Exam III, Chemistry 4610/5560, Fall 2005
Department of Chemistry, University of North Texas, Dr. Mohammad Omary

Student name: _____

1. Fill the following table, which analyzes d-d (ligand-field) transitions in five complexes; refer to the appropriate Tanabe-Sugano diagram. (30 pts)

Complex	d^n , HS/LS	Ground state term symbol/ free ion	Ground state term symbol/ complex	Excited state term symbols /complex (see note* below)
$[Cr(CN)_6]^{4-}$				
$[Mo(H_2O)_6]^{2+}$				
$[WCl_6]^{4-}$				
$[Cr(CO)_6]$				
$[FeCl_4]^{2-}$				

* List only for spin-allowed transitions; if there is more than one, list them in order of increasing energy.

2. Predict which of the above five complexes (if any) will exhibit the following band types in the visible and near UV region, in addition to the d-d bands above: (8 pts)
LMCT bands:

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3. The low energies of d-d transitions in the visible region give most coordination compounds their distinctive visible colors (unlike most organic compounds). However, the following complexes are usually colorless. Explain for each case.
a. Octahedral complexes of Mn^{II} with weak-field ligands: (8 pts)

b. Zn^{II}, Hg^{II}, and Au^{I} complexes:

c. Sc^{III} and V^{V} complexes:

d. The organometallic complex $[Ni(CO)_4]$:

4. Explain the following: (8 pts)
a. In atomic absorption and emission spectroscopy, lines due to s-p and p-d transitions are observed while no lines are seen for s-s, s-d, p-p, and p-f transitions.

b. The electronic absorption spectra of organic compounds such as benzene have bands that can be assigned to $\sigma-\sigma^*$ and $\pi-\pi^*$ transitions but not to $\sigma-\pi^*$ and $\pi-\sigma*$ transitions.

5. a. Name the following compounds: (8 pts)

$[Re(CO)_3(en)Br]$:

$[Pt(NH_3)_3Cl_3]Cl$:

$[Co(en)_3]Cl_2$:

$[Ru(SCN)_2(bipy)_2](NO_3)_2$:

b. Draw ALL possible stereo isomers for the complex species in each compound and indicate which are chiral (*for chiral isomers, do NOT draw their mirror images; just indicate that they are chiral*). (20 pts)

You may use N⌒N to represent "en" and "bipy". Use the back page or a separate sheet if extra space is necessary.

6. Draw the structure of di-μ-chlorobis(tricarbonylcobalt) (0). (4 pts)

7. Use the concepts of the crystal field theory to predict a reasonable splitting of the five *d* orbitals when a transition metal ion is placed in a trigonal bipyramidal ligand field with σ-donor ligands. (7 pts)

8. Explain the consequences of replacing σ-donor ligands <u>in an octahedral complex</u> with ligands that can also act as either (a) <u>π acceptor</u> or (b) <u>π donor</u> in terms of: (12 pts)

- Whether Δ_o will become higher, lower, or unchanged.
- Whether the M-L bonds become stronger, weaker, or unchanged (you can conclude this by depicting how the t_{2g} or e_g orbitals become more or less bonding or antibonding, or whether they remain unchanged).

To get full credit, you need to illustrate the relative energy levels of the five *d* orbitals in the free ion, in the O_h field with only sigma bonding, and when the latter changes as a result of interacting with the ligand's <u>vacant π*</u>orbitals (in the case of <u>π acceptor</u> ligands in (a)) or with the ligand's <u>filled π</u> orbitals (in the case of <u>π donor</u> ligands in (b)).

(a) (b)

5 BONUS POINTS TOTAL - GOOD LUCK!