CHEM-651: Inorganic Chemistry

Midterm II – November 6th, 2014

NAME Solution Set

This exam is comprised of 6 questions and is 10 pages in length. Please be sure that you have a complete exam and place your name on each page.

Answer each question to the best of your ability. Partial credit will be awarded where appropriate. You are not permitted to use any supplemental materials other than what is included in this test booklet. Calculators are not needed and are not permitted to be used. **PLEASE DO NOT REMOVE ANY PAGES FROM THIS EXAM**.

Write all your answers directly in this test booklet and show all work where necessary.

Good Luck!

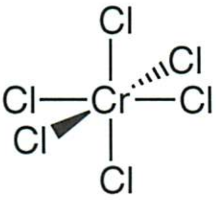
1. ____________ (18 points)
2. ____________ (20 points)
3. ____________ (18 points)
4. ____________ (18 points)
5. ____________ (14 points)
6. ____________ (12 points)

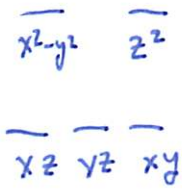
Total ____________

Name: ______________________________

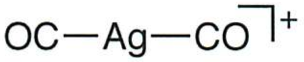
1. (18 total points; 6 points each) Based on your knowledge of Ligand Field Theory, predict the *d*-orbital splitting diagram for the following three complexes in the geometry indicated. Be sure to label each *d*-orbital.

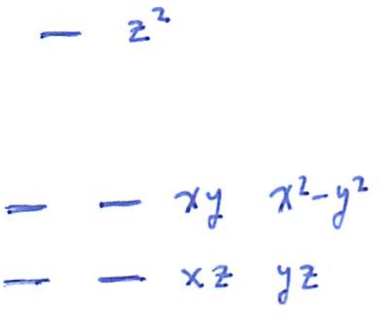
   (a) (6 points) Octahedral $[CrCl_6]$.



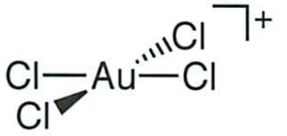


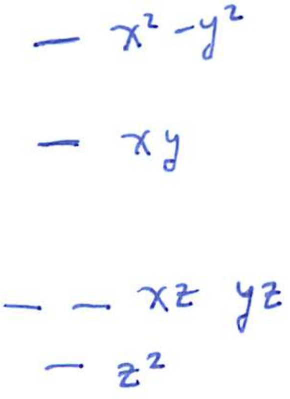
   (b) (6 points) Linear $[Ag(CO)_2]^+$.





   (c) (6 points) Square Planar $[AuCl_4]^+$.





Name: ______________________________

2. (20 total points) For each of the following, please provide the **metal oxidation state, valence electron count, CFSE** and **multiplicity**.

(a) $[Cu(OH_2)_6]^{2+}$ (b) $[FeCl_4]^{2-}$ (c) $[MnF_6]^{3-}$ (d) $[Fe(CN)_6]^{3-}$ (e) $[Pt(NCMe)_6]^{4+}$

a)

↑↓ ↑

↑↓ ↑↓ ↑↓

Cu^{II} VEC = 21

Doublet

CFSE = 6(0.4) - 3(0.6) - 4P

= 0.6 - 4P

b)

↑ ↑ ↑

↑↓ ↑

Fe^{II} VEC = 14

Quintet

CFSE = 3(0.6) - 3(0.4) - P

= 0.6 - P

c)

↑ —

↑ ↑ ↑

Mn^{III} VEC = 16

Quintet

CFSE = 3(0.4) - 0.6

= 0.6

d)

— —

↑↓ ↑↓ ↑

Fe^{III} VEC = 17

Doublet

CFSE = 5(0.4) - 2P

= 2.0 - 2P

e)

— —

↑↓ ↑↓ ↑↓

Pt^{IV} VEC = 18

Singlet

CFSE = 6(0.4) - 3P

= 2.4 - 3P

Name: ____________________________________

3. (18 total points) Using your knowledge of Ligand Field Theory, please address the following. You may find the use of simplified MO diagrams and/or orbital sketches to be helpful in formulating your answers to the questions below.

