5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #29

Transition Metals

Topic: Crystal Field Theory Continued, and Magnetism Chapter 16 p 631-637

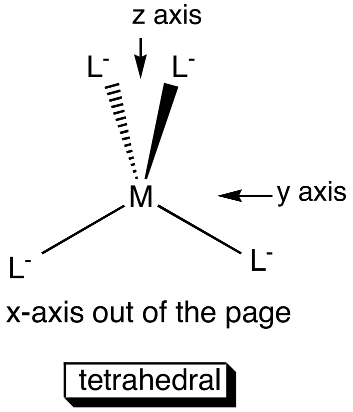
Magnetism

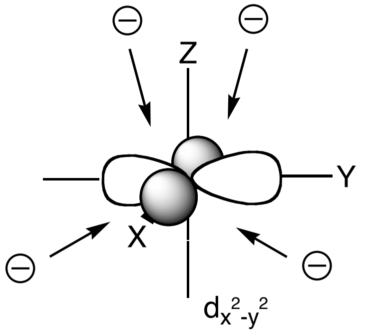
Compounds possessing unpaired electrons are paramagnetic (attracted by magnetic field); those in which the electrons are paired are diamagnetic (repelled by magnetic field).

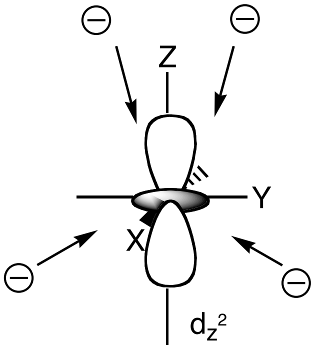
Crystal Field Theory: Octahedral Case (See Lecture #28)

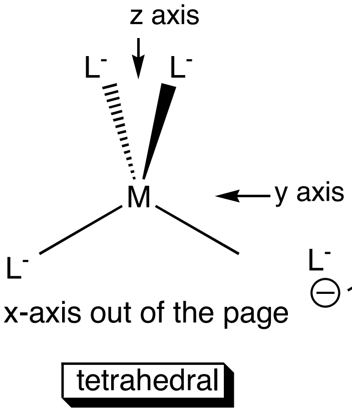
Crystal Field Theory: Tetrahedral Case

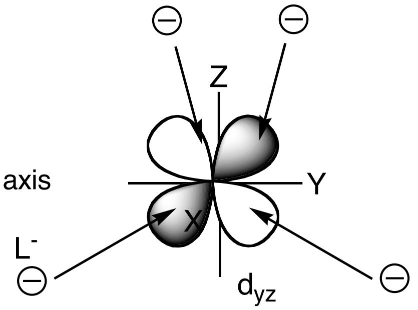
The tetrahedral crystal field splitting energy (Δ_T) is smaller than for octahedral complexes because the point charges are not directed at any orbital set.

