

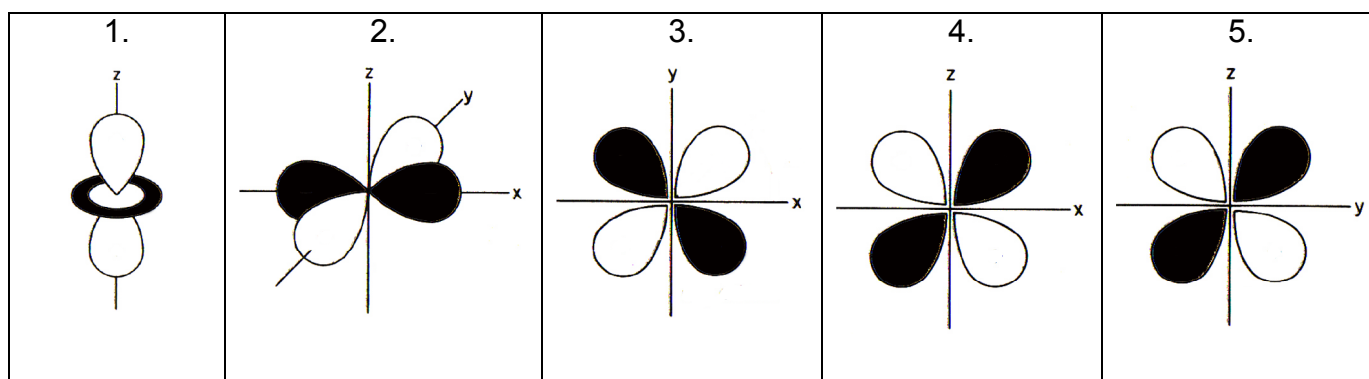
**Inorganic Chemistry with Doc M.**  
**Fall Semester, 2011**  
**Day 17. Transition Metals Complexes II:**  
**Crystal Field Theory**

<b>Name(s):</b>	<b>Element:</b>

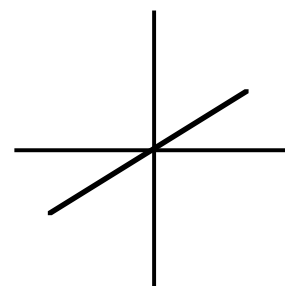
**Topics:**

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| 1. The d-orbitals and the octahedron             | 5. $\Delta_o$ and the spectrochemical series |
| 2. Crystal field splitting of the energy diagram | 6. Tetrahedral complexes                     |
| 3. High-spin and low-spin complexes              | 7. Square planar complexes                   |
| 4. Crystal field stabilization energy            | 8. Other geometries                          |

**A. The d-orbitals.** It is necessary know the d-orbitals by name for this discussion. Name these orbitals.



**B. The energy diagram.** We have routinely sketched the energies of the five d-orbitals as five energetically degenerate lines. Consider an octahedron complex  $ML_6^m$ , where  $m$  = charge on complex. Sketch the six ligands as "L"s and the metal as "M" on the figure at right.



The d-orbitals are no longer equivalent to one another in an octahedral field of ligands. The relative energies of the five orbitals will change. In the first two orbitals shown above (1 and 2), the lobes are directed towards the ligands. If the d-orbitals contained electrons (at least  $d^1$ ), that electron would "prefer" not being in either of those two orbitals due to electron-electron repulsion. (a) Do the other three orbitals (3 – 5) offer a better alternative to the first two in terms of reduced electron (from the d-orbital) – electron (from the E group on the ligand) repulsion? Explain.

(a)	(b)

(b) In Box (b) above, sketch an energy diagram with the five d-orbitals all having the same energy — as they would if no ligands were present. To the right of that, sketch the relative energies of the five d-orbitals with an octahedral field of ligands present. Hint: The three d-orbitals 3 – 5 all behave the same; they are energetically degenerate. The other two are also energetically degenerate among the two of them. While this isn't obvious by looking at the diversely different structures of each, they do have the same symmetry and the same n and l quantum numbers so thus, they transform the same.

