5.111 Lecture Summary #29 **Friday, November 21, 2014**

Reading For Today: 16.8-16.11 in 4th and 5th editions
Reading for Lecture #30: 14.1-14.5 in 5th ed and 13.1-13.5 in 4th ed.

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.

$[NiCl_6]^{4-}$ (greenish)

Absorbs λ that is _____; so Δ_o is _____ ;Cl^- is a _____field ligand

⬇H_2O

$[Ni(H_2O)_6]^{2+}$ (blue-green)

Absorbs λ that is _____than above; so Δ_o is _____than above;

H_2O is a _____field ligand than above

⬇EDTA

Ni-EDTA (blue)

Absorbs λ that is _____than above; so Δ_o is _____than above;

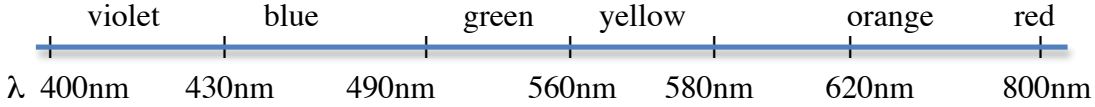
EDTA is a _____field ligand than above

Also **$[Ni(H_2O)_6]^{2+}$ (blue-green)**

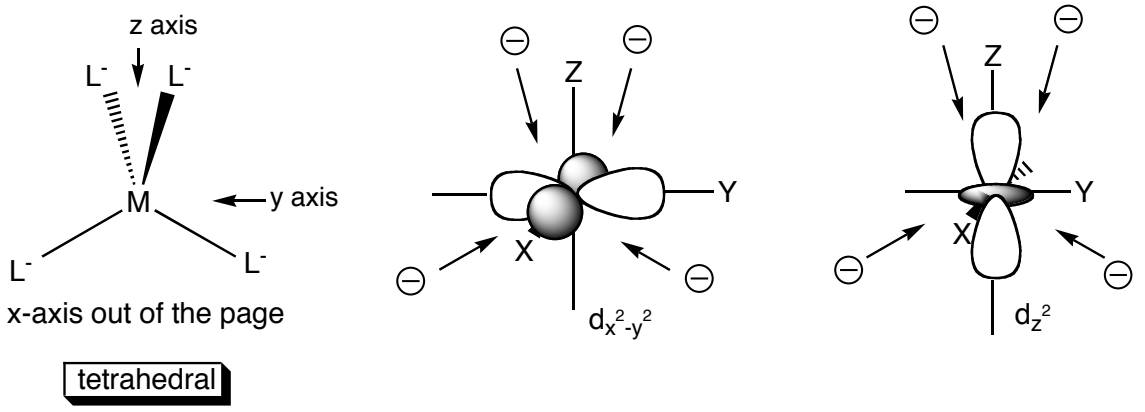
⬇dimethylglyoxine (dmgH)

Ni-$(dmgH)_2$ (red)

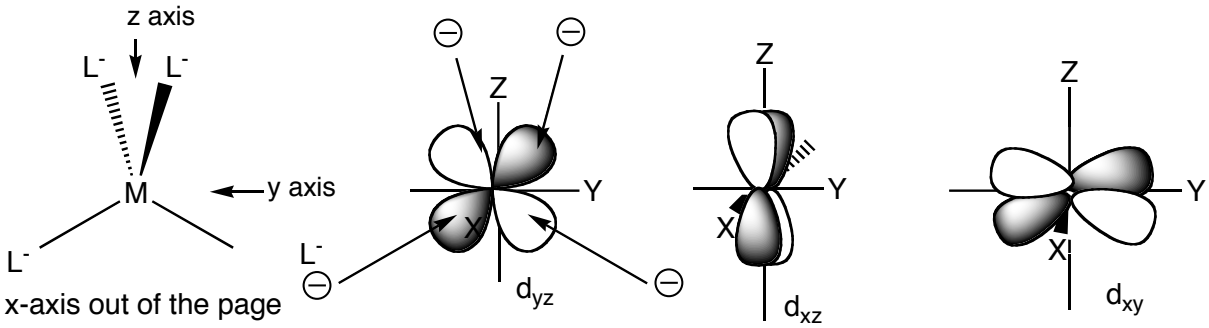
Absorbs λ that is _____than above; so Δ is _____; but the complex is square planar and not octahedral. Geometry matters. Square planar geometry must allow for a large splitting of the energy of the d-orbitals. (We will look at this in a few minutes.)



