Inorganic Exam 3 **Name:**
Chm 451
2 December 2010

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

1. (5 pts) Bonding in metals.

T F Late transition metals have high melting points due to the fact that their molecular orbitals are mostly full and their bond order is low.

T F In metals, molecular orbitals are created involving the s and d valence orbitals.

T F Bond order in metals would be largest for the early metals such as scandium.

T F Valence electrons are moving almost freely through the lower-energy unoccupied molecular orbitals in a metal.

T F A metal with a half-filled shell, such as chromium, [Ar] $4s^1\ 3d^5$, would be expected to have a large band gap due to its stable electron configuration.

2. (6 pts) Which of the following are expected to exhibit metallic bonding?

silicon
cadmium
potassium
brass (65% Cu + 35% Zn)
osmium (IV) oxide
lead

3. (5 pts) Semiconductors

a. The band gap for silicon is 107 kJ/mol and for germanium is 65 kJ/mol. At any given temperature, does germanium have (a) more or (b) fewer electrons in the conduction band.

b. If the silicon is doped with a trace amount of selenium, what sort of semiconductor has been created? Is it an (a) n-type, (b) p-type or (c) neither?

c. If an n-type semiconductor is joined to a p-type semiconductor, the result is a diode. If the diode is connected to a battery, electrons will flow: (a) in either direction, (b) in only one direction.

d. If the diode and battery are connected in a forward-bias arrangement, the electrons will enter the diode through the (a) p-type end or (b) the n-type end.

e. Photovoltaic cells work on the principle that they promote an electron from (a) the conduction band to the valence band; (b) the valence band to the conduction band; (c) the n-type semiconductor to the p-type semiconductor.

4. Periodic trends of the metals.

4a. (2 pts) Given that Co^{+2} has an ionic radius of 89 pm, predict the ionic radius of Ni^{+2} and Co^{+3}, respectively.

(a) both should be > 89 pm
(b) both should be < 89 pm
(c) Ni^{+2} should be larger than 89 pm, but Co^{+3} smaller than 89 pm
(d) Co^{+3} should be larger than 89 pm, but Ni^{+2} smaller than 89 pm

4b. (2 pts) The lanthanide contraction occurs because of the 14 lanthanide elements that occur before the 3rd row transition metals. Based on the trends established by the first two rows, how does the lanthanide contraction affect the atomic radius and first ionization energies of third row metals?

(a) both are smaller than predicted

(b) both are larger than predicted

(c) the atomic radius is smaller than predicted and the first ionization energy is larger than predicted

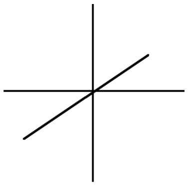
(d) the atomic radius is larger than predicted and the first ionization energy is smaller than predicted

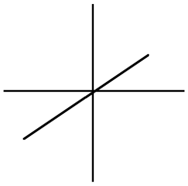
5. (6 pts) Sketch the structure of these transition metal compounds (ignore the counter-ion). Include the charge, if it is an ion.

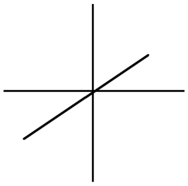
$K_4[Fe(CN)_6]$	$[Co(P(CH_3)_3)_4]_2(SO_4)_3$	$[Ni(H_2O)_6]SO_4$

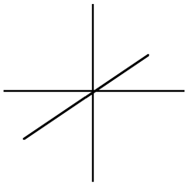
6. (2 pts) The ligand acetylacetonato (2, 4-pentandionate anion) is abbreviated *acac*. It is a bidentate ligand with formula $CH_3COCHCOCH_3^-$. In the space provided at right, sketch the structure of this ligand coordinated to a metal ion of formula M^{+n}.

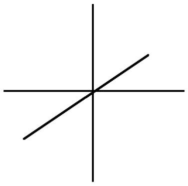
7a. (5 pts) Sketch the geometric isomers (diastereomers) possible for the complex $MA_2B_2C_2$. There are five. Recall that geometric isomers do not include optical isomers.


