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Ligand-Field Theory and Reaction Kinetics

A/Prof Adam Bridgeman
Room: 222
Email: A.Bridgeman@chem.usyd.edu.au
www.chem.usyd.edu.au/~bridge_a/chem2

Office Hours: Monday 2-4pm, Wednesday 2-4pm
Other times by appointment or by chance
Where Are We Going…?

- Week 4: Electronic Spectroscopy
  - Jahn-Teller effect
  - Electronic spectra of multi-electron atoms
  - Nephelauxetic effect and the spectrochemical series
  - Selection rules
  - Charge transfer transitions
- Week 5: Bonding in Complexes, Metalloproteins and Materials
  - $\pi$-Donor and $\pi$-Acceptor Ligands
  - Metal-metal bonding in clusters and solids
  - Role of ligand-field effects in electrochemistry
- Week 6: Kinetics and Ligand-Field Effects
  - Differential rate laws
  - Ligand substitution reactions
By the end of week 4…

Ligand-field (‘d-d’) spectroscopy
- be able to predict/explain number of bands for d\(^{1}\)-d\(^{9}\) (high-spin)
- be able to calculate \(\Delta_{\text{oct}}\) for d\(^{1}\), d\(^{3}\), d\(^{4}\), d\(^{6}\), d\(^{7}\), d\(^{8}\) and d\(^{9}\)
- be able to explain differences in band intensity (spin forbidden, orbitally forbidden, Laporte forbidden)
- be able to explain the appearance of charge transfer transitions
- be able to explain and predict the occurrence of the Jahn-Teller effect and its consequences (structural, spectroscopic, reaction rates)

Resources
- Slides for lectures 1-3
- Shriver and Atkins “Inorganic Chemistry” Chapter 19 (4\(^{\text{th}}\) Edition)
Schedule

• Lecture 1: Electronic absorption spectroscopy
  Jahn-Teller effect and the spectra of $d^1$, $d^4$, $d^6$ and $d^9$ ions

• Lecture 2: Interpreting electronic spectra
  Interelectron repulsion and the nephelauxetic effect

• Lecture 3: Interpreting electronic spectra
  Selection rules and charge transfer transitions
Revision – Ligand-Field Splitting

- In the absence of any ligands, the five d-orbitals of a $M^{n+}$ transition metal ion are degenerate.
- Repulsion between the d-electrons and ligand lone pairs raises the energy of each d-orbital.
Revision – Ligand-Field Splitting

- Two of the d-orbitals point along x, y and z and are more affected than the average (\(e_g\))
- Three of the d-orbitals point between x, y and z and are affected less than the average (\(t_{2g}\))
- The ligand-field splitting (\(\Delta_{oct}\))

\[\Delta_{oct} = \Delta_{t_{2g}} - \Delta_{e_g}\]
Electronic Spectra of $d^1$ Ions

- A $d^1$ octahedral complex can undergo 1 electronic transition
- The ground state $(t_{2g})^1$ comprises three degenerate arrangements
- The excited state $(e_g)^1$ comprises two degenerate arrangements
- The electronic transition occurs at $\Delta_{oct}$
Electronic Spectra of High Spin $d^4$ Ions

- A high spin $d^4$ octahedral complex can also undergo just 1 transition
- The ground state $(t_{2g})^2(e_g)^1$ comprises two degenerate arrangements
- The excited state $(t_{2g})^2(e_g)^2$ comprises three degenerate arrangements
- The electronic transition occurs at $\Delta_{\text{oct}}$
- No other transitions are possible without changing the spin

\[ \text{Cr}^{2+}(\text{aq}) \]
Electronic Spectra of High Spin $d^6$ and $d^9$ Ions

- High spin $d^6$ and $d^9$ octahedral complexes can also undergo just 1 transition.
- The electronic transition occurs at $\Delta_{\text{oct}}$.
- No other transitions are possible changing the spin.
Effect of Distortion on the d-Orbitals

- Pulling the ligands away along z splits $e_g$ and lowers the energy of $d_{z^2}$
- It also produces a \textit{much} smaller splitting of $t_{2g}$ by lowering the energy of $d_{xz}$ and $d_{yz}$
- $\Delta_{\text{oct}} \gg \delta_1 \gg \delta_2$

$e_g$ \hspace{1cm} $t_{2g}$

$\Delta_{\text{oct}}$ \hspace{1cm} $\delta_1$ \hspace{1cm} $\delta_2$

\textbf{tetragonal elongation}
Which Complexes Will Distort?

