Exam Three Part One

CHM 451 (Inorganic Chemistry)

Dr. Mattson 4 December 2012 Name:

Instructions: This exam has two parts. In Part One, only a pencil and a non-programmable calculator may be used. When you have completed Part 1, turn it in and obtain Part Two. In Part Two, your data sheet (on the periodic table) and a non-programmable calculator may be used. Show your work for credit whenever a box is provided.

1. (6 pts) Which of the following could be ligands? Show your work!

(a) BH_3	b) AsH_3
(c) CH_4	(d) SeH_2
(e) SCN^-	(f) NO_2^+

2a. (4 pts) Sketch the following. If more than one enantiomer exists, sketch just one.

mer-$Cr(NH_3)_3(Cl)_3$	*cis*-$[Fe(H_2O)_4(CN)_2]Cl$
cis-$[Ni(en)_2Cl_2]SO_4$	*fac*-$Co(NH_3)_3(CN)_3$

2b. (1 pt) Which one of the compounds sketched above exists as an enantiomeric pair? Identify your answer by the metal it contains:

Cr Fe Ni Co

3. (4 pts) Sketch ALL of the stereoisomers possible for $K[Co(ox)(H_2O)_2Cl_2]$? Two are enantiomers of each other: circle them.

4a. (3 pts) Sketch the crystal field splitting diagram (energy diagram) for octahedral complex. Label all five d-orbitals.

4b. (2 pts) Cyanide is a strong field ligand. Populate the energy diagram (in 4a) for $Co(CN)_6^{-3}$.

4c. (2 pt) How many unpaired electrons are present in $Co(CN)_6^{-3}$? Is it diamagnetic or paramagnetic?

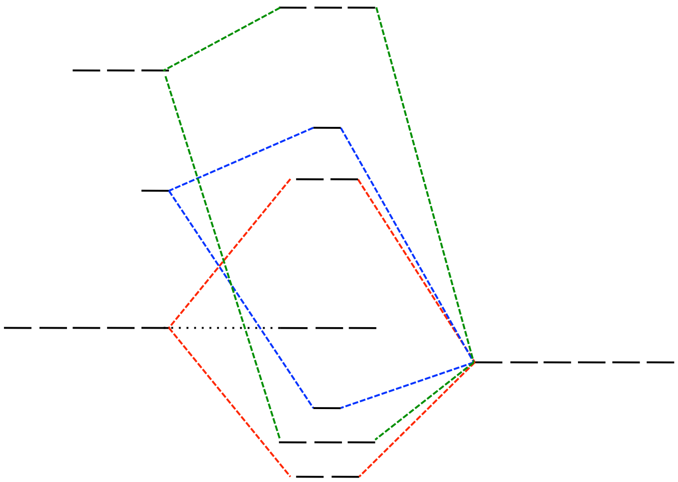
5. (3 pts) Determine the number of unpaired electrons for each of these in a tetrahedral crystal field:

(a) d^4

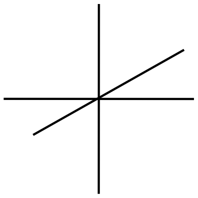
(b) d^6

(c) d^7

6. The following MO diagram is for an octahedral complex.



6a. (2 pts) On the coordinate system below sketch, using circles, the six ligand electron pair groups that go into making the SALC orbitals.



6b. (4 pts) Use the character table to add symmetry labels to the atomic and molecular orbitals in the figure.

6c. (2 pts) Populate the diagram for $V(NH_3)_6^{+3}$.

6d. (1 pt) Indicate Δ_o on the diagram.

7. (4 pts) Suppose you were completing a chart of microstates in order to determine the various term symbols for a d^4 configuration. What microstates would you include in the combination $M_L = 4$ and $M_S = 1$?

8. (1 pt) Suppose L = 4 and S = 1/2. What term symbol corresponds to this combination?

9a. (3 pts) How many d-d spin-allowed electronic transitions are expected for a d^4 high-spin configuration in an octahedral environment? Explain or show your work.