(i)


(ii)


(iii)


(iv)


(v)

7b. (2 pt) One of the above is half of an enantionmeric pair. Which one is it?

(a) i (b) ii (c) iii (d) iv (e) v

7c. (2 pt) Based on your answers to Question 6 and 7a, how many geometric isomers are possible for $MA_2B_2(acac)$? 0 1 2 3 4 5 6 7 8 9

7d. (1 pt) Are any of the geometric isomers of $MA_2B_2(acac)$ optically active? Yes No

8. (15 pts) Sketch the crystal field splitting pattern for each of the following. Populate orbitals accordingly and calculate the crystal field stabilization energy in units of Δ_o and P. Indicate the number of unpaired electrons.

	Crystal field splitting pattern of d-orbitals, populated	CFSE	Number of unpaired electrons
d^3, octahedral			
d^4, octahedral, low-spin			
d^5, octahedral, high-spin			
d^6, octahedral, low-spin			
d^9, octahedral			

9. (4 pts) Tetrahedral complexes are all high spin because Δ_t is smaller than the typical pairing energy, P. Sketch the crystal field splitting pattern for each of the following. Populate orbitals accordingly and indicate the number of unpaired electrons.

	Crystal field splitting pattern of d-orbitals, populated	Number of unpaired electrons
$K_2[FeCl_4]$		
$[Ni(NH_3)_4](NO_3)_2$		

10. (8 pts) The spectrochemical series is reproduced below. For each pair of compounds listed, circle the one most likely to be high-spin.

Spectochemical Series:

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

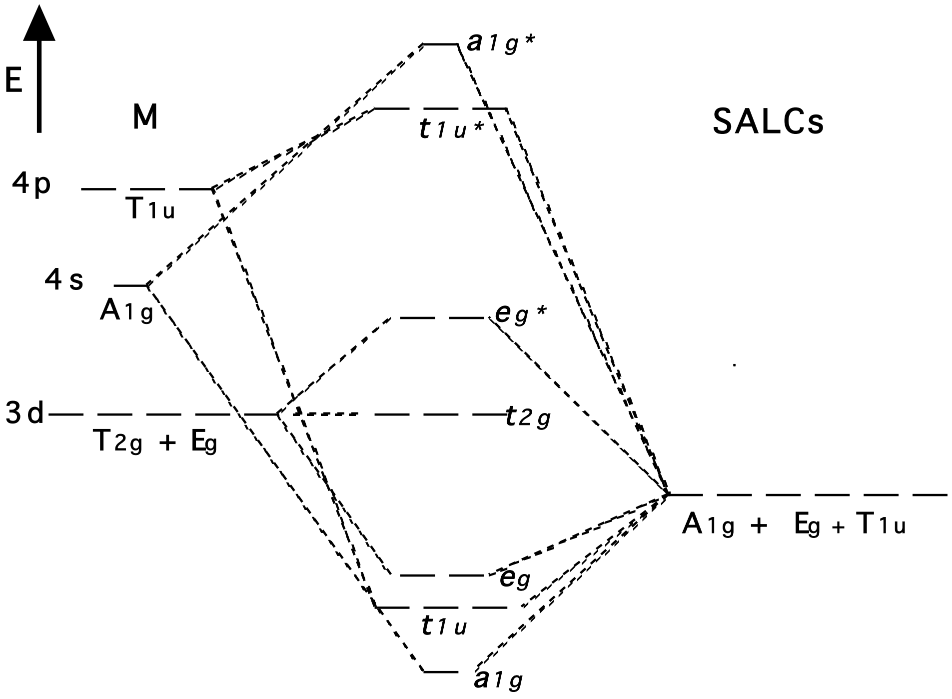
(a) $[Fe(NH_3)_6](NO_3)_2$ or $[Fe(NH_3)_6](NO_3)_3$

(b) $K_4[Mn(CN)_6]$ or $K_4[MnCl_6]$

(c) $[Co(NH_3)_4](NO_3)_2$ or $[Co(en)_2(NH_3)_2](NO_3)_2$

(d) $[Cr(H_2O)_6]SO_4$ or $[Mo(H_2O)_6]SO_4$

11. (12 pts) The MO diagram for a transition metal complex is given below.