- Relative to average: $t_{2g}$ go down by $0.4\Delta_{oct}$ in octahedral complex
- Relative to average: $e_g$ go up by $0.6\Delta_{oct}$ in octahedral complex
- Relative to average $d_z^2$ is stabilized by $\frac{1}{2}\delta_1$ and $d_{x^2-y^2}$ is destabilized by $\frac{1}{2}\delta_1$
- Relative to average $d_{xz}$ and $d_{yz}$ are stabilized by $\frac{2}{3}\delta_2$ and $d_{xy}$ is destabilized by $\frac{1}{3}\delta_2$
Which Complexes Will Distort?

\[ \Delta_{\text{oct}} \ggg \delta_1 \ggg \delta_2 \]

<table>
<thead>
<tr>
<th>( d^n )</th>
<th>configuration</th>
<th>degeneracy</th>
<th>LFSE</th>
<th>stabilized?</th>
<th>distortion</th>
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</thead>
<tbody>
<tr>
<td>( t_{2g} )</td>
<td>( e_g )</td>
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<td>(-0.4\Delta_{\text{oct}} - 0.33\delta_2)</td>
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<td>small</td>
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</tbody>
</table>

\[ e_g \quad +0.6 \Delta_{\text{oct}} \quad +\frac{1}{2}\delta_1 \]

\[ t_{2g} \quad -0.4 \Delta_{\text{oct}} \quad -\frac{1}{3}\delta_2 \quad +\frac{2}{3}\delta_2 \]
Which Complexes Will Distort?

\[ \Delta_{\text{oct}} >>> \delta_1 >> \delta_2 \]

<table>
<thead>
<tr>
<th>(d^n)</th>
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<tr>
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<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
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Diagram:
- \(e_g\) with \(+0.6\Delta_{\text{oct}}\)
- \(t_{2g}\) with \(-0.4\Delta_{\text{oct}}\)
- \(+\frac{1}{2}\delta_1\)
- \(-\frac{1}{2}\delta_1\)
- \(+\frac{2}{3}\delta_2\)
- \(-\frac{1}{3}\delta_2\)
Which Complexes Will Distort?

\[ \Delta_{\text{oct}} \gg \delta_1 \gg \delta_2 \]

<table>
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<th>(d^n)</th>
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Which Complexes Will Distort?

\[ \Delta_{\text{oct}} \gg \delta_1 \gg \delta_2 \]

- Low spin:

<table>
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<th>stabilized?</th>
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<tr>
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<td>( t_{2g} )</td>
<td>6 1</td>
<td></td>
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</table>

\[ e_g \quad +0.6 \Delta_{\text{oct}} \quad +\frac{1}{2} \delta_1 \]

\[ t_{2g} \quad -0.4 \Delta_{\text{oct}} \quad -\frac{1}{3} \delta_2 \]
Which Complexes Will Distort?

- Large distortions (always seen crystallographically):
  - high spin $d^4$
  - low spin $d^7$
  - $d^9$
  - $d^{10}$

- Small distortions (often not seen crystallographically):
  - $d^1$
  - $d^2$
  - low spin $d^4$
  - low spin $d^5$
  - high spin $d^6$
  - high spin $d^7$
Jahn-Teller Theorem

- This is a general result known as the Jahn-Teller theorem:

  *Any* molecule with a degenerate ground state will distort

- antibonding

- bonding
Effect on Spectroscopy

- From Slide 6, there is one d-d transition for an octahedral $d^1$ ion.
- From Slide 15, a $d^1$ complex will distort and will not be octahedral.
- There are now 3 possible transitions.
- (A) is in infrared region and is usually hidden under vibrations.
- (B) and (C) are not usually resolved but act to broaden the band.

![Diagram of d-orbit transitions for Ti$^{3+}$(aq)](image-url)
Summary

By now you should be able to....

• Show why there is a single band in the visible spectrum for $d^1$, high spin $d^4$, high spin $d^6$ and $d^9$ octahedral complexes
• Obtain the value of $\Delta_{\text{oct}}$ from the spectrum of these ions
• Show the electronic origin of the (Jahn-Teller) distortion for high spin $d^4$, low spin $d^7$ and $d^9$ octahedral complexes
• Predict whether any molecule will be susceptible to a Jahn-Teller distortion
• Explain how the Jahn-Teller effect leads to broadening of bands in the UV/Visible spectrum

Next lecture

• Effects of interelectron repulsion
Semester 2 2003

With the aid of a labeled diagram, briefly describe how the operation of the Jahn Teller effect may give rise to an axially compressed tetragonal geometry in the complexes of a $d^9$ metal ion.
Consider the high-spin complexes, \([\text{Mn(OH}_2)_6]^{3+}\) and \([\text{Mn(OH}_2)_6]^{2+}\). The lowest energy d-d band in the spectrum of the \([\text{Mn(OH}_2)_6]^{3+}\) complex is at 476 nm.

Relevant constants and conversions: \(c = \text{speed of light} = 3.00 \times 10^8 \text{ m s}^{-1}\); \(h = \text{Planck constant} = 6.63 \times 10^{-34} \text{ J s}\); \(N_A = \text{Avogadro constant} = 6.02 \times 10^{23} \text{ mol}^{-1}\); Faraday constant = 96,485 C mol\(^{-1}\).

(i) Give the d-electron configuration for each of the Mn centres; and draw appropriate d-orbital energy diagrams and illustrate the distributions of the d electrons within them.

(ii) Explain which of the two complexes has Jahn-Teller distortions in the ground state and how this will effect the electronic absorption spectrum of the complex with such a distortion.

(iii) Calculate the Ligand Field Stabilisation Energy (LFSE) in kJ mol\(^{-1}\) for each of the above complexes.