   (a) (5 points) Although oxygen is more electronegative than nitrogen, ammonia is a significantly stronger field ligand than water. Please provide a model that is consistent with this observation.

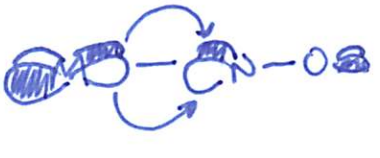
Ligand Field Strength is controlled by the relative ability of ligands to serve as σ-donors, π-donors or π-acceptors. Although the oxygen of water is more electronegative, the water ligand has lone pairs, which allow it to serve as a π-donor. Ammonia lacks lone pairs + therefore does not serve as a π-donor

No lone pairs on Nitrogen to donate to π-symmetric d-orbitals

π-donation by water raises energy of accepting d-orbital producing a weaker ligand field

   (b) (5 points) Although nitrosonium ($[N\equiv O]^+$) is cationic it is an extremely strong field ligand. Please provide a model that is consistent with this observation.

NO^+ is isoelectronic w/ CO. As such, the LUMO of NO^+ (π^*) can interact w/ π-symmetric d-orbitals on a metal + accept e^- density, producing a very strong ligand field interaction



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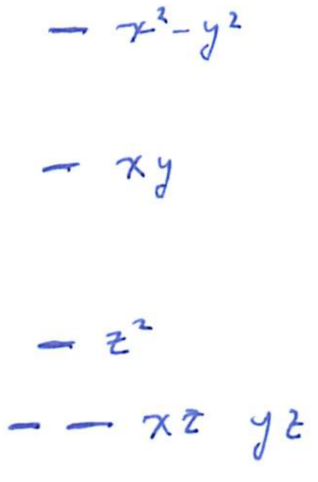
(c) (8 points) Except in cases in which ligand geometry requires it, square-planar geometry occurs most commonly for d^7, d^8 and d^9 metal ions with strong field π-acceptor ligands. Please provide a model that is consistent with this observation.

For SP complexes π-backbonding is maximized which produces an extremely large LFSE + stabilizes the resulting complex. These interactions are not maximized for tetrahedral geometries, leading to a less stable electronic config.

Additionally, SP d-orbital splitting w/ π-acceptor ligands appears as



For d^7 - d^9 configs, there is no instability w/ respect to J-T distortions. The same is not true in a tetrahedral field.

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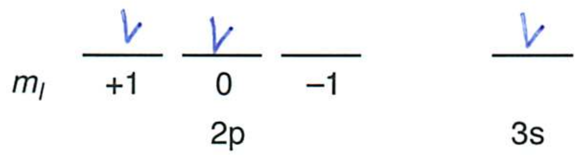
4. (18 total points) The generalized microstate table for the $2p^2 3s^1$ configuration is illustrated below.

		M_S			
		3/2	1/2	−1/2	−3/2
M_L	2		⊙	⊙	
	1	✖	✖⊙◆	✖⊙◆	✖
	0	✖	✖⊙◆△	✖⊙◆△	✖
	−1	✖	✖⊙◆	✖⊙◆	✖
	−2		⊙	⊙	

(a) (3 points) Draw the microstate having quantum numbers $M_S = -3/2$, $M_L = 1$.



(b) (10 points) From the above table, determine all spectroscopic terms that comprise the $2p^2 3s^1$ configuration. To which spectroscopic term does the microstate in part (a) belong.

Δ = ^2S

◆ = ^2P

x = ^4P

⊙ = ^2D

Microstate in Part a) belongs to ^4P

(c) (2 points) Which spectroscopic term is the lowest energy term of the $2p^2 3s^1$ configuration?

^4P

(d) (3 points) Split the ground state spectroscopic term into all possible states via spin-orbit coupling. Indicate which of the new spin-orbit coupled states is the ground state.

$L = 1$ $\quad S = 3/2$ $\quad \therefore\ J = |L+S| \rightarrow |L-S|$

$= 5/2,\ 3/2,\ 1/2$

Ground State = $^4P_{1/2}$ Since shell is less than half filled

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5. (14 total points) Consider the electronic structure of the complexes $[Fe(CN)_6]^{4-}$ and $[Fe(OH_2)_6]^{2+}$ to answer the following (note: you should use the Tanabe-Sugano diagrams provided at the end of this exam to help you answer these questions). Both are d^6

   (a) (2 points) What is the ground state term of $[Fe(CN)_6]^{4-}$?