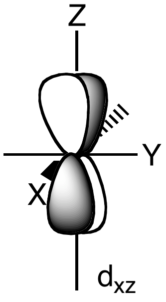


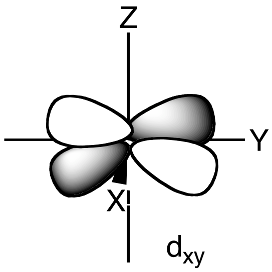




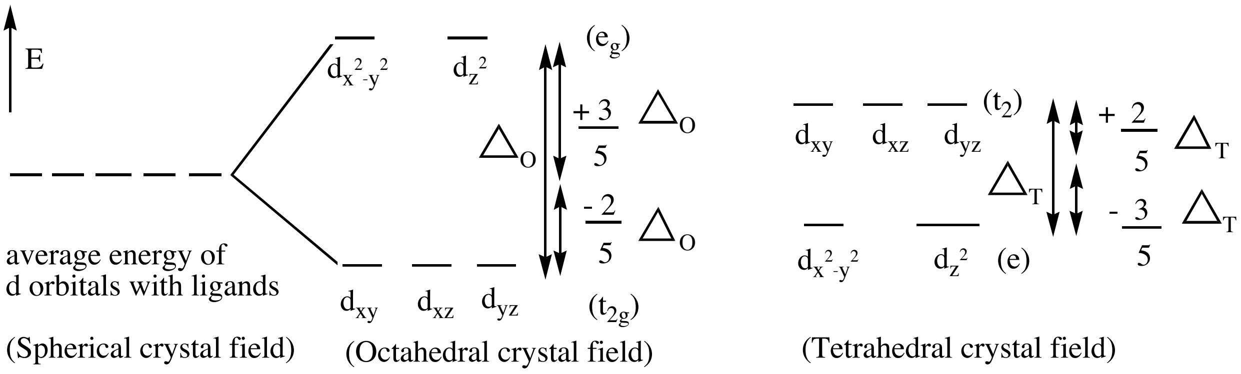








Geometry of tetrahedral complexes result in greater orbital destabilization for d_{yz}, d_{xz}, d_{xy} than for $d_{x^2-y^2}$ and d_{z^2} (opposite of octahedral). There is more repulsion between the ligand negative point charges and the d-orbitals that are 45° off axis (d_{yz}, d_{xz}, d_{xy}) than there is between the ligand negative point charges and the d-orbitals that are on axis (d_{z^2} and $d_{x^2-y^2}$). d_{yz}, d_{xz}, d_{xy} have the same energy with respect to each other (degenerate). d_{z^2} and $d_{x^2-y^2}$ have the same energy with respect to each other (degenerate).



Δ_T is the tetrahedral crystal field splitting energy

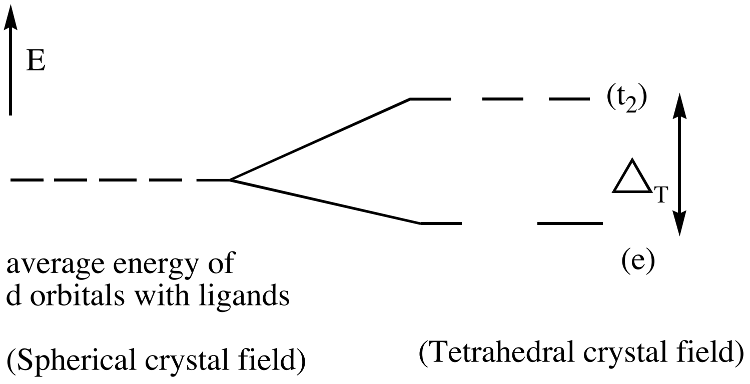
Again, Δ_T is smaller than Δ_o because the point charges are not directed at any orbital set in a tetrahedral crystal field. Because Δ_T is small, many tetrahedral complexes are high spin. You can assume that they are all high spin.

Because the overall energy in the tetrahedral crystal field is maintained, t_2 orbitals (d_{xy}, d_{xz}, and d_{yz}) go up in energy by 2/5, and the e orbitals ($d_{x^2-y^2}$ and d_{z^2}) go down in energy by 3/5.

Tetrahedral Example for Cr^{3+}

(**a**) figure out d electron count

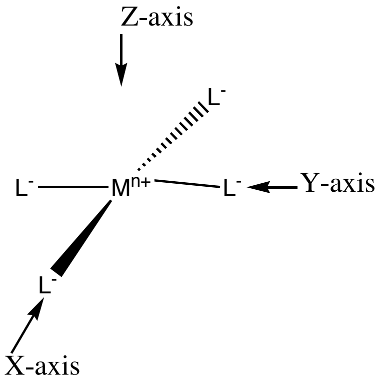
(**b**) draw tetrahedral crystal field splitting diagram, label orbitals, and fill in electrons

