B.Sc. Semester-IV
Core Course-VIII (CC-VIII)
Inorganic Chemistry

I. Coordination Chemistry

5. CFSE in Weak and Strong Fields

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Coordination Chemistry: 20 Lectures

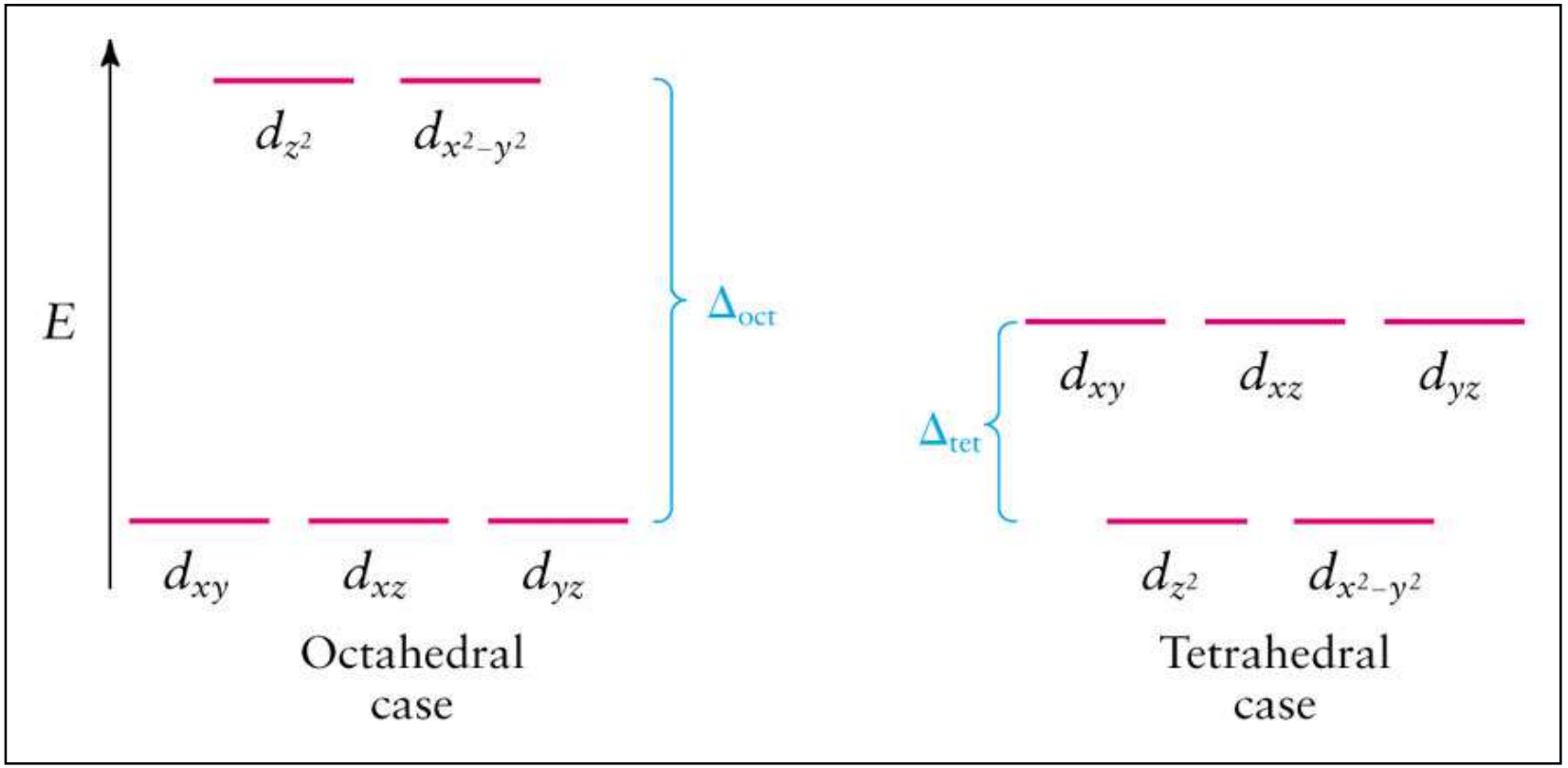
Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of 10 Dq (Δo), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of 10 Dq (Δo, Δt). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coverage:

1. CFSE, Measurement of 10 Dq (Δo)
2. CFSE in Weak and Strong Fields
3. Spectrochemical Series
4. Pairing Energy
5. Factors Affecting the Magnitude of 10Dq (Δo, Δt)

Crystal Field Diagrams for Octahedral and Tetrahedral Complexes



Magnitude of Δ Depends on Following Factors

1. **Oxidation state of the metal ion**

$[Ru(H_2O)_6]^{2+}$ 19800 cm^{-1}

$[Ru(H_2O)_6]^{3+}$ 28600 cm^{-1}

2. **Number of ligands and geometry**

$\Delta_t < \Delta_o$ $\Delta_t = 4/9\Delta_o$

3. **Nature of the ligand**

$I^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < \ldots.. CN^- < CO$

Crystal Field Splitting Energy (CFSE)

- In Octahedral field, configuration is: $t_{2g}^{x} e_{g}^{y}$
- Net energy of the configuration relative to the average energy of the orbitals is:

$$= (-0.4x + 0.6y)\Delta_O$$

$$\Delta_O = 10\ Dq$$

BEYOND d^3

- In weak field: $\Delta_O < P$, => $t_{2g}^{3} e_{g}^{1}$
- In strong field $\Delta_O > P$, => t_{2g}^{4}
- P - paring energy

High-Spin and Low-Spin Complexes for $3d^4$ – $3d^7$ ions

- Octahedral 3*d* Complexes

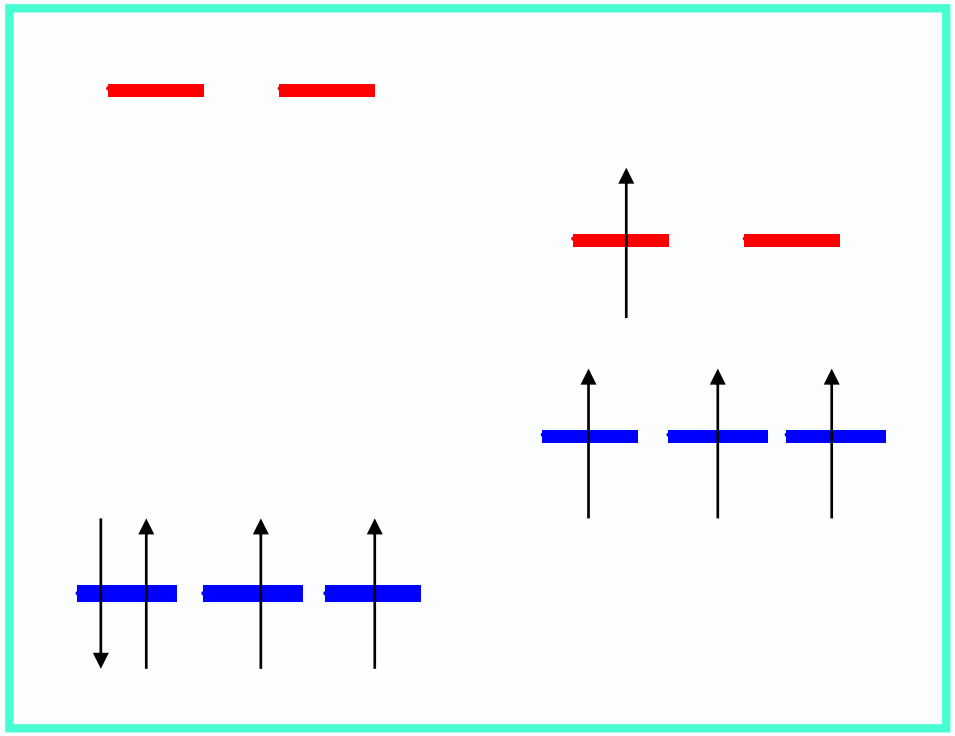
  $\Delta_o \approx$ P(pairing energy)

  Both low-spin ($\Delta_o \leq P$) and high-spin ($P \geq \Delta_o$) complexes are found.