   Strong Field → $^1A_1$

   (b) (2 points) What is the ground state term of $[Fe(OH_2)_6]^{2+}$?

   Weak Field → $^5T_2$

   (c) (7 points) Which transitions are spin allowed for $[Fe(CN)_6]^{4-}$? Which transitions are spin allowed for $[Fe(OH_2)_6]^{2+}$?

$[Fe(CN)_6]^{4-}$	$[Fe(OH_2)_6]^{2+}$
$^1A_1 \rightarrow {}^1T_1$	
$^1A_1 \rightarrow {}^1T_2$	$^5T_2 \rightarrow {}^5E$
$^1A_1 \rightarrow {}^1E$	
$^1A_1 \rightarrow {}^1A_2$	
$^1A_1 \rightarrow {}^1A_2$	

   (d) (3 points) If $[Fe(CN)_6]^{4-}$ were to lose a cyanide ligand to generate the five-coordinate $[Fe(CN)_5]^{3-}$, how many transition would you expect this complex to display, based on the Tanabe-Sugano diagrams provided?

   $[Fe(CN)_5]^{3-}$ is not O_h ∴ Can't use TS diagrams

Name: ____________________________________

6. (12 total points) Consider the following questions dealing with electronic absorption spectroscopy.

   (a) (4 points) The following transitions could occur in an octahedral d^3 complex. Indicate which of the following transitions are formally forbidden and explain why this is the case.

   i. ${}^4A_{2g} \rightarrow {}^4T_{2u}$ Allowed

   ii. ${}^4A_{2g} \rightarrow {}^4T_{2g}$ Forbidden ⇒ Parity/LaPorte Selection Rule

   iii. ${}^4A_{2g} \rightarrow {}^4T_{1u}$ Allowed

   iv. ${}^4A_{2g} \rightarrow {}^2E_{2g}$ Forbidden ⇒ Spin States differ + Parity/LaPorte

   v. ${}^4A_{2g} \rightarrow {}^2T_{2u}$ Forbidden ⇒ Spin States differ

   (b) (3 points) Propose mechanisms by which each of the forbidden transitions shown above could gain intensity.

   - For ${}^4A_{2g} \rightarrow {}^4T_{2g}$ vibronic motion is required to remove inversion center + relax the LaPorte Rule
   - For ${}^4A_{2g} \rightarrow {}^2E_g$ Also need vibronic coupling along w/ spin-orbit coupling to relax the spin forbidden process
   - For ${}^4A_{2g} \rightarrow {}^2T_{2u}$ Need spin orbit coupling

   (c) (5 points) Explain why the ligand field (d—d) bands are shifted only slightly along the series of $[X\text{–}Co(NH_3)_5]^{2+}$ complex ($X = F^-$, Cl^-, Br^- and I^-), but charge-transfer bands are shifted greatly for the series.

The ligand field strength of each complex will be similar since each of the halides is relatively weak field + the overall d-d splitting will be similar for each complex. For the LMCT, however, an e^- is formally transferred from the halide to the metal. Since it is harder to ionize the halogens in the order $F > Cl > Br > I$ it will take a much more energetic photon to ionize more electronegative halogens (i.e. F + Cl) than for Br or I.