11a. What is the geometry of the complex? (a) octahedral (b) tetrahedral (c) square plane

11b. What is the HOMO if the metal ion is Cr^{+3}? ___________

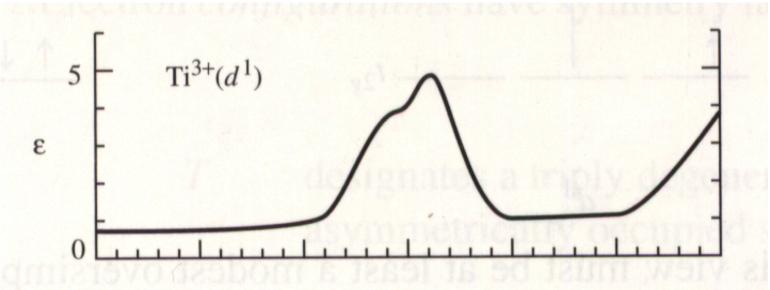
11c. What is the LUMO for a d^0 complex? ____________

11d. Is π-back bonding occurring in this MO diagram? Yes No

11e. Label Δ in this diagram.

11f. Populate the diagram for Fe^{+2} with cyanide ligands.

12. The uv-vis spectrum for $Ti(H_2O)_6^{+3}$ is shown below. The value for λ_{max} is 21,500 cm^{-1}.

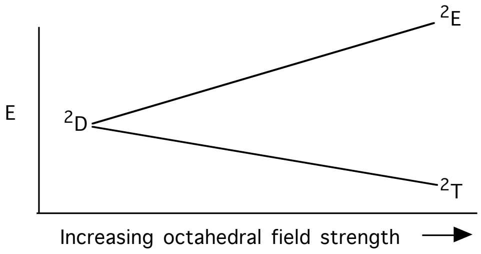


12a. (3 pts) Indicate how you would convert this energy in wave-number to wavelength. You do not need to actually do it; simply list every step that is necessary.

12b. (1 pt) Does the absorption correspond to Δ_{oct}? Yes or No

12c. (2 pts) What is the cause of the shoulder on the peak?

12d. (2 pts) The free ion term symbol for d^1 is ^2D which translates into ^2T and ^2E in an octahedral field of ligands as shown in this energy correlation diagram:



Sketch one microstate next to each of ^2T and ^2E.

12e. (2 pts) Sketch the energy correlation diagram for octahedral d^9.

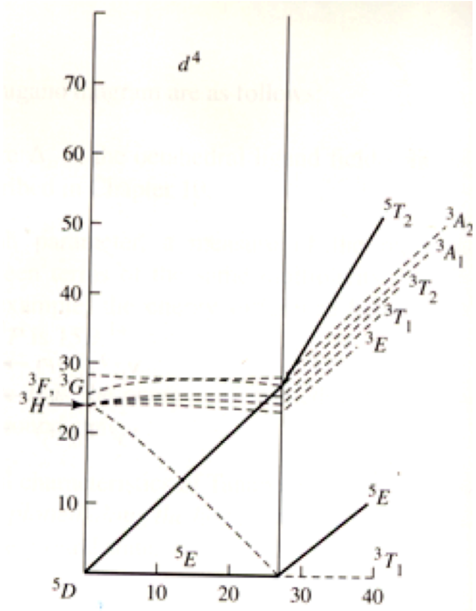
12f. (2 pts) Ignoring the spin multiplicity term, there are two tetrahedral electron configuration with the same energy correlation diagram as octahedral d^1 (T ground state and E excited state). What are they?