- Tetrahedral Complexes

  $\Delta_{Td} = 4/9\ \Delta_o$ hence $P >> \Delta_{Td}$ and tetrahedral complexes are always high spin

When the 4th electron is assigned it will either go into the higher energy e_g orbital at an energy cost of D_q or be paired at an energy cost of P, the pairing energy.



d^4

Strong field = Low spin (2 unpaired)

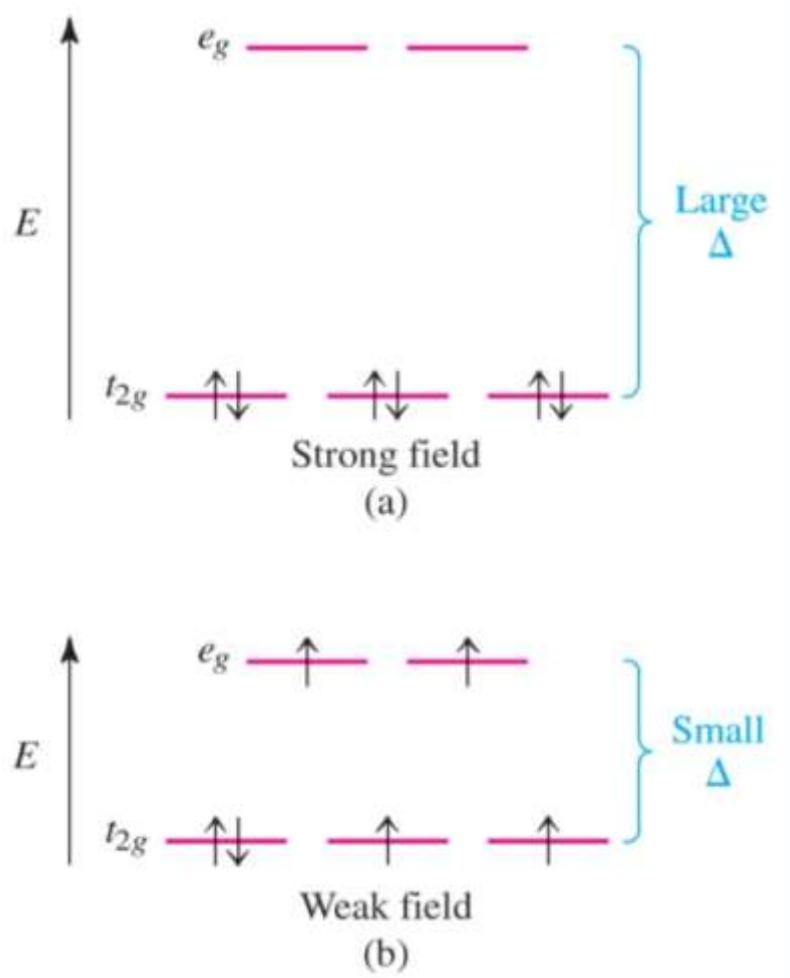
Weak field = High spin (4 unpaired)

