Inorganic Exam 3   Name:
Chm 451
4 December 2008

Instructions. Always show your work where required for full credit.

1. (15 pts) True/False

     a   T   F   Ionization energy decreases as one moves down from Li to Cs in Group 1.

     b   T   F   Group I elements react with O_2 to form different compounds depending on the element. These include oxides, peroxides, and superoxides.

     c   T   F   Hydrogen has an ionization energy more similar to fluorine's than to lithium's.

     d   T   F   Hydrogen forms an extremely strong H-H bond.

     e   T   F   Alkaline earth oxides (e.g. CaO) are base anhydrides.

     f   T   F   In the compound NaH, the δ^+ is on the H atom.

     g   T   F   Boranes contain boron and hydrogen in which hydrogen sometimes bridges two boron centers in a 3-center, 2-electron bond.

     h   T   F   Aluminum reacts with bases but is non-reactive towards acids.

     i   T   F   Silicon and carbon have equal abilities to form double bonds.

     j   T   F   Carbon exists in a variety of allotropes including the tetramer, C_4.

     k   T   F   The nitride ion has formula N^{-2}.

     l   T   F   White phosphorus, P_4, is expected to be more volatile than red phosphorus, $(P_4)_n$.

     m   T   F   Unlike O_2, S_8 is diamagnetic.

     n   T   F   Chlorine has a range in oxidation states from +7 (e.g. $KClO_4$) to –3 (e.g. Rb_3Cl).

     o   T   F   Speckled nitrogen is formed by boiling CH_2 in an osmotic fog until the atoms are fully extracted and the neutrons precipitate.

2. Short answer:

a. (1 pt) What is the periodic trend for atomic radius across the transition metals from Sc to Zn?

     a. Atomic radius increases   b. Atomic radius decreases

b. (1 pt) Transition metals tend to form cations. How does the ionic radius for any given metal change with the magnitude of the charge?

     a. Ionic radius increases with increasing charge
     b. Ionic radius decreases with increasing charge

c. (1 pts) Going down any given triad of transition metals one notices a peculiar trend with respect to ionic radius. For example, the ionic radii of Ni^{+2}, Pd^{+2}, and Pt^{+2} are 83, 100, and 94 pm, respectively. What is the name of this effect? (Or what is the explanation?)

3. (3 pts) Give the oxidation state of iron in each of these complexes:

      $[Fe(NH_3)_6]SO_4$ $K[Fe(NH_3)_2(Cl)_4]$ $Fe(CN)_2(NH_3)_3Cl$
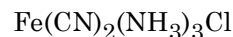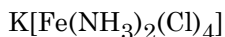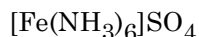
4. (2 pts) The ligand diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$, commonly abbreviated "dien", forms octahedral complexes with metal ions with the formula $M(dien)_2^{+n}$. How many structural isomers are possible for $M(dien)_2^{+n}$?

5. (2 pts) The equilibrium $Cr(NH_3)_6^{+3} + 3\ en \rightleftharpoons Cr(en)_3^{+3} + 6\ NH_3$ (where en = $NH_2CH_2CH_2NH_2$) lies far to the right, despite the fact that ΔH for the reaction is very close to zero. What is the explanation?

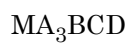a. $\Delta S > 0$ b. $\Delta S = 0$ c. $\Delta S < 0$

d. rate constant > 0   e. rate constant = 0   f. rate constant < 0

6. (2 pts) Which <u>two</u> of these generic octahedral compounds would exhibit chirality (enantiomerism)?

MA_3B_3 MA_3BCD MA_2BC_3 MABCDEF

7. (3 pts) An alternative rare geometry for coordination number six is the trigonal prism shown below. It is shaped like a familiar prism: two equilateral triangles in an eclipsed position with the metal in the center and equal distance from all six ligands. How many structural isomers are possible for trigonal prismatic compounds of the formula MA_2B_4?
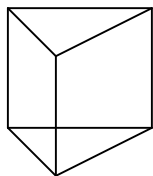
OPTIONAL RISKY BONUS: One of the structures you drew is chiral. Circle it for +1 bonus; circle the wrong one and lose a point!

8. (3 pts) (a) Sketch the crystal field splitting pattern for an octahedral complex. (b) Label all of the orbitals. (c) Populate it for d^5 low spin.