9b. (2 pts) Identify this/these transition(s) using the A, T, E, notation. (e.g., $^2T \rightarrow {}^3A$)

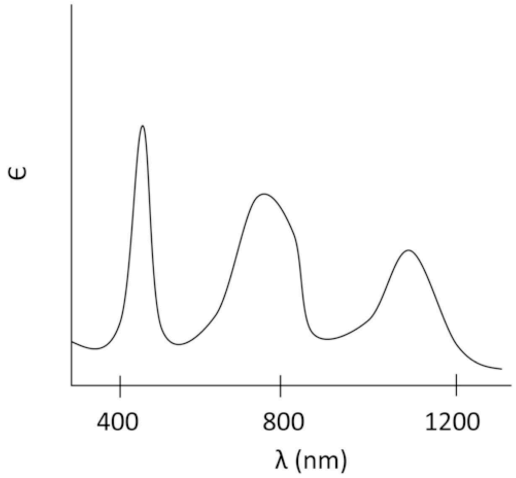
10. (3 pts) Sketch a reasonable Tanabe-Sugano diagram for octahedral d^9. Add all term symbol labels.

11. (3 pts) What tetrahedral environment(s) (d^x) would make use of the same Tanabe-Sugano diagram as for octahedral d^3?

12. (2 pts) What is the cause of the kink in the Tanabe-Sugano diagram for octahedral d^4?

13. (2 pts) Are there any spin-allowed transitions for octahedral d^5? Explain.

14. The spectrum shown below is for $CrCl(NH_3)_5^{+2}$.



14a. (4 pt) Use the appropriate Tanabe-Sugano diagram to assign the absorbance bands on the spectrum above. Use the appropriate term symbols, like you did in 9b.

14b. (2 pts) Which absorption band corresponds to Δ_o?

15. (6 pts) Which of these configurations would be expected to exhibit Jahn Teller distortions in octahedral environments?

d^1	d^3	d^5hs
d^5ls	d^6hs	d^6ls

BONUS (3 pts) Sketch the crystal field splitting pattern expected for a trigonal prism geometry, labeling each orbital.

This ends Part 1. Check your work and turn this portion of the exam in and receive Part 2. In Part 2, you can use the special exam green periodic table with whatever notes you've made on the periodic table.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$z^2, x^2 - y^2$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

EXAM THREE PART TWO

CHM 451 (INORGANIC CHEMISTRY)

DR. MATTSON 4 DECEMBER 2012 NAME:

Instructions: In Part Two, your data sheet (on the green periodic table) and a non-programmable calculator may be used. Always show your work!

16. (0 pts) Print your name on this exam, above, where it says “Name”

17. (4 pts) Suppose only one member of each pair exists. Circle the most plausible compound in each pair.

(a) $[V(NH_3)_4]SO_4$ or $[Cu(NH_3)_4]SO_4$

(b) $[Cr(bipy)_3]_2(SO_4)_3$ or $[Cr(en)_4]_2(SO_4)_3$

(c) $[Fe(NH_3)_2Cl_4]_2SO_4$ or $K[Fe(NH_3)_2Cl_4]$

(d) $[Cu(P(C_6H_5)_3)_3]SO_4$ or $[Cu(P(C_6H_5)_3)_6]SO_4$

18. (4 pts) Determine the crystal field stabilization energy, including pairing energies, for each of the following configurations in an octahedral environment:

(a) d^3

(b) d^4 high spin

(c) d^5 low spin

(d) d^7 high spin

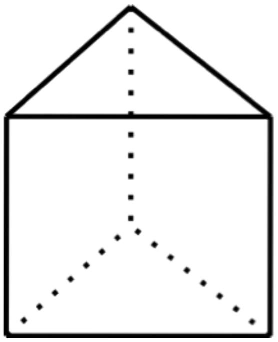
19. (3 pts) What three factors determine whether a complex will be high or low-spin?

1.

2.

3.

20. (5 pts) The trigonal prism is an alternative to the octahedral geometry for complexes with six ligands. It is rare and examples are limited to several bidentate chelate complexes, including $Re(S_2C_2Ph_2)_3$, where Ph = C_6H_5. Use the character table for D_{3h} to determine the <u>irreducible</u> representations for the trigonal prism.