The split energy pattern you have created is called a **crystal field splitting**. Use the  $O_h$  character table to add symmetry labels to the two sets of orbitals in the “split energy” picture shown at right (use lower case)

**C. Populating the energy diagram.** The simplest electron configuration with d-orbitals is  $d^1$ . The ion  $Ti^{+3}$  has a  $d^1$  configuration. When we are considering a complex of  $Ti(I)$  in an octahedral field of ligands, the lone d-electron clearly prefers the lower energy level. Sketch the crystal field splitting pattern (energy diagram) for an octahedron and populate it with one electron.

(a)	(b)
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(b) The electron configuration is sometimes written as (symmetry term, lower energy)<sup>1</sup> (symmetry term upper energy level)<sup>0</sup>. Rewrite this using the correct symmetry terms.

Repeat the process for (c)  $d^2$  and (d)  $d^3$ . Think of at least one ion that actually exhibits these two configurations.

(c)	(d)
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The split between the lower energy levels and the upper energy orbitals is called the crystal field stabilization energy and is abbreviated  $\Delta_o$ . Label  $\Delta_o$  on both of the above energy diagrams.

If we could imagine an average energy for the three orbitals of one energy and the two orbitals of the other energy, the average would lie closer to the three degenerate energies. Determine the exact fraction of the energy difference between the lower energies and the average energy. Label the fraction on the energy diagram. Do the same for the orbitals of higher energy. The two fractions should add up to 1.

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The exact magnitude of  $\Delta_o$  depends on several factors that we will discuss later. All we need to know for now is that  $\Delta_o$  varies. The two fractions written on the energy diagram above should be multiplied by  $\Delta_o$ . Do that now by writing the fractions  $\times \Delta_o$  on the energy diagram above.

When one electron occupies one of the lower energy levels, it has been stabilized (compared to the average energy of all five orbitals) by one the  $\times$  (fraction)  $\times \Delta_o$ . This is called the crystal field stabilization energy or CFSE and is + because of the name “stabilization energy.” The change in energy is negative and simply given by  $\Delta E = -\text{CFSE}$ . Thus, electronic structures with electrons in the lower energy levels and not the upper energy levels have a + CFSE and have  $\Delta E < 0$ . Calculate the CFSE for  $d^1$ ,  $d^2$  and  $d^3$  in an octahedral field of ligands.

When we get to  $d^4$ , the 4<sup>th</sup> electron can either occupy one of the lower energy orbitals or one of the higher energy orbitals. If it occupies the lower level, it also is stabilized by the same amount as the first three were, however, now there is a “pairing energy” that offsets the additional CFSE somewhat. The “pairing energy” is the energy it costs when two electrons share the same orbital. The pairing energy is abbreviated “P.” If  $P > \Delta_o$ , the electron will prefer to occupy which orbital? Both scenarios are possible.

If $P > \Delta_o$ , the electron will prefer to occupy:	If $P < \Delta_o$ , the electron will prefer to occupy:
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When the electrons choose to occupy the higher energy orbitals rather than pairing up, the situation is called **high-spin** because the number of unpaired electron is maximized. When they pair up, the situation is called **low-spin**. High/low-spin possibilities only occur for a few d-electron configurations. What are they?

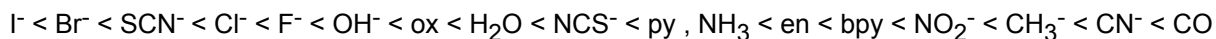
Complete the following table for octahedral metal ions in an octahedral crystal field. For each situation, sketch the energy splitting pattern, fill the orbitals, determine the total stabilization ( $= a \Delta_o - bP$ ) and the number of unpaired electrons. For electron configurations such as  $d^1$ , where high/low spin is not an option, just show your work in the “high-spin” columns in the table and leave the low spin columns blank.

	High Spin			Low Spin		
	Energy diagram	Energy, $a\Delta_o - bP$	Number unpaired electrons	Energy diagram	Energy, $a\Delta_o - bP$	Number unpaired electrons
<b>d<sup>0</sup></b>						
<b>d<sup>1</sup></b>						
<b>d<sup>2</sup></b>						
<b>d<sup>3</sup></b>						
<b>d<sup>4</sup></b>						
<b>d<sup>5</sup></b>						
<b>d<sup>6</sup></b>						
<b>d<sup>7</sup></b>						
<b>d<sup>8</sup></b>						
<b>d<sup>9</sup></b>						
<b>d<sup>10</sup></b>						

#### D. Factors affecting $\Delta_o$

1. The binding ability of the ligand affects  $\Delta_o$ . Ligands that bind strongly increase the size of  $\Delta_o$  and are called "strong field ligands." Weak field ligands do not increase the size of  $\Delta_o$ . All ligands can be listed in an order called the *spectrochemical series*.

