Reading For Today: 16.8-16.11 in 4th and 5th editions

Topic: I. Spectroscopic Theory: Both Ligand Type and Geometry Make a Difference
II. Crystal Field Theory: Tetrahedral Case
III. Crystal Field Theory: Square Planar Case
IV. Other Geometries and Applications

I. Spectroscopic Theory: Both Ligand Type and Geometry Make a Difference

Nickel Demonstration
Recall the color of light transmitted is complementary to the color of light that is absorbed. Red is complementary to green; orange is complementary to blue; yellow is complementary to violet.

\[
\text{[NiCl}_6\text{]}^{4-} \text{ (greenish)}
\]
Absorbs \( \lambda \) that is __________; so \( \Delta_o \) is __________; Cl\(^-\) is a _________field ligand

\( \downarrow \text{H}_2\text{O} \)

\[
\text{[Ni(H}_2\text{O})_6\text{]}^{2+} \text{ (blue-green)}
\]
Absorbs \( \lambda \) that is ________________ than above; so \( \Delta_o \) is ________________ than above;

\text{H}_2\text{O} \text{ is a ________________field ligand than above}

\( \downarrow \text{EDTA} \)

\[
\text{Ni-EDTA (blue)}
\]
Absorbs \( \lambda \) that is ________________ than above; so \( \Delta_o \) is ________________ than above;

\text{EDTA} \text{ is a ________________field ligand than above}

Also

\[
\text{[Ni(H}_2\text{O})_6\text{]}^{2+} \text{ (blue-green)}
\]
\( \downarrow \text{dimethylglyoxine (dmgH)} \)

\[
\text{Ni-(dmgH)}_2 \text{ (red)}
\]
Absorbs \( \lambda \) that is ________________ than above; so \( \Delta \) is ________________; but the complex is square planar and not octahedral. Geometry matters. Square planar geometry must allow for a large splitting of the energy of the d-orbitals.

(We will look at this in a few minutes.)

\begin{center}
\begin{tabular}{cccccccc}
violet & blue & green & yellow & orange & red \\
\hline
\( \lambda \) & 400nm & 430nm & 490nm & 560nm & 580nm & 620nm & 800nm
\end{tabular}
\end{center}
II. Crystal Field Theory: Tetrahedral Case

- There is __________ repulsion between the ligand negative point charges and the d-orbitals that are 45° off axis (d_{yz}, d_{xz}, d_{xy}) than there is between the ligand negative point charges and the d-orbitals that are on axis (d_{z}^{2} and d_{x}^{2}-y^{2}).

- As a result of the above, there is greater orbital destabilization for d_{yz}, d_{xz}, d_{xy} than for d_{z}^{2} and d_{x}^{2}-y^{2} (of octahedral).

- d_{z}^{2} and d_{x}^{2}-y^{2} have the __________ energy with respect to each other (degenerate).

- d_{yz}, d_{xz}, d_{xy} have the same energy with respect to each other (degenerate).

- The tetrahedral crystal field splitting energy ($\Delta_{T}$) is __________ than for octahedral complexes because the point charges are not directed at any orbital set.
• $\Delta_o$ and $\Delta_T$ are the octahedral and tetrahedral crystal field splitting energy, respectively.
• Again, the positioning of the orbitals is opposite for tetrahedral and octahedral.
• $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals are now called $t_2$ and $d_{x^2-y^2}$ and $d_{z^2}$ are $e$.
• $\Delta_T$ is ________________ than $\Delta_o$ because the point charges are not directed at any orbital set in a tetrahedral crystal field.
• Because $\Delta_T$ is small, many tetrahedral complexes are ________________.
• You can assume that they are all high spin!
• Because the overall energy in the tetrahedral crystal field is maintained, $t_2$ orbitals go up in energy by $2/5$, and the $e$ orbitals go down in energy by $3/5$.

Tetrahedral Example for Cr$^{3+}$

(a) figure out d electron count

(b) draw tetrahedral crystal field splitting diagram, label orbitals, and fill in electrons

(c) Write $d^n$ electron configuration:

(d) How many unpaired electrons?

(e) If this compound is [CrCl$_6$]$^{3-}$ and the wavelength of most intensely absorbed light is 740 nm, predict the color of the complex.
III. Crystal Field Theory: Square Planar Case

Square planar

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ligand point charges directed at orbitals

**Destabilized** compared to all other d-orbitals

much less repulsion than in octahedral crystal field.

Less repulsion than for \( d_{x^2-y^2} \) and for \( d_{xy} \)

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stabilized compared to \( d_{xy} \) and \( d_{x^2-y^2} \)

stabilized compared to \( d_{xy} \) and \( d_{z^2} \)

---

repulsion than for \( d_{x^2-y^2} \), \( d_{z^2} \), and \( d_{xy} \).

Less repulsion than for \( d_{x^2-y^2} \) since orbitals are 45° off axis in \( d_{xy} \).

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The overall energy of the square planar crystal field is also maintained, but the relative energies of each of the d-orbitals are more complicate d and you are not expected to know them.
IV. Other Geometries

What about square pyramidal?

\[ d_{z^2} \] is \_____________ for square pyramidal compared to square planar
\[ d_{xz} \] and \[ d_{yz} \] are \_____________ for square pyramidal compared to square planar
\[ d_{x^2-y^2} \] and \[ d_{xz} \] are \_____________ degenerate for square pyramidal

And Applications to metalloenzymes (Nickel enzyme example)

Nickel dependent enzymes are responsible for removing ~100 million tons of CO from the atmosphere each year and producing ~1 trillion kg of acetate from greenhouse gases and other carbon sources. We want to know what these nickel-based catalysts look like, so that we can mimic this chemistry.

To probe the geometry of the nickel cofactor, spectroscopy was used and it was found that the Ni\(^{2+}\) (d\(^8\)) center was diamagnetic. Predict whether it has square planar, tetrahedral, or octahedral geometry?

\[ d_{x^2-y^2} \]

\[ E \]

\[ d_{x^2-y^2} \]

\[ d_{z^2} \]

\[ d_{xy} \]

\[ d_{xy} \]

\[ d_{xz} \]

\[ d_{yz} \]

\[ d_{x^2-y^2} \]

\[ d_{z^2} \]

\[ d_{xy} \]

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Answer:
The Ni center in the enzyme must be \______________.