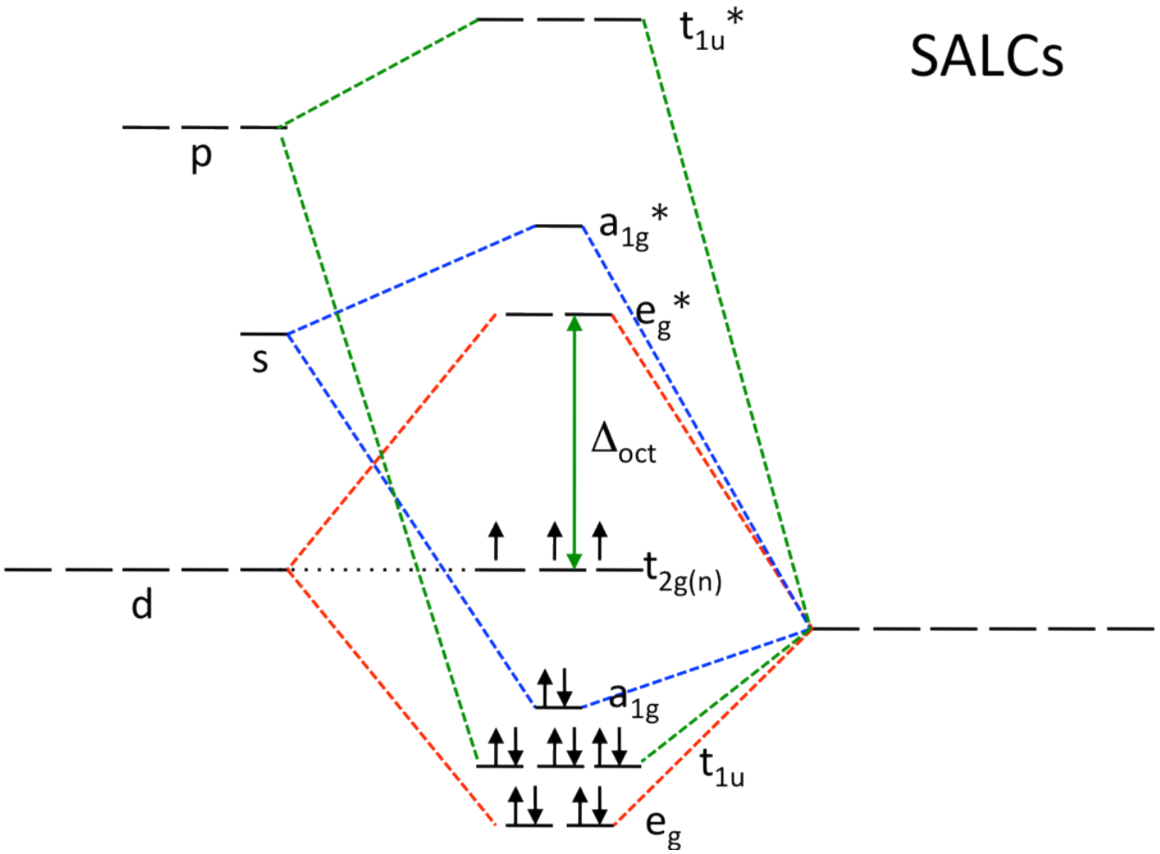


D_{3h}	E	2 C_3	3 C_2	σ_h	2S_3	3σ_v		
A_1'	1	1	1	1	1	1		
A_2'	1	1	-1	1	1	-1		
E'	2	-1	0	2	-1	0		
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1		
E''	2	-1	0	-2	1	0		

21. (3 pts) Square planar complexes often feature d^8 electron configurations on the metal and are always diamagnetic. Sketch the crystal field splitting pattern for the square plane and populate it with electrons.

22a. (4 pts) Sketch the following MOs (using orbital shape drawings)

e_g	a_{1g}^*	t_{1u}	t_{2g}



22b. (1 pt) Give an example of a ligand-to-metal charge transfer. You can show this with an arrow on the diagram above.

22c. (3 pts) We categorized transition metal complexes into three scenarios, the third of which was those compounds that could have only 18 electrons because the t_{2g} orbitals shown above were lowered in energy and became bonding due to π-back-bonding. This sort of bonding (π -back bonding) is not applicable for Scenarios 1 and 2. What are the other two scenarios and what differentiates them from each other?

23. (3 pts) The complex ion $Cu(NH_3)_4^{+2}$ absorbs at 620 nm. (a) Describe this absorbance using the ligand field term symbol notation (A, T, E) (b) Does this absorbance correspond to Δ? Explain.

24.Consider the complexes $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$.

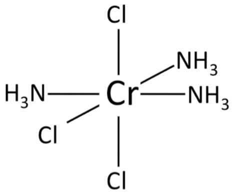
24a. (2 pts) Which is the most likely to have a more intense color than the other? Explain.