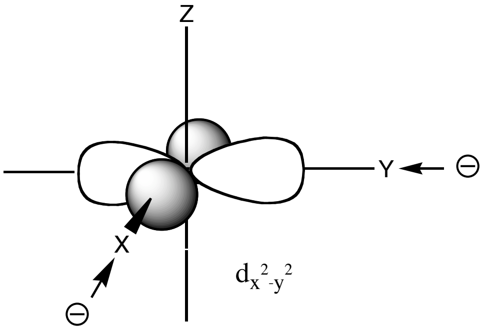


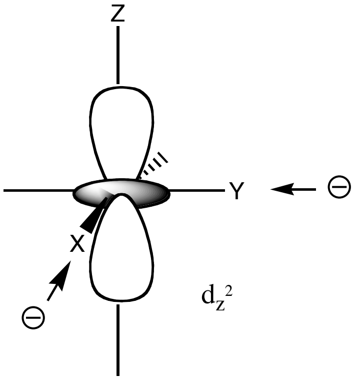
(**c**) Write d^n electron configuration:

(**d**) How many unpaired electrons?

Crystal Field Theory: Square Planar Case



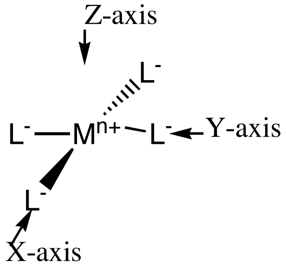


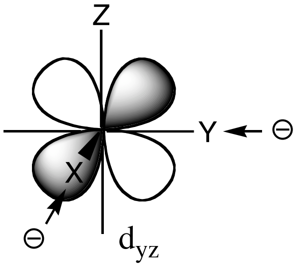


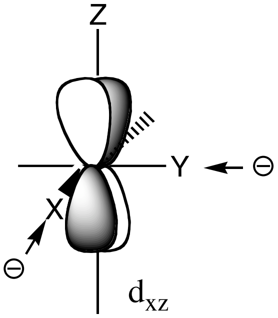
Square planar

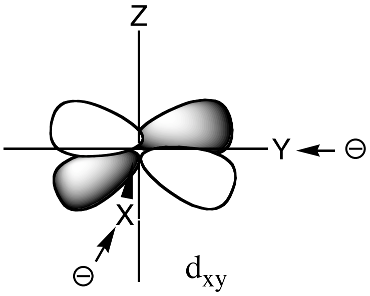
lots of repulsion
ligand point charges
directed at orbitals
Destablized compared
to all other d-orbitals

much less repulsion than
in octahedral crystal field.
Less repulsion than
for $d_{x^2-y^2}$ and for d_{xy}