**Spectrochemical Series:**



Weak field ligands ... Strong field ligands  
 High-spin complexes ... Low-spin complexes

2. The nature of the metal ion has an impact on whether the complex will be high- or low-spin. List two important factors that contribute to the metal's role.

3. The metal's and the ligand's contributions to estimating  $\Delta_o$  can be summarized in Jørgensen's relationship,  $\Delta_o = f \times g$ . The f-factor follows the spectrochemical series. The units are in "wavenumbers" —  $1000 \text{ cm}^{-1}$ .

**f-factor**

Br <sup>-</sup>	0.72
Cl <sup>-</sup>	0.78
F <sup>-</sup>	0.9
ox	0.99
H <sub>2</sub> O	1.00
NCS <sup>-</sup>	1.02
py	1.23
NH <sub>3</sub>	1.25
en	1.28
bpy	1.33
CN <sup>-</sup>	1.7

**g-factor**

Mn <sup>+2</sup>	8.0	Rh <sup>+3</sup>	27
Ni <sup>+2</sup>	8.7	Ir <sup>+3</sup>	32
Co <sup>+2</sup>	9	Pt <sup>+4</sup>	36
V <sup>+2</sup>	12.0		
Fe <sup>+3</sup>	14.0		
V <sup>+3</sup>	15.9		
Cr <sup>+3</sup>	17.4		
Co <sup>+3</sup>	18.2		
Ru <sup>+2</sup>	20.0		
Mn <sup>+4</sup>	23.0		
Mo <sup>+3</sup>	24.6		

Estimate $\Delta_o$ for $Cr(CN)_6^{-3}$ , experimentally found to be $26,600 \text{ cm}^{-1}$ .	Estimate $\Delta_o$ for $Fe(H_2O)_6^{+3}$ , experimentally found to be $14,000 \text{ cm}^{-1}$ .	Estimate $\Delta_o$ for $Ru(H_2O)_6^{+2}$ , experimentally found to be $19,800 \text{ cm}^{-1}$ .
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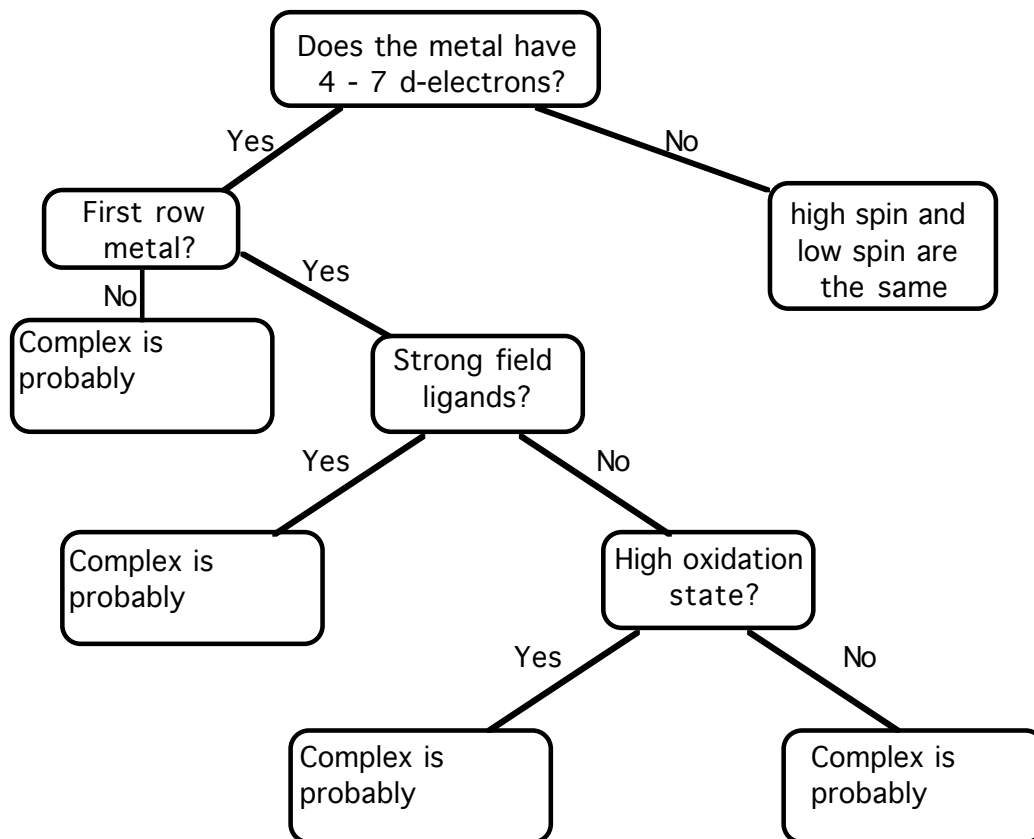
4. Here some pairing energies for some first-row  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  complexes:

$d^n$	Ion	P, kJ/mol ( $\text{cm}^{-1}$ )
$d^4$	Cr <sup>+2</sup>	244.3 (20,425)

	Mn <sup>+3</sup>	301.6 (25,215)
d <sup>5</sup>	Mn <sup>+2</sup>	285.0 (23,825)
	Fe <sup>+3</sup>	357.4 (29,875)
d <sup>6</sup>	Fe <sup>+2</sup>	229.1 (19,150)
	Co <sup>+3</sup>	282.6 (23,625)
d <sup>7</sup>	Co <sup>+2</sup>	250 (20,800)

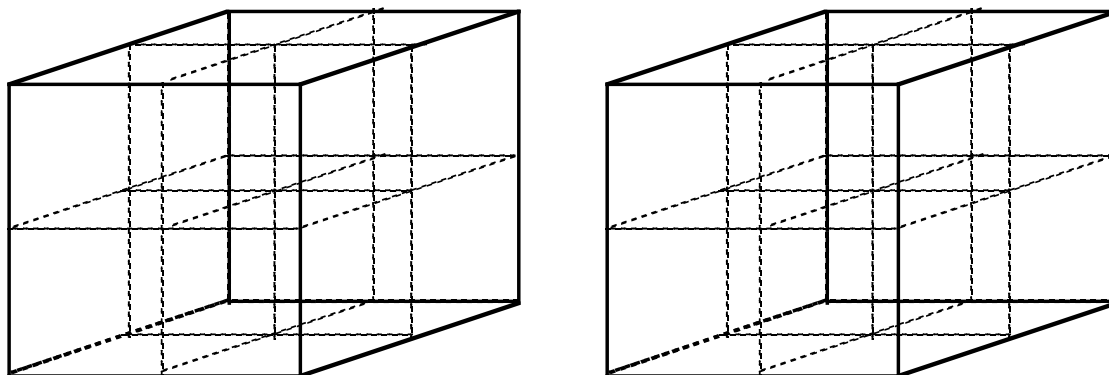
Should the complex  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$  be high-spin or low-spin?

Complete the following flowchart, useful for determining if an octahedral complex is high or low spin.



**E. The tetrahedron.** The octahedron lends itself well to predicting the d-orbital splitting pattern. When attempting to predict the splitting pattern for other geometries, two important tools make the job easier. 1. The character table lets you know which of the d-orbitals are transform the same (have the same symmetry) and are thus degenerate. 2. The d-orbitals can be sketched into a Cartesian coordinate system as part of a cube

and the tetrahedron can be inscribed in a cube by placing the ligands at four opposite corners of the eight-cornered cube.



Predict the energy splitting pattern for the d-orbitals in a tetrahedral field. Provide symmetry labels along with d-orbital designations (e.g.  $d_{xz}$ ) for each orbital. Provide an explanation using the cubes above or just words below.

**F. The square plane.** Predict the energy splitting pattern for the d-orbitals in a square plane field. Using the appropriate character table will let you know which orbitals are degenerate. Provide symmetry labels along with d-orbital designations (e.g.  $d_{xz}$ ) for each orbital.

**G. Other geometries.** The table below summarizes all regular geometries and the relative energies of the d-orbitals. Note the octahedron, for example: the +0.6 indicates higher energy than the starting value of 0 and -0.4 indicates a stabilization (lower energy). Keep this in mind as you use the other entries in the table. Note: For the sake of making comparisons, *all* energies for all geometries are in units of  $\Delta_0$ .