$\mathbf{P < \Delta_o}$ $\mathbf{P > \Delta_o}$

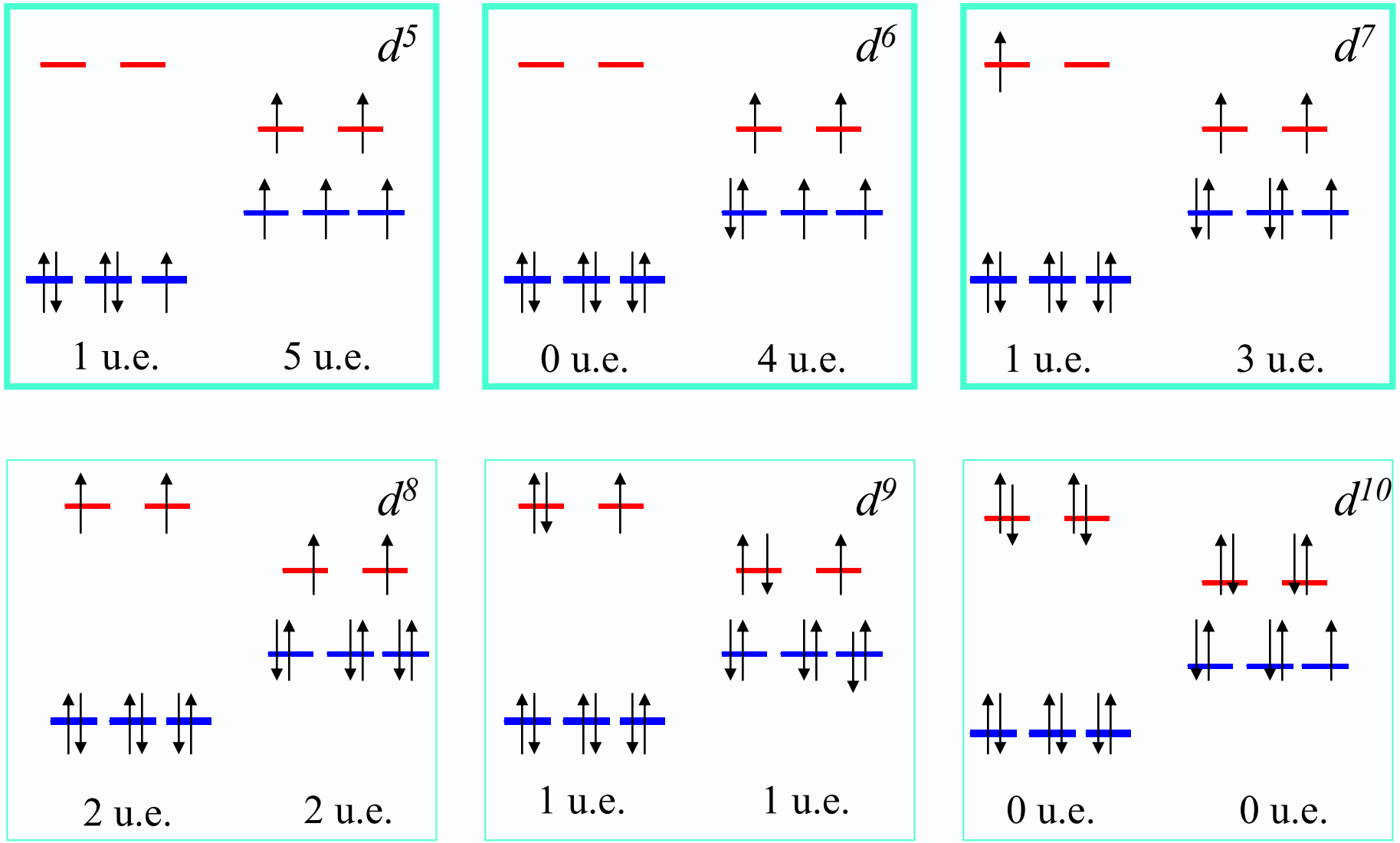
Coulombic repulsion energy and exchange energy

Possible Electron Arrangements in the Split 3*d* - Orbitals in an Octahedral Complex of Co^{3+}

- Strong - field (low - spin):
  - Yields the minimum number of unpaired electrons.
- Weak - field (high - spin):
  - Gives the maximum number of unpaired electrons.
- Hund's rule still applies.