9. (2 pts) Calculate the crystal field stabilization energy in units of Δ_o and P.

10. (1 pts) An octahedral complex of Fe^{+2} is diamagnetic. Is the complex high-spin or low-spin?

a. high spin   b. low spin

11. (2 pts) $Ni(NH_3)_4^{+2}$ is paramagnetic while isoelectronic (having the same number of electrons) $Pd(NH_3)_4^{+2}$ is diamagnetic. Explain in a few words how this could be so.

12. (3 pts) List the three conditions that are necessary for an octahedral complex to be high spin.

   a.

   b.

   c.

13. (3 pts) What do you think the crystal field splitting pattern for the trigonal prism (See Question 9 for a diagram) would look like? (Hint: There are degenerate orbitals.) Label each d-orbital.

14. (12 pts) Predict the geometry and the number of unpaired electrons for each of these transition metal complexes. Given: Spectrochemical Series:

   $I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < ox < H_2O < NCS^- < py$, $NH_3 < en < NO_2^- < CH_3^- < CN^- < CO$

Compound	Geometry	Number of unpaired electrons
$[Cr(NH_3)_6]_2(SO_4)_3$	Octahedron Tetrahedron Square plane	
$K_2[CoCl_4]$	Octahedron Tetrahedron Square plane	
$Pt(NH_3)_2Cl_2$	Octahedron Tetrahedron Square plane	
$K_4[Mn(CN)_6]$	Octahedron Tetrahedron Square plane	

15. The transition metal complex $PdCl_4{}^{2-}$ is square planar. The bonding of the four chlorides can be considered as σ-only (no π-bonding). Use the D_{4h} character table and the started MO diagram to complete the questions that follow.

| D_{4h}	E	$2C_4$	C_2	C'_2	C''_2	i	$2S_4$	s_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(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	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

SALCs

p   ─ ─ ─

s   ─

d─ ─ ─ ─ ─

                    ─ ─ ─ ─

(a) (2 pts) Use the character table to write symmetry labels by the 4d, 5s and 5 p atomic orbitals on the diagram.

(b) (2 pts) Sketch the set of four atomic orbitals that are used to form the SALC set on this Cartesian coordinate system:
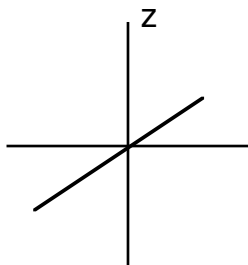
(b) (1 pts) If you determined the reducible representation for the SALC set, you would have concluded that the SALC set transforms as $A_{1g} + B_{1g} + E_u$. Add these labels to the SALC orbitals in the diagram (such as "a_{1g}" — use lower case.)

(c) (4 pts) Finish the MO diagram. Caution! There are three orbitals that transform as A_{1g}! Recall how we handled this! Double check: Did you create 13 MOs from the 13 AOs? Add symmetry labels to each MO (such as "a_{1g}" — use lower case.)

(d) (2 pts) Square planar compounds such as $PdCl_4{}^{2-}$ are diamagnetic, d^8, 16-electron compounds (8 e$^-$ from the d^8 metal and 2 each from the four ligands. Populate the MO diagram in order to give a diamagnetic result.

(e) (3 pts) Suppose one of the ligands in $PdCl_4{}^{2-}$ is replaced with a π-back bonding ligand such as CO, producing $Pd(CO)Cl_3{}^-$. Ignore the minor adjustments that would take place for the σ-SALC set by having two types of σ-donor ligands. Sketch in the two π* orbitals that the one CO would add to the ligand column (under the word SALC), and then indicate how you think these would form π-bonding and antibonding orbitals with the metal. To do this, decide what orbital(s) is/are involved from the metal and use arrows and lines or whatever you feel is necessary to explain the role of π-back bonding in the MO diagram.

16. (3 pts) What is the ground state free ion term symbol for the electron configuration f^2, such as $4f^2$?

17. (3 pts) Suppose you were filling in a table of microstates for a d^4 situation. List the microstates that would go in the box for $M_L = 4$ and $M_S = 1$.

18. The following questions pertain to $Cu(H_2O)_6^{+2}$

   a. (3 pts) Into what term symbols does the free ion term ^2D, change in an octahedral field of ligands? Sketch the split that occurs and label each energy level with the appropriate term symbol.

   b. (2 pts) Sketch a sample microstates by each of the energy levels sketched above.

   c. (2 pts) Add a label for Δ_o.

