

LECTURE 28

1. For each of the following ions, (i) **draw** an crystal field splitting diagrams to show orbital occupancies in both weak and strong octahedral fields, and (ii) indicate the number of unpaired electrons in each case. **Label** the diagrams (iii) weak or strong field, (iv) high spin or low spin (as appropriate), (v) with the names of the d-orbitals, and (vi) with the appropriate orbital sets e_g and t_{2g} designators.

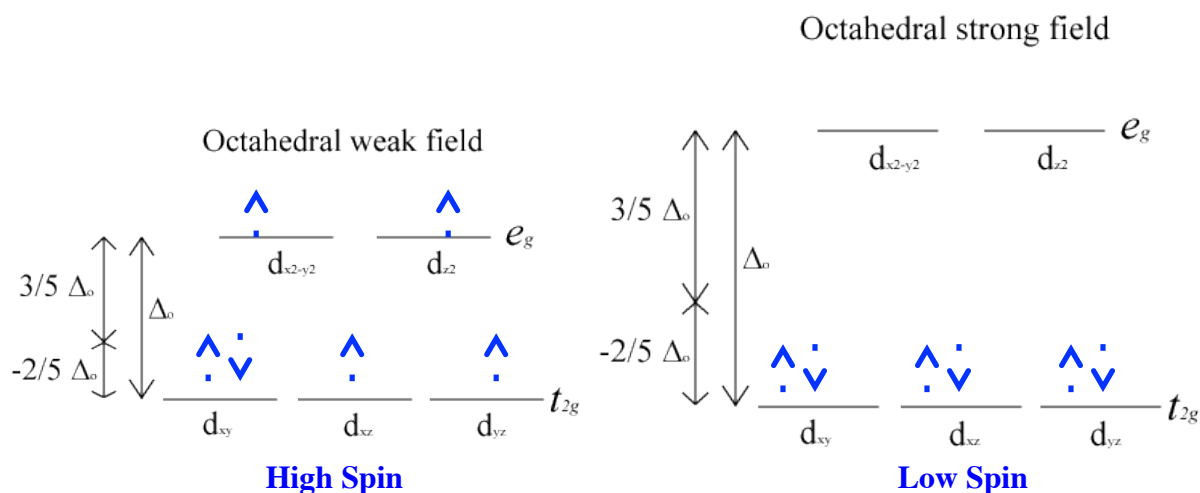
(a) Fe^{2+}

(b) Cr^{3+}

(c) Cd^{2+}

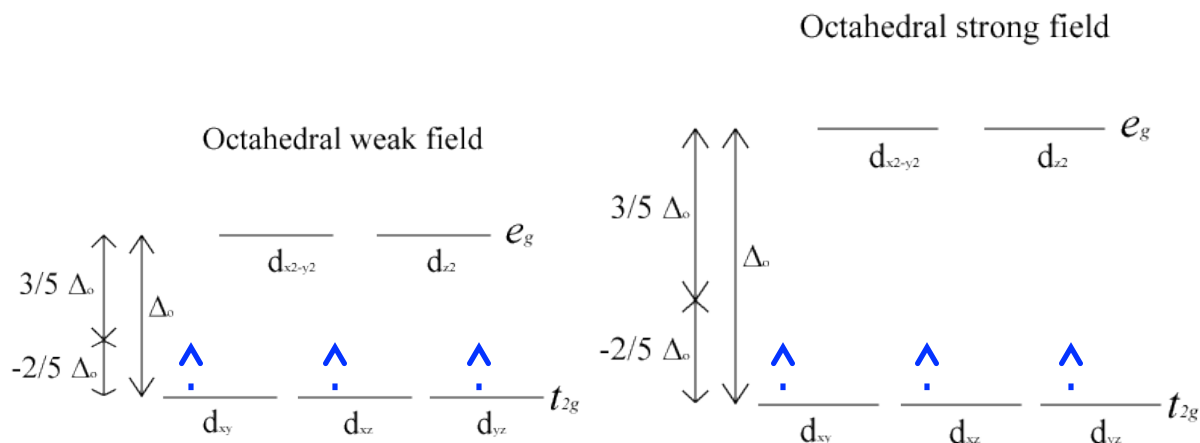
(a) Fe^{2+}

The Fe^{2+} ion is a d^6 case. The weak field case has **four unpaired electrons** and the strong field has **zero unpaired electrons**.



(b) Cr^{3+}

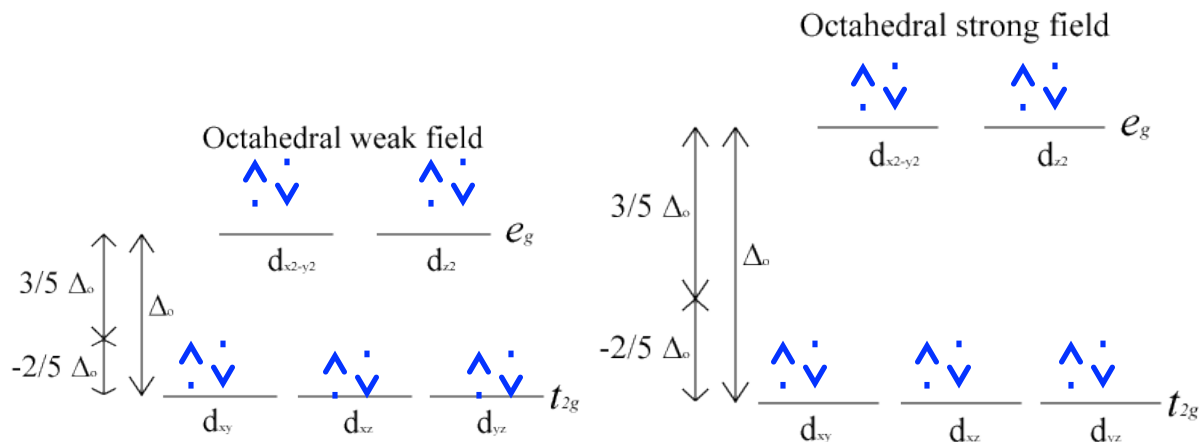
The Cr^{3+} ion is a d^3 case. Both weak and strong field complexes have **three unpaired electrons**. Note: you do not need to show both diagrams, as they are the same



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(c) Cd^{2+}

The Cd^{2+} ion is a d^{10} case. Both weak and strong field complexes have **no unpaired electrons**. Note: you do not need to show both diagrams, as they are the same.



