The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system.

Introduction

In 1937, Hermann Jahn and Edward Teller postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," in regards to its electronic state.[1] This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecroft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy."[2] This is most commonly observed with transition metal octahedral complexes, however, it can be observed in tetrahedral compounds as well.

For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: \( \{t_{2g}\} \) \( \{d_{xz},d_{yz},d_{xy}\} \) and \( \{e_g\} \) \( \{d_{z^2}\} \) and \( \{d_{x^2−y^2}\} \). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the \( z \) ligand bonds as shown in Figure (PageIndex{1}) below:

![Elongated and Compressed Octahedral Complexes](image)

_Elongated_  _Compressed_

*Figure (PageIndex{1}): Jahn-Teller distortions for an octahedral complex.*

When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.
Elongation

Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, while the orbitals without a z component are destabilized (higher in energy) as shown in Figure \(\PageIndex{2}\) below:

![Figure \(\PageIndex{2}\): Illustration of tetragonal distortion (elongation) for an octahedral complex.](image)

This is due to the \(\{d_{xy}\}\) and \(\{d_{x^2−y^2}\}\) orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the \(\{d_{x^2−y^2}\}\) orbital is antibonding, it is expected to increase in energy due to elongation. The \(\{d_{xy}\}\) orbital is still nonbonding, but is destabilized due to the interactions. Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in Figure \(\PageIndex{3}\).
Notice that the two axial bonds are both elongated and the four shorter equatorial bonds are the same length as each other. According to the theorem, the orbital degeneracy is eliminated by distortion, making the molecule more stable based on the model presented in Figure \(\PageIndex{2}\).

**Compression**

Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals without a z component, while the orbitals with a z component are destabilized (higher in energy) as shown in Figure \(\PageIndex{4}\) below:

![Diagram of tetragonal distortion (compression)](image)

This is due to the z-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the \(d_{z^2}\) orbital is antibonding, it is expected to increase in energy due to compression. The \(d_{xz}\) and \(d_{yz}\) orbitals are still nonbonding, but are destabilized due to the interactions.
Electronic Configurations

For Jahn-Teller effects to occur in transition metals there must be degeneracy in either the \( t_{2g} \) or \( e_g \) orbitals. The electronic states of octahedral complexes depend on the number of d-electrons and the splitting energy, \( \Delta \). When \( \Delta \) is large and is greater than the energy required to pair electrons, electrons pair in \( t_{2g} \) before occupying \( e_g \). On the other hand, when \( \Delta \) small and is less than the pairing energy, electrons will occupy \( e_g \) before pairing in \( t_{2g} \). The \( \Delta \) of an octahedral complex is dictated by the chemical environment (ligand identity), and the identity and charge of the metal ion. If there electron configurations for any d-electron count is different depending on \( \Delta \), the configuration with more paired electrons is called low spin while the one with more unpaired electrons is called high spin.

The electron configurations diagrams for d1 through d10 with large and small \( \Delta \) are illustrated in the figures below. Notice that the electron configurations for d\(^1\), d\(^2\), d\(^3\), d\(^8\), d\(^9\), and d\(^10\) are the same no matter what the magnitude of \( \Delta \). Low spin and high spin configurations exist only for the electron counts d\(^4\), d\(^5\), d\(^6\), and d\(^7\).

**Large \( \Delta \)**

Figure \( \PageIndex{5} \) (below) shows the various electronic configurations for octahedral complexes with large \( \Delta \), including the low-spin configurations of d\(^4\), d\(^5\), d\(^6\), and d\(^7\):

![Electron Configuration Diagram](image)

\[ \text{Figure } \PageIndex{5} \text{: Electron configuration diagram of octahedral complexes (red indicates no degeneracies possible, thus no Jahn-Teller effects).} \]

The figure illustrates the electron configurations in the case of large \( \Delta \). The electron configurations highlighted in red (d\(^3\), low spin d\(^6\), d\(^8\), and d\(^10\)) do not exhibit Jahn-Teller distortions. On the other hand d\(^1\), d\(^2\), low spin d\(^4\), low spin d\(^5\), low spin d\(^7\), and d\(^9\), would be expected to exhibit Jhan-Teller distortion. These electronic configurations correspond to a variety of transition metals. Some common examples include Cr\(^{3+}\), Co\(^{3+}\), and Ni\(^{2+}\).
Small $\langle \Delta \rangle$

Figure \(\PageIndex{6}\) (below) shows the various electronic configurations for octahedral complexes with small \(\langle \Delta \rangle\), including the high-spin configurations of \(d^4\), \(d^5\), \(d^6\), and \(d^7\): 

![Diagram of electronic configurations]

*Figure \(\PageIndex{6}\)*: High spin octahedral coordination diagram (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates the electron configurations in the case of small \(\langle \Delta \rangle\). The electron configurations highlighted in red (\(d^3\), high spin \(d^5\), \(d^8\), and \(d^{10}\)) do not exhibit Jahn-Teller distortions. In general, degenerate electronic states occupying the \(\langle e_g \rangle\) orbital set tend to show stronger Jahn-Teller effects. This is primarily caused by the occupation of these high energy orbitals. Since the system is more stable with a lower energy configuration, the degeneracy of the \(e_g\) set is broken, the symmetry is reduced, and occupations at lower energy orbitals occur.