19. (2 pts) With d^3 configurations, we could easily obtain values for Δ_o directly from the spectrum. (Unlike d^2 where we had to do some subtracting of absorbances.) Suppose a d^3 complex featured absorbance maxima at 10,500, 18,800, and 28,900 cm^{-1}. What is the value of Δ_o?

20. (4 points) What four tetrahedral d^n configurations have a ground state term symbol of ^nA?

      d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

21. (8 pts) Count electrons in each of these organometallic formulas involving technecium. Some of them do not exist because they do not obey the 18-electron rule.

$Tc(CO)_6$	$(OC)_4TcBr$
$(\pi\text{-}C_5H_5)Tc(CO)_3$	$(OC)_5TcCH_3$

22. (3 pts) The compound "$(\pi\text{-}C_5H_5)Ir(CO)$" exists as a dimer, $[(\pi\text{-}C_5H_5)Ir(CO)]_2$ with a metal-metal bond between. The compound obeys the 18-electron rule. Is the Ir-Ir bond a single, double or triple bond? Show work.

Answers:

1. T, T, T, T, T   F T F F F   F T T F (F) (last one was a silly statement meant to be false – it was not counted.

2. b. b   3. +2, +3, +3   4. Two: fac and mer   5. a

6. MA_3BCD MABCDEF

7. There are three structural isomers: (1) the two A groups can be on the same triangular face, (2) they can be on separate triangular faces directly above one another or (3) they can be on separate triangular faces not directly above one another. This third possibility is chiral.

8. lower: the t_{2g} orbitals (d_{xy}, d_{xz} d_{yz}) higher: the e_g orbitals: $d_{x^2-y^2}$ and d_{z^2}. Population: $(t_{2g})^5$ $(e_g)0$

9. $5 \times 0.4\ \Lambda_o - 2\ P\ (= -5 \times 0.4\ \Lambda_o + 2\ P)$

10. b   11. $Ni(NH_3)_4^{+2}$ is tetrahedral $Pd(NH_3)_4^{+2}$ is square planar

12. a. first row metal, b. low oxidation state, c. weak field ligands

13. Here, several answers would be acceptable. If the prism is short and wide, the splitting will be different than if it were tall and skinny. Either way, there are two doubly degenerate pairs: d_{xz} d_{yz} are degenerate and $d_{x^2-y^2}$ and d_{xy} are degenenerate. The remaining orbital d_{z^2} is unique. The best guess is that d_{xz} d_{yz} are highest in energy while the others are lower.

14. $[Cr(NH_3)_6]_2(SO_4)_3$, Octahedron, 3 unpaired electrons; $K_2[CoCl_4]$, Tetrahedron, 3 unpaired electrons; $Pt(NH_3)_2Cl_2$, Square plane, 0 unpaired electrons; $K_4[Mn(CN)_6]$, Octahedron, 1 unpaired electrons

15. (a) d_{xy}: b_{2g}; d_{xz} and d_{yz}: eg; $d_{x^2-y^2}$: b_{1g} d_{z^2} : a_{1g}; (b) four circles, one on each end of the x and y axes.; (c) See MO diagram in textbook; (d) populated up through and including : $a_{1g}(n)$; (e) The π^* orbital will overlap with the filled $e_g(n)$ in the original σ-only diagram.

16. ^3H

17. There are only two microstates possible for the four electrons: (m_l, m_s):
(2, ½); (2, -½); (1, ½); (-1, ½) and (2, ½); (1, ½); (1, -½); (0, ½)

18. a. Lower energy state: ^2E, higher energy state ^2T. b. The lower energy state has configuration $(t_{2g})^6$ $(e_g)^3$ and the higher energy state has configuration $(t_{2g})^5$ $(e_g)^4$. c. Energy difference between ^2E ^2T is Λ_o.

19. $\Lambda_o = 10{,}500\ cm^{-1}$ 20. d^2 d^5 d^7 d^{10}

21. $Tc(CO)_6$: 19 e^- $(OC)_4TcBr$: 16 e^- $(\pi\text{-}C_5H_5)Tc(CO)_3$: 18 e^- $(OC)_5TcCH_3$: 18 e^-

22. double bond