t_{2g} \uparrow \_ \_ \_ \_ \uparrow \_ \_ \_ \_ \uparrow
    \]

  Example: With equal probability, any one of the three \(t_{2g}\) orbitals could be vacant in the ground state for \(d^2\) \((t_{2g}^2)\), so this too is a triply degenerate state.

    \[
    t_{2g} \uparrow \uparrow \_ \_ \_ \_ \uparrow \_ \_ \_ \_ \uparrow
    \]
Degenerate and Non-degenerate $d^n$ Ground States

Only non-degenerate states are immune to Jahn-Teller Distortion.

<table>
<thead>
<tr>
<th>Degeneracy</th>
<th>$d^n$ Configuration</th>
<th>$t_{2g} e_g$ Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triply degenerate</td>
<td>$d^1$</td>
<td>$t_{2g}^1$</td>
</tr>
<tr>
<td></td>
<td>$d^2$</td>
<td>$t_{2g}^2$</td>
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<tr>
<td></td>
<td>$d^4$ low spin</td>
<td>$t_{2g}^4$</td>
</tr>
<tr>
<td></td>
<td>$d^5$ low spin</td>
<td>$t_{2g}^5$</td>
</tr>
<tr>
<td></td>
<td>$d^6$ high spin</td>
<td>$t_{2g}^4 e_g^2$</td>
</tr>
<tr>
<td></td>
<td>$d^7$ high spin</td>
<td>$t_{2g}^5 e_g^2$</td>
</tr>
<tr>
<td>Doubly degenerate</td>
<td>$d^4$ high spin</td>
<td>$t_{2g}^3 e_g^1$</td>
</tr>
<tr>
<td></td>
<td>$d^7$ low spin</td>
<td>$t_{2g}^6 e_g^1$</td>
</tr>
<tr>
<td></td>
<td>$d^9$</td>
<td>$t_{2g}^6 e_g^3$</td>
</tr>
<tr>
<td>Non-degenerate</td>
<td>$d^3$</td>
<td>$t_{2g}^3$</td>
</tr>
<tr>
<td></td>
<td>$d^5$ high spin</td>
<td>$t_{2g}^3 e_g^2$</td>
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<tr>
<td></td>
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<td></td>
<td>$d^8$</td>
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</tr>
<tr>
<td></td>
<td>$d^{10}$</td>
<td>$t_{2g}^6 e_g^4$</td>
</tr>
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</table>
Strong and Weak Jahn Teller Distortions of ML$_6$

- Distortions will be more pronounced for the doubly degenerate configurations, which have an imbalance in the filling of the $e_g$ level.

- Lesser distortions result from triply degenerate states, which have an imbalance in the distribution among $t_{2g}$ orbitals.

- The difference can be understood by considering shielding effects and the orientations of the $t_{2g}$ and $e_g$ orbitals.
Shielding Effects and Distortion for $d^9$

$$d^9 = t_{2g}^6 e_g^3 = t_{2g}^6 [(d_{x^2-y^2})^2(d_{z^2})^1] \text{ and } t_{2g}^6 [(d_{x^2-y^2})^1(d_{z^2})^2]$$

- $t_{2g}^6 [(d_{x^2-y^2})^2(d_{z^2})^1]$: The pair of electrons in the $d_{x^2-y^2}$ orbital would more effectively shield ligands in the $xy$ plane from the metal ion’s charge than the single electron in the $d_{z^2}$ orbital would shield ligands along the $z$ axis.

  - If this were to occur, the ligands along $z$ would be **more strongly** attracted to the central metal ion and their M-L bond lengths would be **shortened** relative to those in the $xy$ plane.

- $t_{2g}^6 [(d_{x^2-y^2})^1(d_{z^2})^2]$: The single electron in the $d_{x^2-y^2}$ orbital would less effectively shield ligands in the $xy$ plane from the metal ion’s charge than the pair of electrons in the $d_{z^2}$ orbital would shield ligands along the $z$ axis.

  - If this were to occur, the ligands along $z$ would be **less strongly** attracted to the central metal ion and their M-L bond lengths would be **lengthened** relative to those in the $xy$ plane.