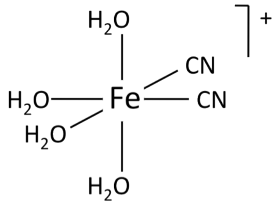
24b. (2 pts) Which one is diamagnetic? Explain.

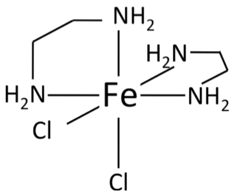
Answers:

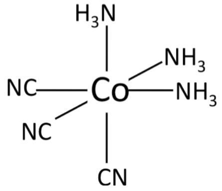
1. (a) AB_3 not a ligand; (b) AB_3E a ligand; (c) AB_4 not a ligand; (d) AB_3E a ligand; SCN^- is a ligand via the E groups on S or N; (f) AB_2 not a ligand

2a.



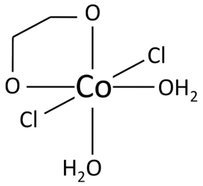


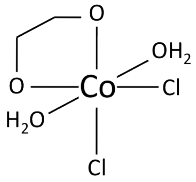


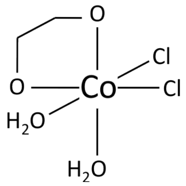


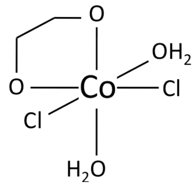
2b. Ni

3. The bottom two are enantiomers:

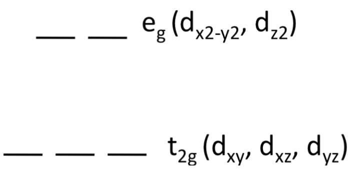




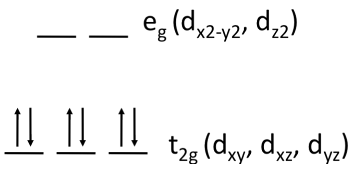




4a.



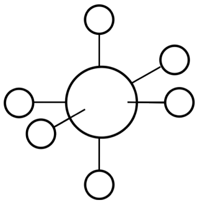
4b.



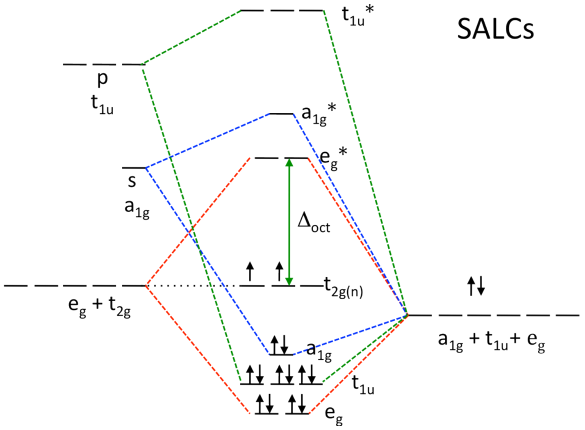
4c. 0, diamagnetic

5. (a) 4; (b) 4; (c) 3

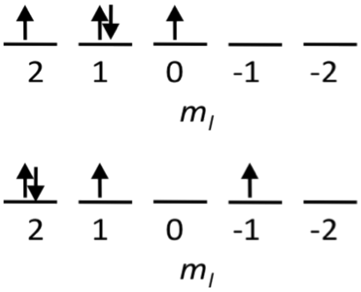
6a.



6b, c, and d.

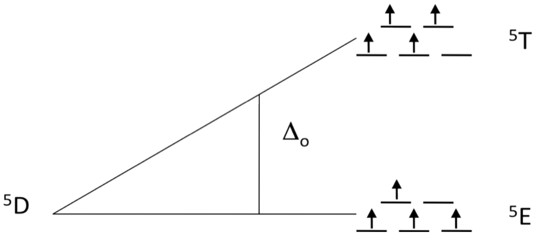


7.

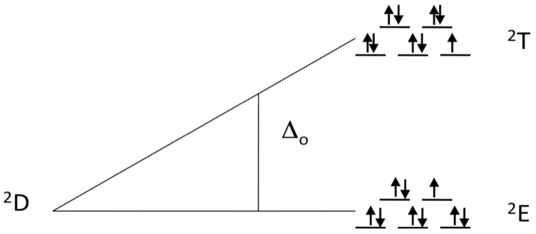


8. ^2G

9a and b. one:



10.