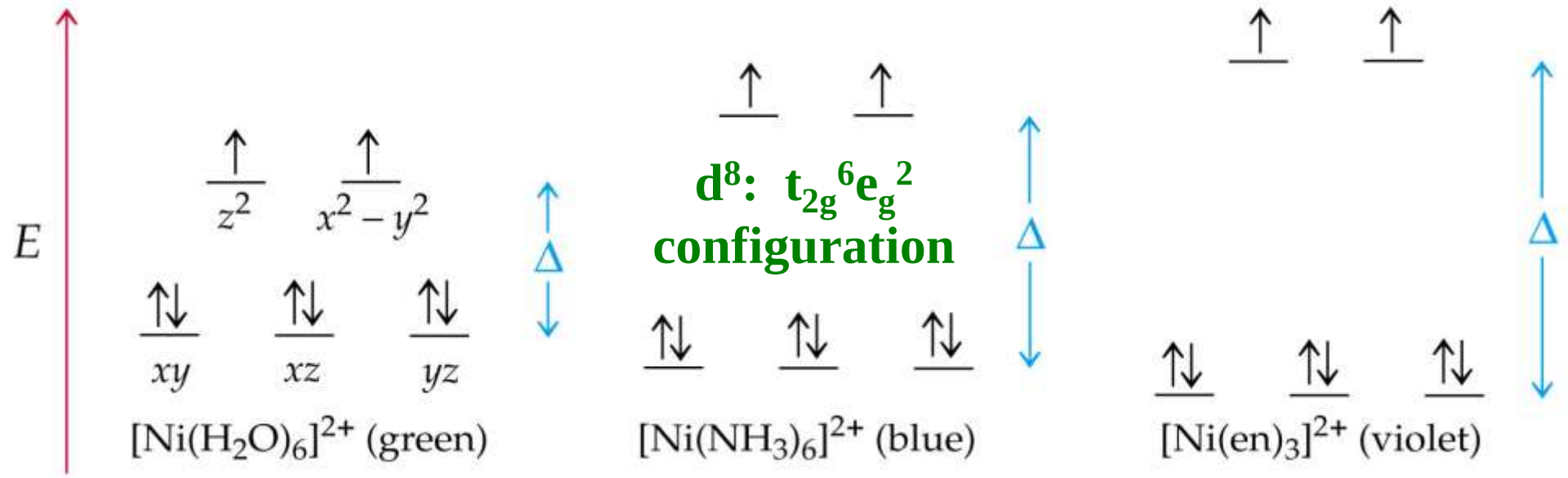


Placing Electrons in *d*-Orbitals



u.e. – Unpaired Electrons

The Splitting of *d*-Orbitals Depends on the Ligands Bonded to Ni^{2+} in It's Octahedral Complexes



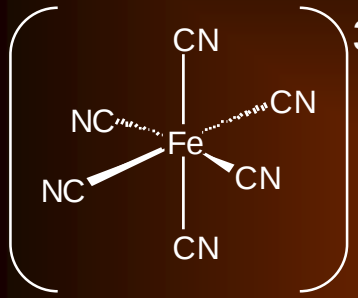
The Spectrochemical Series

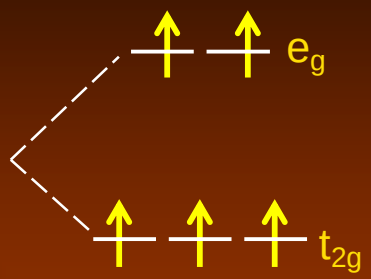
Weak-field ligands $I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < CN^-$ Strong-field ligands

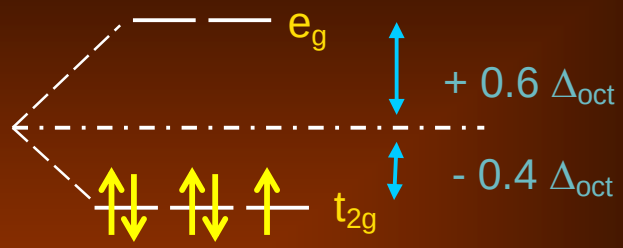
Increasing Δ

What is the CFSE of $[Fe(CN)_6]^{3-}$?

C.N. = 6 ∴ O_h Fe(III) ∴ d^5 h.s. l.s. CN^- = s.f.l.