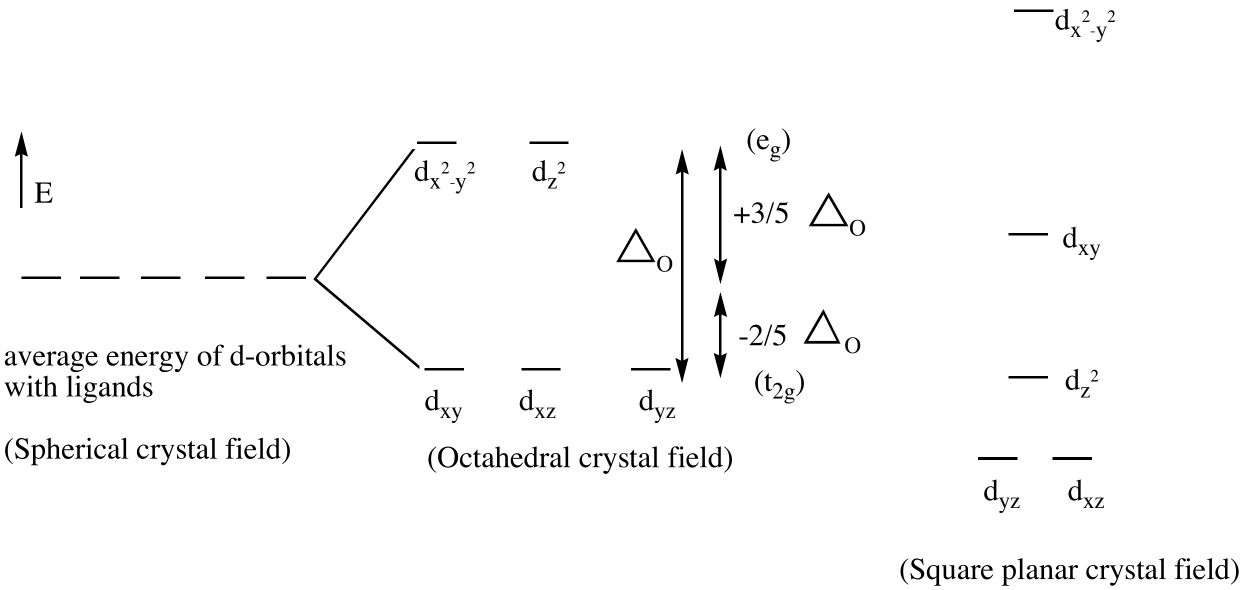


Square planar

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

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

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



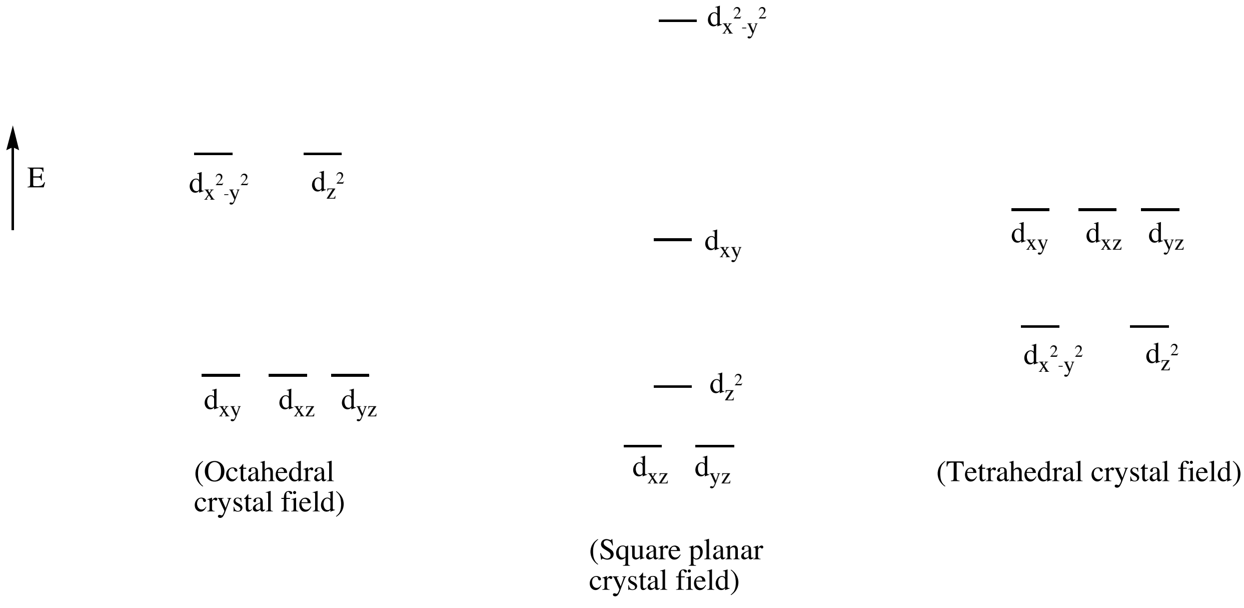
(Spherical crystal field)

(Octahedral crystal field)

(Square planar crystal field)

The overall energy of the square planar crystal field is maintained as well, but the relative energies of each of the d-orbitals are more complicated and you are not expected to know them.

<u>Putting it all together</u>: If a Ni^{2+} (d^8) center in an enzyme is found to be diamagnetic, does it have square planar, tetrahedral, or octahedral geometry?



(Octahedral crystal field)

(Square planar crystal field)

(Tetrahedral crystal field)

Answer:

An example of a square planar Ni site in Nature is found in enzyme called acetyl-CoA synthase.