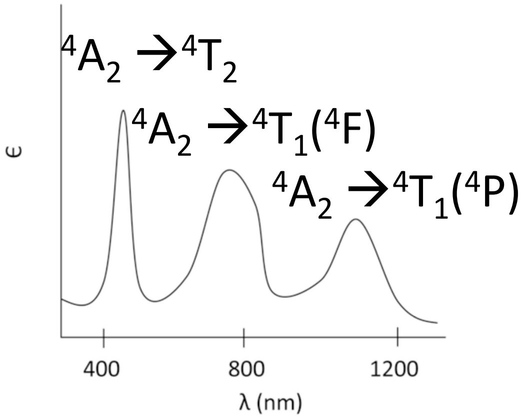


11. d^2, d^7

12. the transition from hs to ls.

13. not for hs, but for ls there are multiple spin-allowed transitions

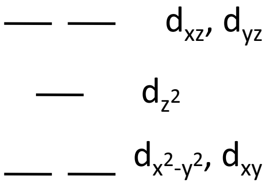
14a.



14b. Δ_o corresponds to the absorbance at about 450 nm.

15. d^1, d^5ls, and d^6hs

BONUS (3 pts) Sketch the crystal field splitting pattern expected for a trigonal prism geometry, labeling each orbital.



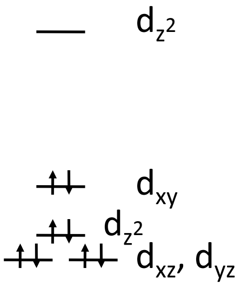
17. (a) $[Cu(NH_3)_4]SO_4$; (b) $[Cr(bipy)_3]_2(SO_4)_3$; (c) $K[Fe(NH_3)_2Cl_4]$; (d) $[Cu(P(C_6H_5)_3)_3]SO_4$

18. (a) d^3 CFSE = 1.2 Δ_o; (b) d^4 high spin CFSE = 0.6 Δ_o; (c) d^5 low spin CFSE = 2.0 Δ_o - 2 P; (d) d^7 high spin CFSE = 0.8 Δ_o - 2 P

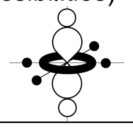
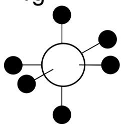
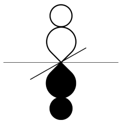
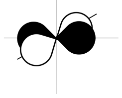
19. ligand strength (strong vs. weak-field ligand, transition metal: first row or 2nd/3rd row, and oxidation state on metal

20. A_1' + E'+ A_2''+ E'' (Note: Γ = 6, 0, 0, 0, 0, 2)

21.



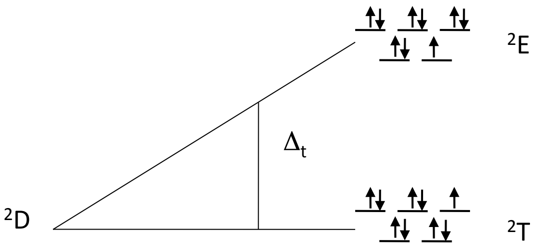
22a.

e_g(1 of 2 possibilities)	a_{1g}^*	t_{1u}	t_{2g}
			

22b. This can be shown with a line sketched from a_{1g} (or t_{1u} or e_g) molecular orbitals to the e_g^* antibonding orbital.

22c. Scenario 1 includes all situations in which Δ_o is small (e.g. weak field ligands). These complexes can have a total of 12 – 22 electrons in MO diagram (12 from six ligands + d^0 – d^{10} for the metal). Scenario 2 includes all situations in which Δ_o is large (e.g. strong field ligands). These complexes can have a total of 12 – 18 electrons in MO diagram (12 from six ligands + d^0 – d^6 for the metal); the e_g^* orbitals are too high in energy to be populated.

23. (3 pts) The complex ion $Cu(NH_3)_4^{+2}$ is tetrahedral d^9. The absorbance at 620 nm corresponds to Δ_t.



24. The complexes $K_3[Fe(CN)_6]$ contains Fe^{+3} which is d^5 hs; the complex $K_4[Fe(CN)_6]$ contains Fe^{+2} which is d^6hs. The former has one unpaired electron and has spin-allowed transitions and is intensely colored. The latter is a pale yellow, is diamagnetic with no spin-allowed transitions.