## The Energy Levels of $d$ Orbitals in Crystal Fields of Different Symmetries

C.N.	Structure	$d_{z^2}$	$d_{x^2 - y^2}$	$d_{xy}$	$d_{xz}$	$d_{yz}$
1	Linear	0.514	-0.314	-0.314	0.057	0.057
2	Linear	1.028	-0.628	-0.628	0.114	0.114
3	Trigonal plane	-0.321	0.546	0.546	-0.386	-0.386
4	Tetrahedral	-0.267	-0.267	0.178	0.178	0.178
4	Square planar	-0.428	1.228	0.228	-0.514	-0.514
5	Trigonal bipyramid	0.707	-0.082	-0.082	-0.272	-0.272
5	Square pyramid	0.086	0.914	-0.086	-0.457	-0.457
6	Octahedron	0.600	0.600	-0.400	-0.400	-0.400
6	Trigonal prism	0.096	-0.584	-0.584	0.536	0.536
7	Pentagonal bipyramid	0.493	0.282	0.282	-0.528	-0.528
8	Cube	-0.534	-0.534	0.356	0.356	0.356
8	Square antiprism	-0.534	-0.089	-0.089	0.356	0.356
9	$\text{ReH}_9$ structure	-0.225	-0.038	-0.038	0.151	0.151
12	Icosahedron	0	0	0	0	0

Use the values in the table to sketch the energy diagram for the trigonal bipyramid and the pentagonal bipyramid. Label each orbital.

trigonal bipyramid:	pentagonal bipyramid:
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The difference between the high and low energies in the octahedron is, of course,  $\Delta_o$ . What is the value of  $\Delta_{\text{tetrahedron}}$  in terms of  $\Delta_o$ ?

As a continuation of the previous problem, what is the value of  $\Delta_{\text{sq pl}}$  in terms of  $\Delta_o$ ?

Do any other geometries have relatively large  $\Delta$  values, similar in size to  $\Delta_o$ ? Aside from the square plane and octahedron, what is the geometry with the next largest difference between energy levels?

### Review for ACS Final Exam

1. Which of these compounds is paramagnetic?

- (a)  $K_3[FeCl_6]$
- (b)  $KMnO_4$
- (c)  $ZnSO_4$
- (d)  $TiCl_4$
- (e)  $XeF_4$

2. The number of unpaired electrons in  $K_4[Co(CN)_6]$  is

- (a) 0
- (b) 1
- (c) 2
- (d) 3
- (e) None of these

3. Which compound is diamagnetic?

- (a)  $K_4[Co(CN)_6]$
- (b)  $[Cr(NH_3)_6]SO_4$
- (c)  $[Mn(H_2O)_6](Cl)_2$
- (d)  $K_2[ZnCl_4]$
- (e)  $K_3[FeCl_6]$

4. Which would have the largest value of D?

- (a)  $Fe(CN)_6^{-3}$
- (b)  $Fe(CN)_6^{-4}$
- (c)  $Co(NH_3)_6^{+2}$
- (d)  $Ni(NH_3)_4^{+2}$
- (e)  $Co(NH_3)_3(Cl)_3$

5. Which would have the largest crystal field stabilization energy?

- (a) octahedral complex with  $d^3$  configuration
- (b) octahedral complex with  $d^4$  low spin configuration
- (c) tetrahedral complex with  $d^5$  configuration

- (d) octahedral complex with  $d^6$  low spin configuration
- (e) octahedral complex with  $d^6$  high spin configuration

6. In which of the compounds is the one most likely to be high spin listed first?

- (a)  $Ru(H_2O)_6^{+3}$  and  $Fe(H_2O)_6^{+3}$
- (b)  $Mn(Cl)_6^{-3}$  and  $Mn(Cl)_6^{-4}$
- (c)  $Fe(Cl)_6^{-3}$  and  $Fe(Cl)_4^-$
- (d)  $Ni(NH_3)_4^{+2}$  and  $Pt(NH_3)_4^{+2}$
- (e)  $Fe(CN)_6^{-3}$  and  $Fe(H_2O)_6^{+3}$

7. Which is **not** a factor when predicting  $D_o$ ?

- (a) oxidation state of metal
- (b) Spectrochemical series
- (c) whether the metal is from  $n = 3, 4$  or  $5$ .
- (d) the geometry of the complex.
- (e) the charge on the ligand

Answers: A, B, D, A, D, D, E