* Can't tell which distortion will occur.

- Shielding effects are less pronounced for triply degenerate configurations, because the orbitals’ lobes are oriented between the ligands.

  - Thus, the resulting distortions are not as severe.
**Tetragonal Distortion**

- Although the exact nature of the resulting distortion cannot be predicted from the Jahn-Teller theorem, the foregoing analysis of the $d^9$ case suggests that a *tetragonal distortion* might result.
  - A tetragonal distortion to an octahedron results from any change in geometry that preserves a $C_4$ axis.
  - Tetragonal distortion occurs whenever two *trans* related ligands are differentiated from the remaining four.

- Jahn-Teller tetragonal distortions must result in a centrosymmetric group (e.g., $D_{4h}$).

- Tetragonal distortions to non-centrosymmetric groups (e.g., $C_{4v}$) are possible, but not by the Jahn-Teller effect.
Jahn-Teller Tetragonal Distortions

- A tetragonal distortion would occur if the M-L bonds of two ligands lying along the $z$ axis were either stretched or compressed equally while maintaining equivalence among the four remaining ligands in the $xy$ plane.

![Diagram of tetragonal distortion](image)

- By either process, the symmetry would descend from $O_h$ to $D_{4h}$.
  - The descent in symmetry causes a partial lifting of the degeneracies among the $d$ orbitals in the octahedral field.
Splitting of $d$ Orbital Degeneracies – $O_h \to D_{4h}$

- From the correlation table that links the groups $O_h$ and $D_{4h}$ (Appendix B) we see that the two $e_g$ orbitals of the octahedral field become nondegenerate as $a_{1g}$ and $b_{1g}$ in the tetragonal field.

- From the direct product listings in the $D_{4h}$ character table (Appendix A) we see

$$a_{1g} = d_{2z^2-x^2-y^2} (= d_{z^2})$$
$$b_{1g} = d_{x^2-y^2}$$

- From the correlation table we also see that the degeneracy among the $t_{2g}$ orbitals in $O_h$ is partially lifted to become $b_{2g}$ and $e_g$ in the $D_{4h}$ tetragonal field.

- From the direct product listings in the $D_{4h}$ character table we see

$$b_{2g} = d_{xy}$$
$$e_g = (d_{xz}$ and $d_{yz}$)
Relative Energies of \( d \) Orbitals in \( D_{4h} \)

- The relative energy ordering of the orbitals depends on the direction and magnitude of the tetragonal distortion.

- A distortion in which the two M-L bonds along \( z \) are progressively stretched is an interesting case to consider, because at its limit the two ligands would be removed, resulting in a square planar ML\(_4\) complex.

- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in \( d \) orbitals that have substantial electron distribution along \( z \).
  
  \( \circ \) Thus the energies of the \( d_{xz} \), \( d_{yz} \), and \( d_{z^2} \) orbitals are lowered.

- If we assume that the stretch along \( z \) is accompanied by a counterbalancing contraction in the \( xy \) plane, so as to maintain the overall energy of the system, then the orbitals with substantial electron distribution in the \( xy \) plane will experience increased repulsions.
  
  \( \circ \) Thus, the \( d_{xy} \) and \( d_{x^2-y^2} \) orbitals rise in energy.
Orbital Splitting from Stretching Tetragonal Distortion

- The upper $e_g$ orbitals of the perfect octahedron split equally by an amount $\delta_1$, with the $d_{x^2-y^2}$ orbital ($b_{1g}$ in $D_{4h}$) rising by $+\delta_1/2$ and the $d_{z^2}$ orbital ($a_{1g}$ in $D_{4h}$) falling by $-\delta_1/2$.

- The lower $t_{2g}$ orbitals of the perfect octahedron split by an amount $\delta_2$, with the $d_{xy}$ orbital ($b_{2g}$ in $D_{4h}$) rising by $+2\delta_2/3$, and the degenerate $d_{xz}$ and $d_{yz}$ orbitals ($e_g$ in $D_{4h}$) falling by $-\delta_2/3$. 
Magnitudes of the $\delta_1$ and $\delta_2$ Splittings

- Both the $\delta_1$ and $\delta_2$ splittings, which are very small compared to $\Delta_o$, maintain the barycenters defined by the $e_g$ and $t_{2g}$ levels of the undistorted octahedron.

