

**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

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## 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

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## Selection Rules and Band Intensity

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

	$\epsilon$ (mol <sup>-1</sup> cm <sup>-1</sup> )	type of transition	type of complex
very pale colours  ↓  intense colours	$10^{-3} - 1$	spin forbidden orbitally forbidden, Laporte forbidden	octahedral d <sup>5</sup> complexes (e.g. [Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> )
	$1 - 10$	spin forbidden orbitally forbidden,	tetrahedral d <sup>5</sup> complexes (e.g. [MnCl <sub>4</sub> ] <sup>2-</sup> )
	$10 - 10^2$	spin allowed, orbitally forbidden Laporte forbidden	octahedral and square planar complexes
	$10 - 10^3$	spin allowed, orbitally forbidden	tetrahedral complexes
	$> 10^3$	LMCT, MLCT, IVT	

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## Oxidation States of Manganese: +7



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

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

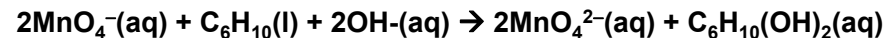


- high metal charge (+7) makes it highly oxidizing (and easily reduced)
- $\text{O} \rightarrow \text{M}$  charge transfer occurs at relatively low energy (in the visible region)
- LMCT - orbitally allowed and spin allowed so highly intense

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## Oxidation States of Manganese: VI

- $[\text{MnO}_4]^{2-}$ : the manganate ion



- high metal charge (+6) makes it highly oxidizing (and easily reduced)
- $\text{O} \rightarrow \text{M}$  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

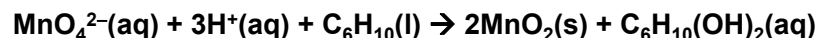
deep green colour  
(absorbs purple  $\sim 25000 \text{ cm}^{-1}$ )

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## Oxidation States of Manganese: IV and II

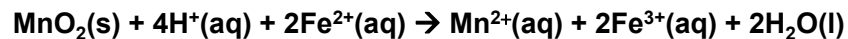
- $\text{MnO}_2$ : manganese dioxide

brown



- $\text{Mn}^{2+}(\text{aq})$ : manganese ion

pale pink

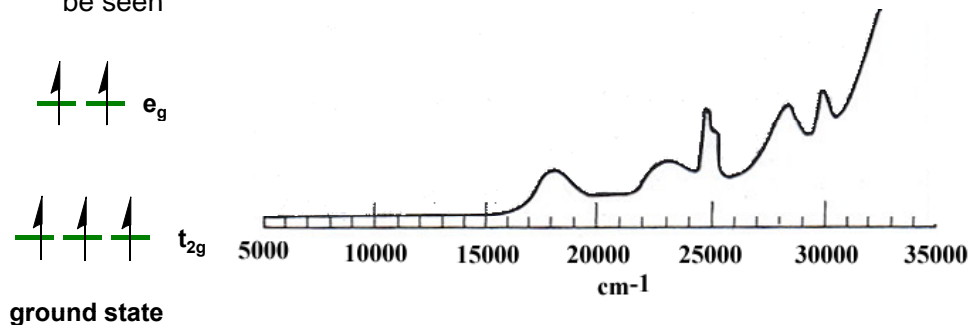


- low metal charge (+2) so  $\text{O} \rightarrow \text{M}$  charge transfer in ultraviolet
- high spin  $d^5$  - all transitions are spin forbidden
- similar *colour* to permanganate but very different *intensity*

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## Manganese(II)

- $\text{Mn}^{2+} d^5$ : 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

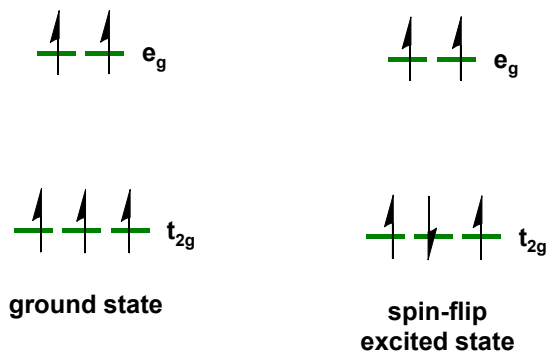


AJB lecture 3

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## Manganese(II)

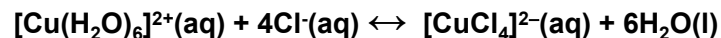
- $\text{Mn}^{2+}$   $d^5$ : all transitions are spin forbidden
  - turning a spin over requires energy even if the orbital is not changed
  - called a “spin flip transition”
  - as the orbital occupation does not change, there is very little change in the M-L bond lengths



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## Octahedral and Tetrahedral $\text{Cu(II)}$

- $\text{Cu}^{2+}$



pale blue

absorbs  $\sim 13000 \text{ cm}^{-1}$

green

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

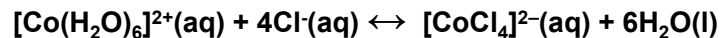
- $d^9$ : one d-d transition with frequency =  $\Delta_{\text{oct}}$  or  $\Delta_{\text{tet}}$ 
  - $\Delta_{\text{oct}} > \Delta_{\text{tet}}$  (fewer ligands in a tetrahedron)
- Higher intensity for tetrahedral complex
  - d-p mixing possible in tetrahedron
  - d-p mixing only due to vibrations for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



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## Octahedral and Tetrahedral $\text{Co(II)}$

- $\text{Co}^{2+}$



pale pink

absorbs at 8680,  
18400 and 19200  $\text{cm}^{-1}$

blue

absorbs at 4780,  
15700 and 16230  $\text{cm}^{-1}$

- $d^7$ : three d-d transitions
  - $\Delta_{\text{oct}} = \nu_2 - \nu_1 = (18400 - 8680) = 9720 \text{ cm}^{-1}$
- Higher intensity for tetrahedral complex
  - d-p mixing possible in tetrahedron
  - d-p mixing only due to vibrations for octahedron



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## 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

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