Dr. Aquino **CHEMISTRY 341 FINAL** December 15, 2011

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 an s^1d^1 electronic configuration for a free ion and arrange them in a microstate table (M_L vs. M_S). (10 marks)

b) Determine the terms for this configuration. (4 marks)

c) What is the ground-state term? (1 mark)

[16] Question 2

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

a) BH_3 b) *fac*-$[FeCl_3Br_3]^{3-}$ c) ethane (staggered) d) NCS^-

[10] Question 3

An example of a linear 2-coordinate complex is $[Au(CN)_2]^-$.

a) Draw and label (with the appropriate d orbital) the d-orbital splitting diagram for this complex and fill it with the appropriate number of electrons. (Remember that your z axis should correspond to your principal rotation axis!). (6 marks)

b) Assuming $Ti(CN)_2$ and $[Co(CN)_2]^+$ adopt the same structure estimate their μ_{eff}. (4 marks)

[12] Question 4

Sketch all the isomers of the following complex ions:

a) i) $Pt(bipy)_2BrCl$ ii) $Re(dien)Br_2Cl$ (bipy = 2,2'-bipyridine; dien = diethylenetriamine)

b) Name the two complexes in a)

[8] Question 5

Construct molecules that have the following point groups: a) C_i b) D_{2d}

(4 marks each). (Note: Molecules must be reasonably chemically consistent!)

[15] Question 6

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

a) Why is $[FeCl_6]^{3-}$ essentially colourless?

b) List all the spin-allowed transitions (originating from the ground-state) for $[Cr(CN)_6]^{4-}$.

c) Why is the nephelauxetic parameter, β, significantly smaller for $[MnI_6]^{3-}$ than for $[MnF_6]^{3-}$?

d) Determine the ground-state term symbol for: i) Te ii) Ir^{4+} iii) $[CoCl_6]^{4-}$

[14] Question 7

a) 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. (6 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

b) Explain, with the aid of a rough graph, why a plot of hydration enthalpy versus number of d-electrons in the first-row transition metals (Sc to Zn) is *not* linear for the following reaction (4 marks):

$$M^{2+} + 6\ H_2O \longrightarrow [M(H_2O)_6]^{2+} \qquad \Delta H_{hydration}$$

c) Almost all first-row transition metals prefer octahedral geometry over tetrahedral. This is the case for Co(II) and Ni(II) complexes. However, Co(II) is more likely to form a tetrahedral complex than Ni(II). Why? (Explain in terms of LFSE). (4 marks)

[10] Question 8

Given a molecule with C_{4v} symmetry:

a) Draw a SALC corresponding to each of the following symmetry labels: i) a_2 ii) e iii) b_1 (There may be more than one SALC possible for each label. Make sure you define your coordinate axes).

b) Which metal orbitals are of appropriate symmetry to mix with the SALC's in a)?

c) Which SALC(s) of the above would have an IR active band associated with it (them)?