II. Crystal Field Theory: Tetrahedral Case



tetrahedral



tetrahedral

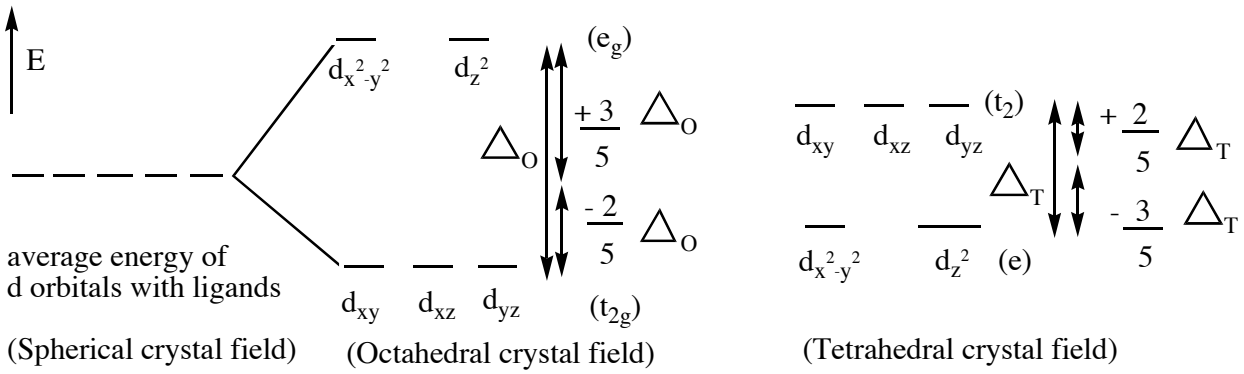
- There is _____repulsion between the ligand negative point charges and the d-orbitals that are 45° off axis (d_{yz}, d_{xz}, d_{xy}) than there is between the ligand negative point charges and the d-orbitals that are on axis (d_{z^2} and $d_{x^2-y^2}$).

- As a result of the above, there is greater orbital destabilization for d_{yz}, d_{xz}, d_{xy} than for $d_{x^2-y^2}$ and d_{z^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 (Δ_T) is _____than for octahedral complexes because the point charges are not directed at any orbital set.

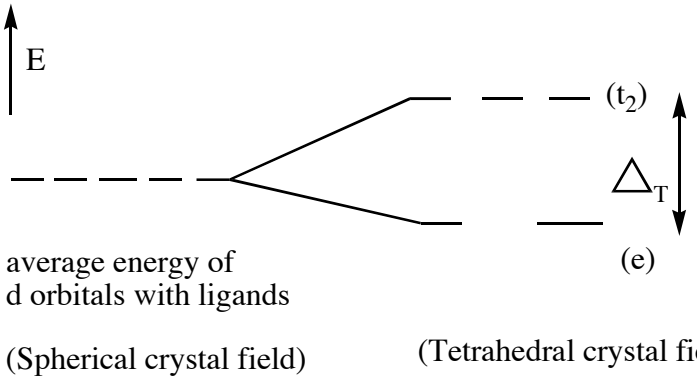


- Δ_o and Δ_T are the octahedral and tetrahedral crystal field splitting energy, respectively
- Again, the positioning of the orbitals is opposite for tetrahedral and octahedral
- d_{xy}, d_{xz}, and d_{yz} orbitals are now called $\mathbf{t_2}$ and $d_{x^2-y^2}$ and d_{z^2} are **e**
- Δ_T is _____ than Δ_o because the point charges are not directed at any orbital set in a tetrahedral crystal field.
- Because Δ_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

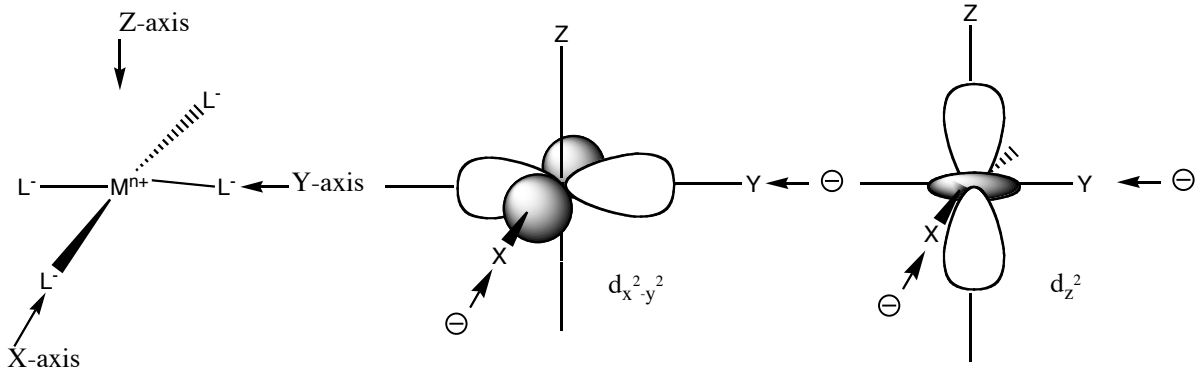


(c) Write d^n electron configuration:

(**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.

