COMMONWEALTH OF AUSTRALIA

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Schedule

• Last Week: Electronic spectroscopy
  Interelectron repulsion, covalency and spin-orbit coupling

• Lecture 4: Re-cap

• Lecture 5: \(\pi\)-Acceptor Ligands and Biology
  \(N_2\), \(CO\), \(N_2\) and \(O_2\) complexes

• Lecture 6: M-M bonding
  Multiple bonds and metal clusters
Summary of the Last Lecture

Spin selection rule
- The spin cannot change during an electronic transition
- ‘Relaxed’ by spin-orbit coupling for heavy elements

Orbital selection rule
- ‘d-d’ transitions cannot occur
- ‘Relaxed’ by d-p mixing in complexes without centre of inversion (e.g. tetrahedron)

Laporte selection rule
- No ‘d-p’ mixing possible in complexes with a centre of inversion (e.g. octahedron or square planar complex)
- ‘Relaxed’ due to molecular vibrations

Charge transfer transitions
- LMCT, MLCT and IVT – cover up ‘d-d’ if in visible region
Selection Rules and Band Intensity

- The height of the band in the spectrum is called the 'molar extinction coefficient' - symbol $\varepsilon$:

<table>
<thead>
<tr>
<th>$\varepsilon$ (mol(^{-1}) cm(^{-1}))</th>
<th>type of transition</th>
<th>type of complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3} - 1$</td>
<td>spin forbidden</td>
<td>octahedral d(^5) complexes (e.g. [Mn(H(_2)O)(_6)]^{2+}$)</td>
</tr>
<tr>
<td></td>
<td>orbitally forbidden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Laporte forbidden</td>
<td></td>
</tr>
<tr>
<td>$1 - 10$</td>
<td>spin forbidden</td>
<td>tetrahedral d(^5) complexes (e.g. [MnCl(_4)]^{2-+}$)</td>
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<tr>
<td></td>
<td>orbitally forbidden</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10 - 10^2$</td>
<td>spin allowed</td>
<td>octahedral and square planar complexes</td>
</tr>
<tr>
<td></td>
<td>orbitally forbidden</td>
<td></td>
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<tr>
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<td></td>
<td>orbitally forbidden</td>
<td></td>
</tr>
<tr>
<td>$&gt; 10^3$</td>
<td>LMCT, MLCT, IVT</td>
<td></td>
</tr>
</tbody>
</table>
Oxidation States of Manganese: +7

- $[\text{MnO}_4]^-$: the permanganate ion

  - deep purple colour
  - (absorbs green/yellow $\sim 18000 \text{ cm}^{-1}$)

  - high metal charge (+7) makes it highly oxidizing (and easily reduced)
  - O $\rightarrow$ M charge transfer occurs at relatively low energy (in the visible region)
  - LMCT - orbitally allowed and spin allowed so highly intense
Oxidation States of Manganese: VI

• \([\text{MnO}_4]^{2-}\): the manganate ion

\[
2\text{MnO}_4^- (\text{aq}) + C_6H_{10}(l) + 2\text{OH}^- (\text{aq}) \rightarrow 2\text{MnO}_4^{2-} (\text{aq}) + C_6H_{10}(\text{OH})_2(\text{aq})
\]

➢ high metal charge (+6) makes it highly oxidizing (and easily reduced)

➢ O \rightarrow M \text{ charge transfer occurs at relatively low energy (in the visible region but at higher energy than for permanganate)}

➢ LMCT - orbitally allowed and spin allowed so highly intense

➢ \(d^1\) - ligand-field transition lost under LMCT bands

---

deep green colour

(absorbs purple \(\sim 25000 \text{ cm}^{-1}\))
Oxidation States of Manganese: IV and II

- **MnO$_2$:** manganese dioxide  
  \[ \text{MnO}_4^{2-}(aq) + 3\text{H}^+(aq) + \text{C}_6\text{H}_{10}(l) \rightarrow 2\text{MnO}_2(s) + \text{C}_6\text{H}_{10}(\text{OH})_2(aq) \]

- **Mn$^{2+}$(aq):** manganese ion  
  \[ \text{MnO}_2(s) + 4\text{H}^+(aq) + 2\text{Fe}^{2+}(aq) \rightarrow \text{Mn}^{2+}(aq) + 2\text{Fe}^{3+}(aq) + 2\text{H}_2\text{O}(l) \]

- Pale pink
- Brown

- Low metal charge (+2) so O → M charge transfer in ultraviolet
- High spin d$^5$ - all transitions are spin forbidden
- Similar *colour* to permanganate but very different *intensity*
Manganese(II)

- Mn$^{2+}$ d$^5$: all transitions are spin forbidden:
  - become possible through spin-orbit coupling
  - spin-forbidden transitions are *extremely* weak for 3d metal complexes
  - bands due to spin-forbidden transitions are normally hidden under the spin allowed bands
  - for d$^5$, there are no spin-allowed bands allowing spin-forbidden bands to be seen
Manganese(II)

- Mn$^{2+}$ d$^5$: all transitions are spin forbidden
  - turning a spin over requires energy even if the orbital is not changed
  - called a “spin flip transition”
  - as the orbital occupation does not change, there is very little change in the M-L bond lengths

![Diagram showing eg and t$_{2g}$ orbitals in the ground and excited states.](image-url)
Octahedral and Tetrahedral Cu(II)

- Cu$^{2+}$

\[
[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \leftrightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)
\]

- pale blue
  - absorbs $\sim 13000$ cm$^{-1}$

- green
  - absorbs $\sim 10000$ cm$^{-1}$

- $d^9$: one $d$-$d$ transition with frequency = $\Delta_{\text{oct}}$ or $\Delta_{\text{tet}}$
  - $\Delta_{\text{oct}} > \Delta_{\text{tet}}$ (fewer ligands in a tetrahedron)
- Higher intensity for tetrahedral complex
  - $d$-$p$ mixing possible in tetrahedron
  - $d$-$p$ mixing only due to vibrations for octahedron
Octahedral and Tetrahedral Co(II)

- \( \text{Co}^{2+} \)

\[
[\text{Co(H}_2\text{O)}_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \leftrightarrow [\text{CoCl}_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O} (\text{l})
\]

- pale pink absorbs at 8680, 18400 and 19200 cm\(^{-1}\)
- blue absorbs at 4780, 15700 and 16230 cm\(^{-1}\)

- \( \text{d}^7 \): three d-d transitions
  - \( \Delta_{\text{oct}} = v_2 - v_1 = (18400 - 8680) = 9720 \text{ cm}^{-1} \)
- Higher intensity for tetrahedral complex
  - d-p mixing possible in tetrahedron
  - d-p mixing only due to vibrations for octahedron
Summary

By now you should be able to

• explain the *number* of bands
• obtain $\Delta_{\text{oct}}$ from spectrum for $d^1, d^3, d^4, d^6, d^7, d^8$ and $d^9$
• predict relative intensity of spin-allowed vs spin forbidden, octahedral vs tetrahedral and ligand-field vs charge-transfer transitions