Name: ______________________________

PERIODIC TABLE OF THE ELEMENTS

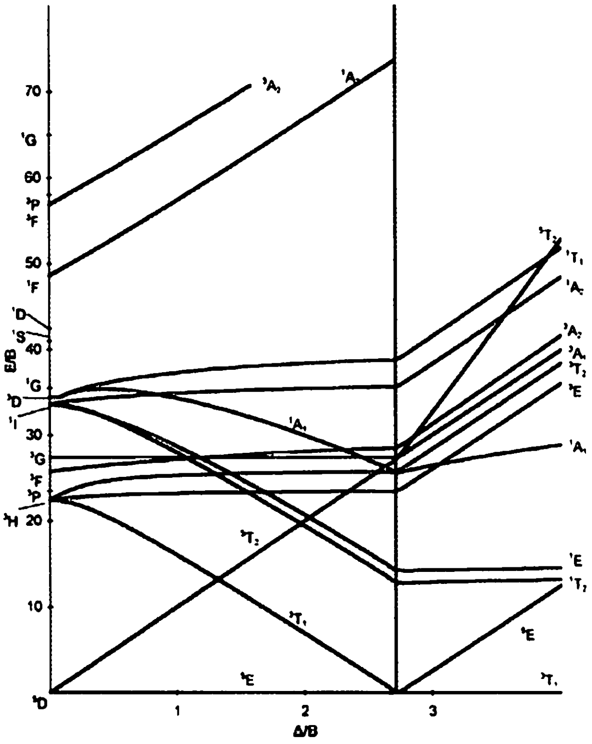
1 H 1.0079																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.179
11 Na 22.9898	12 Mg 24.305											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.905	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)									

58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

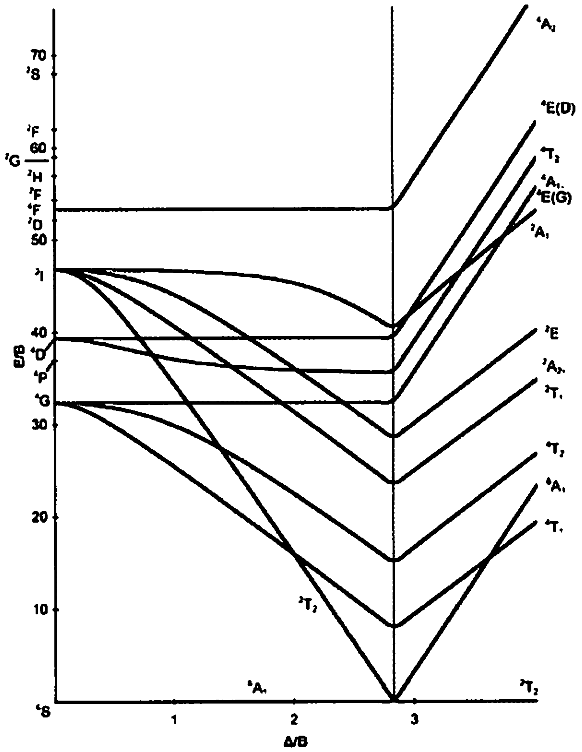
Name: ____________________________________

Selected Tanabe-Sugano Diagrams

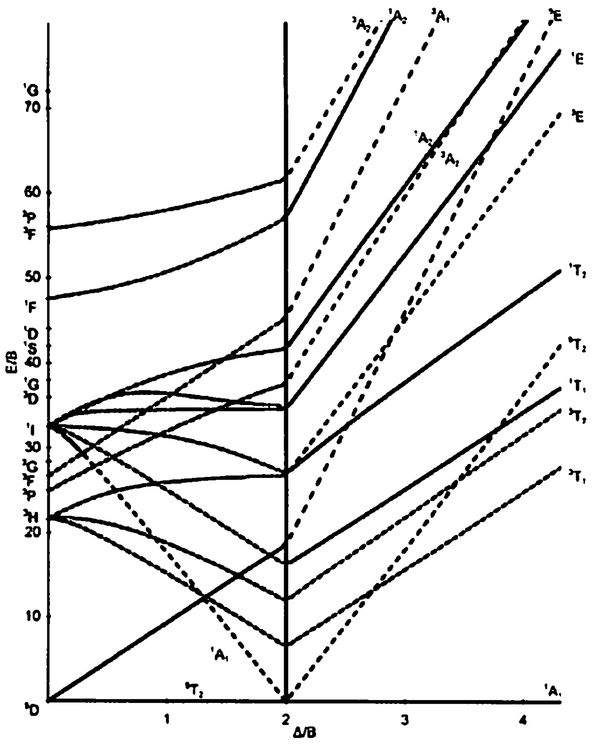
d^4



d^5



d^6



d^7