**Spectroscopic Observation**

Jahn-Teller distortions can be observed using a variety of spectroscopic techniques. In UV-VIS absorption spectroscopy, distortion causes splitting of bands in the spectrum due to a reduction in symmetry (\(O_h\) to \(D_{4h}\)). Consider a hypothetical molecule with octahedral symmetry showing a single absorption band. If the molecule were to undergo Jahn-Teller distortion, the number of bands would increase as shown in Figure \(\PageIndex{7}\) below:
A similar phenomenon can be seen with IR and Raman vibrational spectroscopy. The number of vibrational modes for a molecule can be calculated using the 3n - 6 rule (or 3n - 5 for linear geometry) rule. If a molecule exhibits an $O_h$ symmetry point group, it will have fewer bands than that of a Jahn-Teller distorted molecule with $D_{4h}$ symmetry. Thus, one could observe Jahn-Teller effects through either IR or Raman techniques. This effect can also be observed in EPR experiments as long as there is at least one unpaired electron.

**Table 1:** Examples of Jahn-Teller distorted complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr₂</td>
<td>$D_{3d}$</td>
<td>Br at 240 pm, Br at 318 pm</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>$D_{2d}$</td>
<td>Cl at 230 pm, Cl at 295 pm</td>
</tr>
<tr>
<td>CuCl₂.2H₂O</td>
<td>$D_{2d}$</td>
<td>O at 193 pm, Cl at 228 pm, Cl at 295 pm</td>
</tr>
<tr>
<td>CsCuCl₃</td>
<td>$D_{3d}$</td>
<td>Cl at 230 pm, Cl at 265 pm</td>
</tr>
<tr>
<td>CuF₂</td>
<td>$D_{3d}$</td>
<td>F at 193 pm, F at 227 pm</td>
</tr>
<tr>
<td>CuSO₄.4NH₃.H₂O</td>
<td>$D_{3d}$</td>
<td>N at 205 pm, O at 259 pm, O at 337 pm</td>
</tr>
<tr>
<td>K₂CuF₄</td>
<td>$C_{2v}$</td>
<td>F at 191 pm, F at 237 pm</td>
</tr>
<tr>
<td>KCuAlF₆</td>
<td>$C_{2v}$</td>
<td>F at 188 pm, F at 220 pm</td>
</tr>
<tr>
<td>CrF₂</td>
<td>$C_{2v}$</td>
<td>F at 200 pm, F at 243 pm</td>
</tr>
<tr>
<td>KCrF₃</td>
<td>$C_{2v}$</td>
<td>F at 214 pm, F at 200 pm</td>
</tr>
</tbody>
</table>
The Jahn-Teller Theorem predicts that distortions should occur for any degenerate state, including degeneracy of the $t_{2g}$ level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the $e_g$ level.

References


Practice Questions

1. Why do $d^3$ complexes not show Jahn-Teller distortions?
2. Does the spin system (high spin v. low spin) of a molecule play a role in Jahn-Teller effects?
3. What spectroscopic method would one utilize in order to observe Jahn-Teller distortions in a diamagnetic molecule?
4. What spectroscopic method(s) would one utilize in order to observe Jahn-Teller distortions in a paramagnetic molecule?
5. Why are Jahn-Teller effects most prevalent in inorganic (transition metal) compounds?

Answers

1. Complexes with $d^3$ electron configurations do not show Jahn-Teller distortions because there is no ground state degeneracy.
2. Yes. Examining the $d^5$ electron configuration, one finds that the high spin scenario contains all singly occupied d orbitals (no degeneracy). However, the low spin $d^5$ electron configuration shows degeneracy, which then leads to possible Jahn-Teller effects.
3. UV-VIS absorption spectroscopy is one of the most common techniques for observing these effects. In general, it is independent of magnetism (diamagnetic v. paramagnetic). Thus, one would see the effect in the spectrum of UV-VIS absorption analysis. Note that EPR requires at least one unpaired electron, and therefore not EPR active.
4. Inorganic, specifically transition metal, complexes are most prevalent in showing Jahn-Teller distortions due to the availability of d orbitals. The most common geometry that the Jahn-Teller effect is observed is in octahedral complexes (see Figures 2, 4, 5 and 6 above) due to the splitting of d orbitals into two degenerate sets. Due to stabilization, the degeneracies are removed, making a lower symmetry and lower energy molecule.

5. In addition to UV-VIS absorption, one can also employ EPR spectroscopy if a molecule possesses an unpaired electron.

Contributors

- Kamran Ghiassi (UC Davis)
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)