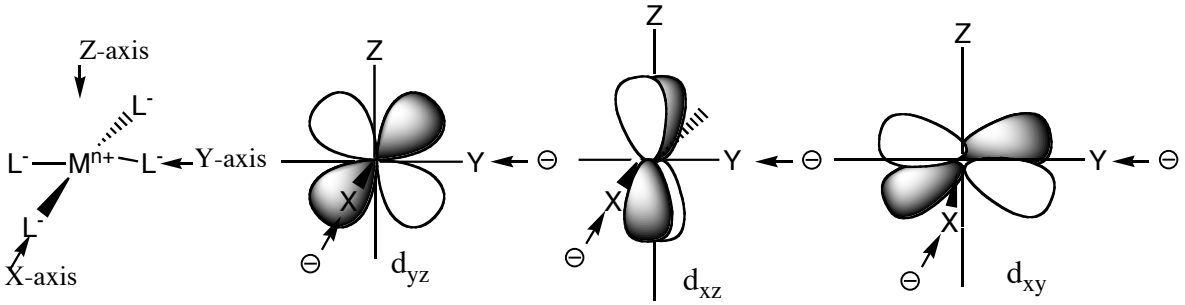
III. Crystal Field Theory: Square Planar Case



Square planar

_____ repulsion ligand point charges directed at orbitals **Destablized** 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}