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

13a. (3 pts) The complexes $[Mn(H_2O)_6]Cl_2$ and $K_4[Mn(CN)_6]$ both contain Mn^{+2}. One is deep red in color and the other almost colorless – just a pale pink. What is the explanation?

13b. (2 pts) K_2CrO_4 is a d^0 tetrahedral complex that is bright yellow in color. What accounts for this color? (a) M→LCT (b) L→MCT (c) $e \rightarrow t_2$ d-d transition (d) $t_2 \rightarrow e$ d-d transition

14. The Tanabe-Sugano diagram for d^4 is shown below.



14a. (2 pts) What is the ground state term symbol for a d^4 low-spin complex?

14b. (2 pts) How many spin-allowed transitions are there for a high-spin d^4 complex?

14c. (2 pts) What are the values for L and S for the ^3H term symbol?

15 (3 pt bonus) Sketch the basic features of the Tanabe-Sugano diagram for d^5. Include the free-ion label (term symbol with no field) and the octahedral field term symbols (e.g. ^3T).

Answers:

1. F T F T F

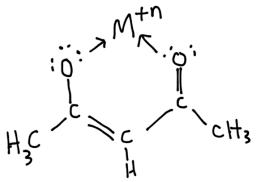
2. cadmium, potassium, brass, lead

3a. (a); b. (a); c. (b); d. (b); e. (b)

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

5. $[Fe(CN)_6]^{4-}$ (octahedral); $[Co(P(CH_3)_3)_4]^{3+}$ (tetrahedral); $[Ni(H_2O)_6]^{2+}$ (octahedral)

6.



7a. In any order:
(a) As trans + Bs trans + Cs trans
(b) As trans + Bs cis + Cs cis
(c) As cis + Bs trans + Cs cis
(d) As cis + Bs cis + Cs trans
(e) As cis + Bs cis + Cs cis

7b. (e) v; 7c. 3; 7d. Yes

8.

	Crystal field splitting pattern of d-orbitals, populated	CFSE	Number of unpaired electrons
d^3, octahedral	$t_{2g}^3\ e_g^0$	$1.2\ \Delta_o$	3
d^4, octahedral, low-spin	$t_{2g}^4\ e_g^0$	$1.6\ \Delta_o - P$	2
d^5, octahedral, high-spin	$t_{2g}^3\ e_g^2$	0	5
d^6, octahedral, low-spin	$t_{2g}^6\ e_g^0$	$2.4\ \Delta_o - 3\ P$	0
d^9, octahedral	$t_{2g}^3\ e_g^0$	$0.6\ \Delta_o - 4\ P$	1

9.

	Crystal field splitting pattern of d-orbitals, populated	Number of unpaired electrons
$K_2[FeCl_4]$	$e_g^3\ t_{2g}^3$	4
$[Ni(NH_3)_4](NO_3)_2$	$e_g^4\ t_{2g}^4$	2

10. (a) $[Fe(NH_3)_6](NO_3)_2$; (b) $K_4[MnCl_6]$; (c) $[Co(NH_3)_4](NO_3)_2$; (d) $[Cr(H_2O)_6]SO_4$

11a. octahedral; 11b. t_{2g}; 11c. t_{2g}; 11d. No; 11e. Δ goes between t_{2g} and e_g^*

11f. Orbitals are filled up through t_{2g}^6

12a. take the reciprocal, 1/21,500 cm^{-1}; 12b. Yes; 12c. Jahn-Teller

12d. The ^2T term should have a microstate of t_{2g}^1 e_g^0 and the ^2E term should have a microstate of t_{2g}^0 e_g^1

12e. Opposite of diagram given: ground state is ^2E.

12f. d^4 d^9

13a. High-spin d^5 $[Mn(H_2O)_6]^{2+}$ has no spin-allowed states and is almost colorless, while low-spin d^5 $[Mn(CN)_6]^{4-}$ is a doublet state with spin-allowed transitions and is hence, colored red.

13b. (b)

14a. $^3T_1$; 14b. one; 14c. L = 5 and S = 1