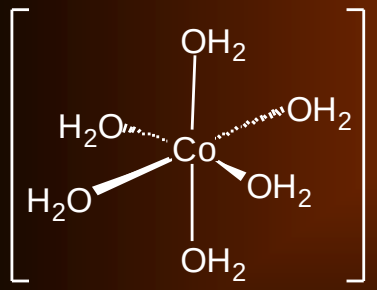
CFSE = 3 x - 0.4 Δ_{oct} + 2 x 0.6 Δ_{oct} = 0

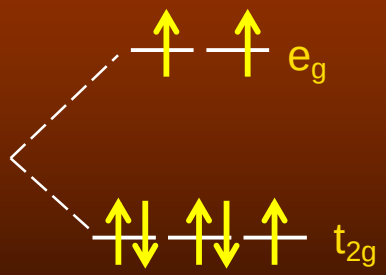
CFSE = 5 x - 0.4 Δ_{oct} + 2P = - 2.0 Δ_{oct} + 2P

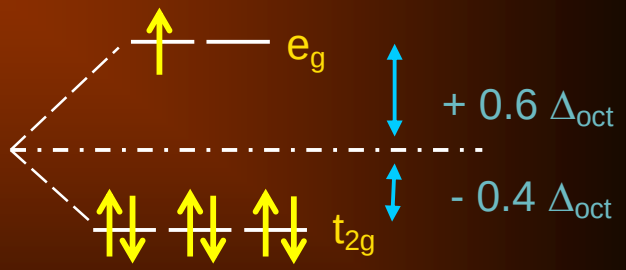
Because CN^- is a strong field ligand, CFSE = - 2.0 Δ_{oct} + 2P

If the CFSE of $[Co(H_2O)_6]^{2+}$ is -0.8 Δ_{oct}, what spin state is it in?

C.N. = 6 ∴ O_h Co(II) ∴ d^7 h.s. l.s.







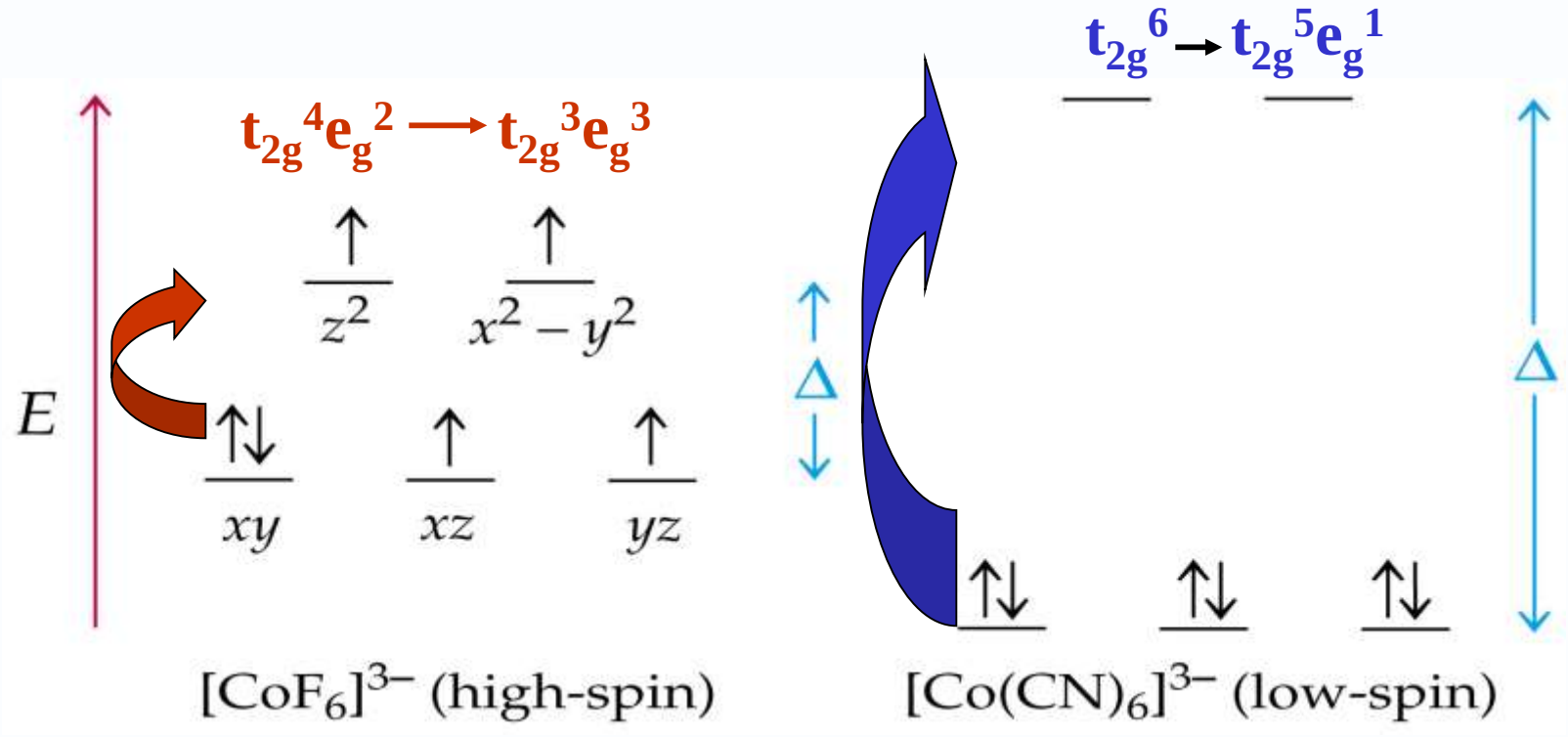
CFSE = (5 x - 0.4 Δ_{oct}) + (2 x 0.6 Δ_{oct}) +2P

