Dr. Aquino **CHEMISTRY 341 FINAL** December 15, 2010

Answer all questions in the booklet(s) provided. A point group flow chart, periodic table and other information are attached. Please write your name on each booklet used. You have 3 hours.

[15] Question 1

a) Determine the possible microstates for $2p^3$ electronic configuration and arrange them in a microstate table (M_L vs. M_S). (10 marks)

b) Determine the terms for the $2p^3$ configuration. (3 marks)

c) List the terms from *lowest* (ground state) to *highest* energy. (2 marks)

[12] Question 2

Determine the *symmetry elements* and *point group* for (4 marks each):

a) CS_2 b) *cis*-$[FeCl_4Br_2]^{3-}$ c) Λ-$[Co(en)_3]^{2+}$ (en = ethylenediamine)

[10] Question 3

a) Use VSEPR theory to draw and then predict the *actually geometry* of a) SbF_4^- and b) SeF_3^+ (3 marks each)

b) Explain the trend in the following set of bond angles: NCl_3 (∠ Cl-N-Cl = 107.1°), NF_3 (∠ F-N-F = 102.3°), PCl_3 (∠ Cl-P-Cl = 100.3°), and PF_3 (∠ F-P-F = 97.7°). (4 marks)

[8] Question 4

Glycine has the structure $NH_2CH_2C(=O)OH$. It can lose a proton from the carboxyl group and form chelate rings bonded through the N and the deprotonated O atom. Draw out all the possible isomers of tris(glycinato)cobalt(III).

[14] Question 5

(Use of the attached Tanabe-Sugano diagrams may help in answering the following).

a) Why is $[MnBr_6]^{4-}$ essentially colourless?

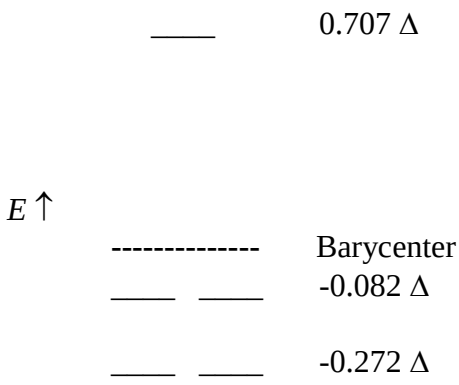
b) List all the spin-allowed transitions (originating from the ground-state) for $[Co(CN)_6]^{3-}$.

c) Why is the nephelauxetic parameter, β, significantly smaller for $[CoBr_6]^{3-}$ than for $[CoF_6]^{3-}$?

d) What is the ground-state term symbol for: i) As ii) Os^{2+} iii) $[Fe(CN)_6]^{3-}$

[13] Question 6

The splitting diagram for a trigonal bipyramidal (tbp) crystal field is given below. (The z-axis is coincident with the C_3 axis of the trigonal bipyramid).



a) *Redraw the splitting diagram above* in your booklets and label the energy levels with the appropriate *d* orbitals. (5 marks)

b) Calculate the LFSE for a d^3 (low-spin) and a d^7 (high-spin) ion *using the above diagram*. (4 marks)

c) For which *high-spin* and which *low-spin* d configurations is a Jahn-Teller distortion ***theoretically*** possible for a trigonal bipyramidal structure. Use the above splitting diagram to determine this. (4 marks)

[8] Question 7

a) Label the following transitions as either: spin-forbidden, Laporte forbidden, Laporte allowed, ligand-to-metal charge transfer (LMCT) or metal-to-ligand charge transfer (MLCT). Choose the most *appropriate* label. There is only **one** label for each transition! (Copy into your exam book).

i) $CO(\pi^*) \longleftarrow Co(3d\ t_{2g})$ _____

ii) $^3E_u \longleftarrow {}^3T_{2g}$ _____

iii) $^4T_{1g} \longleftarrow {}^2T_{2g}$ _____

iv) $^4T_{1g} \longleftarrow {}^4T_{2g}$ _____

v) $Au(5d\ e_g^*) \longleftarrow S^{2-}(\pi)$ _____

b) Rank the above transitions in order from weakest to strongest in intensity. (3 marks)

[9] Question 8

a) The ligand field splitting energies, Δ (cm^{-1}), are listed below for a series of cobalt compounds and a series of chromium compounds. Explain the two trends thoroughly. (7 marks)

i)

Complex	**Δ (cm^{-1})**
$[Co(NH_3)_6]^{3+}$	22,900
$[Co(NH_3)_6]^{2+}$	10,200
$[Co(NH_3)_4]^{2+}$	5,900

ii)

Complex	**Δ (cm^{-1})**
$[CrF_6]^{3-}$	15,000
$[Cr(H_2O)_6]^{3+}$	17,400
$[CrF_6]^{2-}$	22,000
$[Cr(CN)_6]^{3-}$	26,600

b) Briefly explain why far more tetrahedral complexes have *high-spin* configurations than octahedral complexes. (2 marks)

[11] Question 9

a) Derive the splitting pattern (you do not need to fully draw it) and determine the total number of lines in the EPR spectrum of $Cs_4[LaF_6]$. (unpaired electron on La) (4 marks)

(NOTE: for La, I = 7/2; for F, I = 1/2; and for Cs, I = 7/2)

b) The experimental magnetic moments of four manganese complexes are given below. Write down the electronic configurations (in terms of t_{2g} and e_g orbitals in an octahedral field) that is consistent with the data and state whether the complexes are high spin or low spin. (4 marks)

Complex	**μ_{exp} (B.M.)**
$[Mn(CN)_6]^{4-}$	1.8
$[Mn(CN)_6]^{3-}$	3.2
$[Mn(NCS)_6]^{4-}$	6.1
$[Mn(acac)_3]$	5.0

c) Suggest an electronic structure (configuration and geometry) for the complex $[(H_2O)_5FeNO]^{2+}$ that is consistent with a μ_{eff} = 3.9 BM. (3 marks)