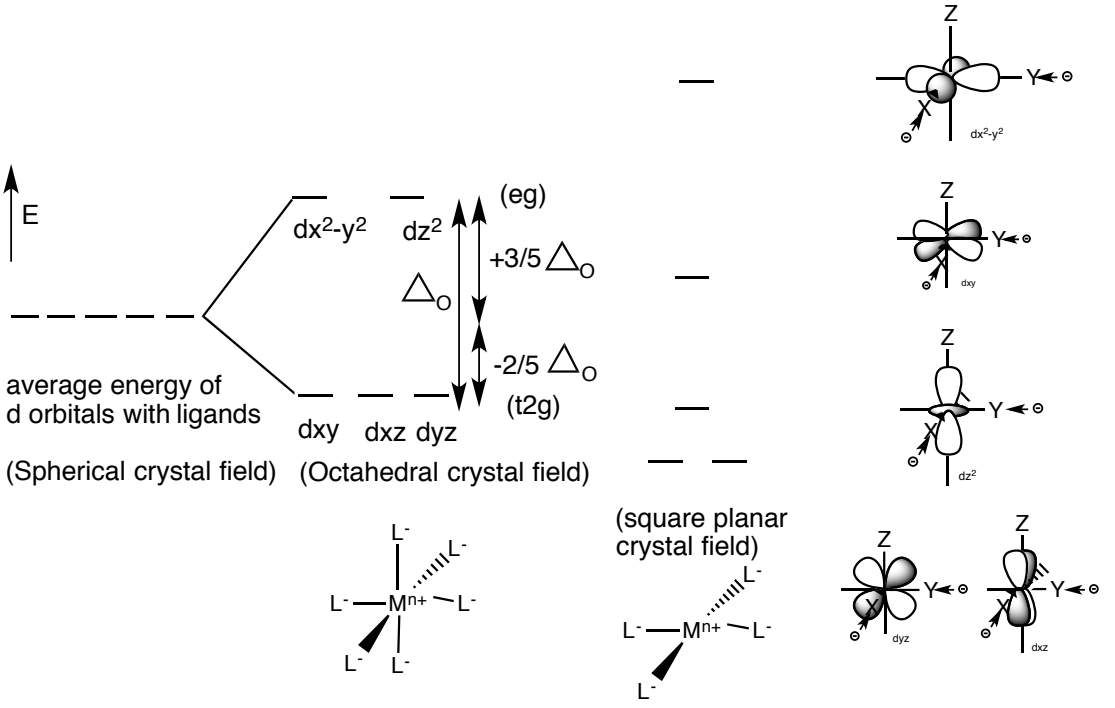


Square planar

stabilized compared to d_{xy} and $d_{x^2-y^2}$

stabilized compared to d_{xy} and $d_{x^2-y^2}$

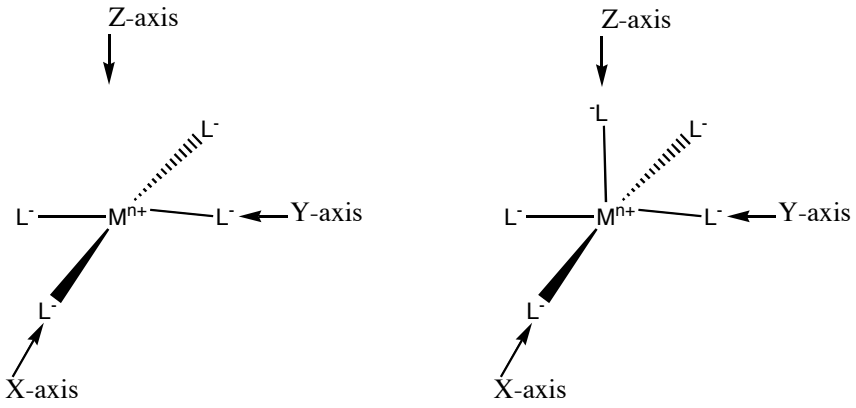
_____repulsion than for d_{xz}, d_{xz}, and d_{z^2}. **Less** repulsion than for $d_{x^2-y^2}$ since orbitals are 45° off axis in d_{xy}.



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?



square planar square pyramidal

d_{z^2} is _____ for square pyramidal compared to square planar

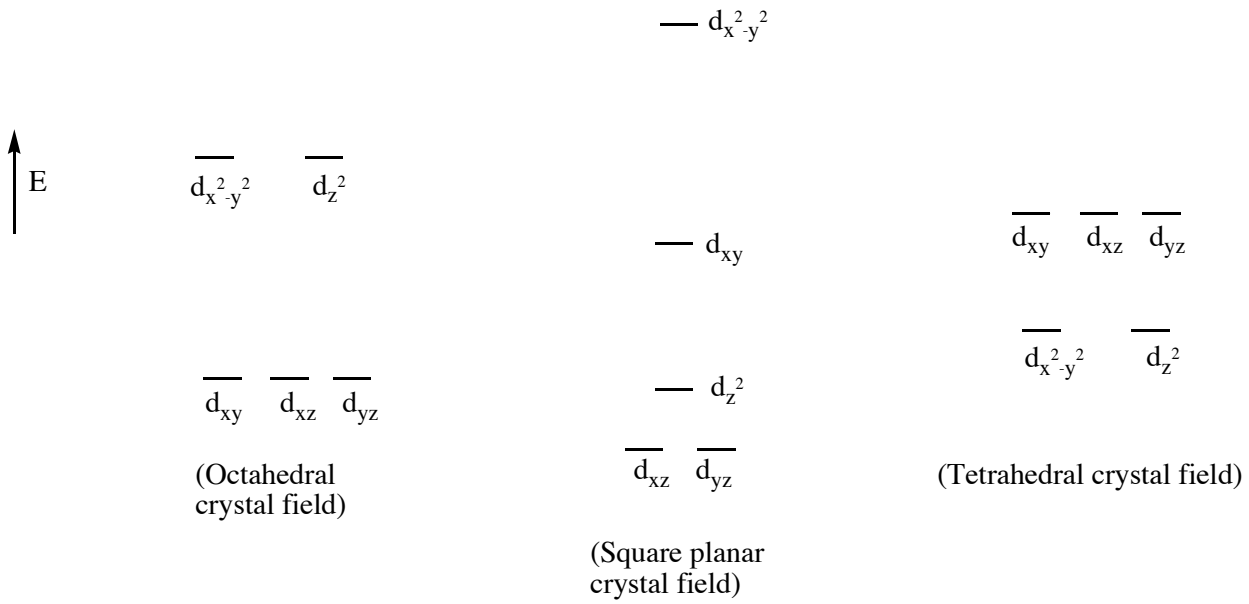
d_{xz} and d_{yz} are _____ for square pyramidal compared to square planar

$d_{x^2-y^2}$ 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?



Answer:
The Ni center in the enzyme must be _____.

5.111 Principles of Chemical Science
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