= - 0.8 Δ_{oct}+2P

CFSE = (6 x - 0.4 Δ_{oct}) + (0.6 Δ_{oct}) +3P

= - 1.8 Δ_{oct} + P

Correlation of High and Low Spin Complexes with Spectrochemical Series



Weak-field ligands $I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < CN^-$ Strong-field ligands

Increasing Δ

Factors Influencing the Magnitude of Δ-Splitting

- Oxidation State

  $\Delta_o (M^{3+}) > \Delta_o(M^{2+})$

  e.g. Δ_o for Fe(III) > Fe(II).

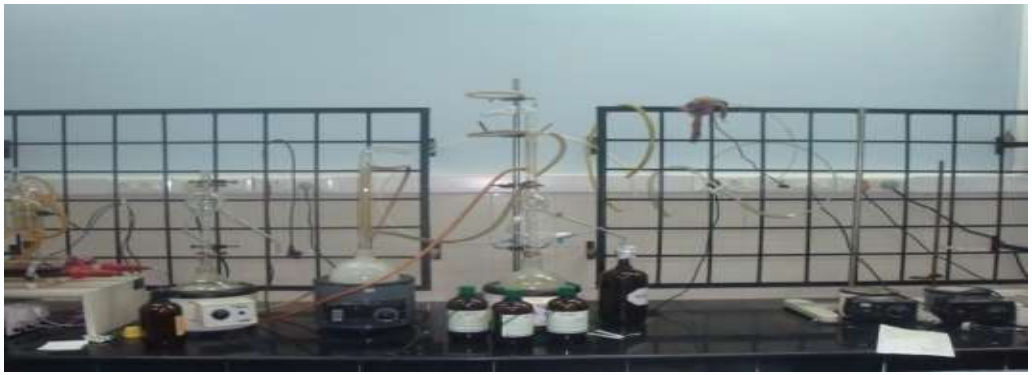
  The higher oxidation state is likely to be low-spin

- 5*d* > 4*d* >3*d*

  e.g. Os(II) > Ru(II) > Fe(II)

  All 5*d* and 4*d* complexes are low-spin.

Thank You



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