  - The energy gap $\delta_1$ is larger than that of $\delta_2$, because the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are directed at ligands.

  - The distortion has the same effect on the energies of both the $d_{x^2-y^2}$ and $d_{xy}$ orbitals; i.e. $\delta_1/2 = 2\delta_2/3$.

  As a result, their energies rise in parallel, maintaining a separation equal to the $\Delta_o$ of the undistorted octahedral field.
Tetragonal Compression Jahn-Teller Distortion

- If we carry out the opposite tetragonal distortion (compression along $z$), the octahedral degeneracies will be lifted in the same manner, as required by symmetry, but the ordering of the orbitals across both the $\delta_1$ and $\delta_2$ gaps will be reversed.

  - The energy of the $d_{x^2-y^2}$ orbital ($b_{1g}$) will fall by $-\delta_1/2$, and the energy of the orbital $d_{z^2}$ ($a_{1g}$) will rise by $+\delta_1/2$.

  - The energy of the $d_{xy}$ ($b_{2g}$) orbital will fall by $-2\delta_2/3$, and the energy of the $d_{xz}$ and $d_{yz}$ ($e_g$) orbitals will rise by $+\delta_2/3$.

- In this case, the energy of the $d_{xy}$ ($b_{2g}$) and $d_{x^2-y^2}$ ($b_{1g}$) orbitals will fall equally with increasing compression along $z$ (i.e., $-\delta_1/2 = -2\delta_2/3$), maintaining a separation equal to $\Delta_o$. 
Square Planar ML₄ Complexes

- If we imagine continuing the stretching of M-L bonds along z, the orbital splittings will become progressively greater, producing successively larger values of δ₁ and δ₂.

- Eventually the two ligands will be removed, resulting in a square planar ML₄ complex.

- At some point before this extreme the a₁g (d₂z) level may cross and fall below the b₂g (dₓy) level, resulting in the following splitting scheme.¹

¹The ordering of the lower four d orbitals probably varies among square planar complexes and has been the subject of much debate. See A. B. P. Lever, Inorganic Electron Spectroscopy, 2nd ed., Elsevier, Amsterdam, 1984, p. 537ff. and references therein.
ML$_4$ ($D_{4h}$) vs. ML$_4$ ($T_d$)

- Most square planar complexes are $d^8$ and less often $d^9$.
- In virtually all $d^8$ cases a low spin configuration is observed, leaving the upper $b_{1g}$ ($d_{x^2-y^2}$) level vacant in the ground state.
  - This is expected, because square planar geometry in first-row transition metal ions is usually forced by strong field ligands.
  - Strong field ligands produce a large $\Delta_o$ value.
  - The energy gap between the $b_{2g}$ ($d_{xy}$) and $b_{1g}$ ($d_{x^2-y^2}$) levels is equivalent to $\Delta_o$.

$\Rightarrow$ A large $\Delta_o$ value favors pairing in the $b_{2g}$ ($d_{xy}$) level, a low-spin diamagnetic configuration for $d^8$.

- Tetrahedral $d^8$ is a high-spin paramagnetic configuration $e^4t^4_2$.

$\Rightarrow$ ML$_4$ ($D_{4h}$) and ML$_4$ ($T_d$) can be distinguished by magnetic susceptibility measurements.

- Ni$^{2+}$ ion tends to form square planar, diamagnetic complexes with strong-field ligands (e.g., [Ni(CN)$_4$]$^{2-}$), but tends to form tetrahedral, paramagnetic complexes with the weaker-field lands (e.g., [NiCl$_4$]$^{2-}$).

- With second and third row transition metal ions the $\Delta_o$ energies are inherently larger, and square planar geometry can occur even with relatively weak field ligands (e.g., square planar [PtCl$_4$]$^{2-}$).