2. For each of the above ions in problem one, (i) Write the expected d^n electron configuration and (ii) calculate the CFSE (both the high and low spin states, as appropriate, and indicate pairing energies PE if electrons are paired).

(a) (i) *Weak octahedral field (high spin):* d^n configuration is $(t_{2g})^4(e_g)^2$
Strong octahedral field (low spin): d^n configuration is $(t_{2g})^6$

(ii) *Weak octahedral field (high spin):* $-\frac{2}{5} \Delta_o + 1\text{P.E.}$

Strong octahedral field (low spin): $-\frac{12}{5} \Delta_o + 3\text{P.E.}$

(b) (i) In both a weak octahedral field (high spin) and strong octahedral field (low spin), it has the ground-state configuration of $(t_{2g})^3$

(ii) $-\frac{6}{5} \Delta_o$

(c) (i) In both a weak octahedral field and a strong octahedral field the configuration

$(t_{2g})^6(e_g)^4$

(ii) $0 \cdot \Delta_o + 5\text{P.E.}$

3. For $[\text{CoCl}_6]^{3-}$

(a) Determine the coordination number of the cobalt

(b) Determine the oxidation number of the cobalt

(c) Predict whether this compound is high or low spin. Briefly explain your answer.

(d) Estimate the octahedral crystal field splitting energy (Δ_o) in joules/mol if the wavelength most intensely absorbed is 740nm.

(a) The coordination number of the cobalt is **6**

(b) The oxidation number on the cobalt is **+3**.

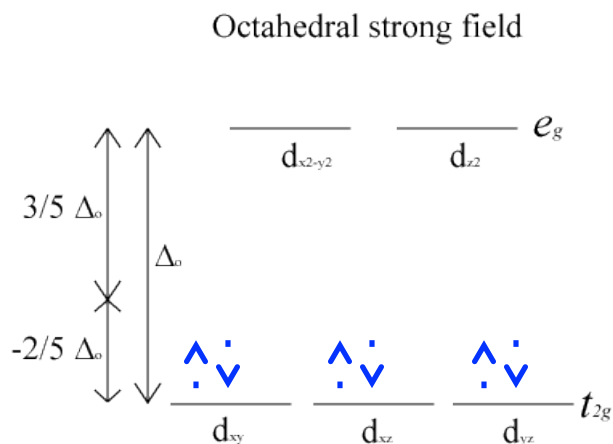
(c) We would predict that the compound be high spin. Cl^- is a weak field ligand.

(d) **$1.6 \times 10^5 \text{ J mol}^{-1}$** .

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4. Octahedral platinum(IV) complexes are used in protein crystallography to help determine three-dimensional protein structures. If the octahedral crystal field splitting energy (Δ_o) is large for these complexes,

- Predict whether they are diamagnetic or paramagnetic
- Write the expected d^n electron configuration

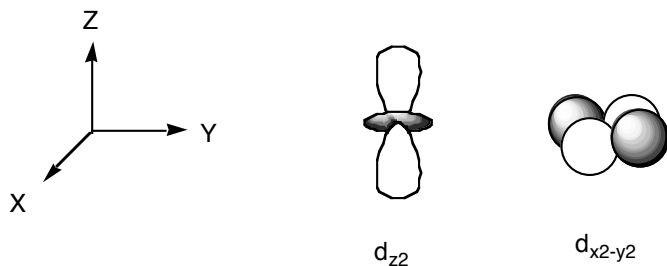


- Diamagnetic.**
- $(t_{2g})^6$

5. For the following, consider a field that has a z-axis that is vertical, a y-axis that is horizontal, and x-axis that is coming out of page.

- Draw pictures of the $d_{x^2-y^2}$ and d_{z^2} orbitals
- Predict the relative energy of $d_{x^2-y^2}$ in an octahedral crystal field compared to a linear crystal field that is along the y-axis
- Predict the relative energy of d_{z^2} in an octahedral crystal field compared to a linear crystal field that is along the y-axis
- Predict the relative energies of $d_{x^2-y^2}$ to d_{z^2} to each other in a(n)
 - octahedral field
 - linear field along the y-axis.

(a)



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(b) The $d_{x^2-y^2}$ orbital in the octahedral complex should be more destabilized, as they will be interacting directly with ligands on both the x- and y-axis, whereas the linear complex will only be directly interacting with the orbital along the y-axis.

(c) The d_z^2 orbital in the octahedral complex should be more destabilized, as the majority of the d_z^2 orbital's density lies on the z-axis. The octahedral complex has ligands on the z-axis to directly interact with the d_z^2 orbital, unlike a linear complex that is along the y-axis.

(d) (i) The d_z^2 and $d_{x^2-y^2}$ orbitals should be degenerate. The orbitals will both be destabilized equally.

(ii) The d_z^2 orbital should be a lower energy (stabilized) than the $d_{x^2-y^2}$ orbital. No ligands are directed toward the d_z^2 orbitals in the linear (along y-axis) case whereas ligands are directed toward $d_{x^2-y^2}$.

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