Name

Chem 370 - Spring, 2018 Hour Exam III - Part 1 May 7, 2018

- 1. (32 points; 4 points each) Fill in the blanks. In some cases, answer choices are shown in *bold italics*.
- a. From your recall of the appropriate Orgel diagram, indicate the number of bands expected in the visible spectra of the following complexes. (Disregard any possible bands resulting from Jahn-Teller effects or spin-forbidden transitions.)

 $[Cr(H_2O_6]^{3+}(d^3, O_h)] = [Fe(H_2O_6]^{2+}(d^6, O_h)] = [Fe(H_2O_6)^{3+}(d^6, O_h)]$

b. Circle the ground state term for each of the following complexes:

$[Cr(H_2O)_6]^{3+}(d^3, O_h)$	${}^{4}E_{g}$	${}^{4}T_{1g}$	${}^{4}\!A_{2g}$	${}^{4}T_{2g}$
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} (d^6, O_h)$	${}^{5}E_{g}$	${}^{5}T_{1g}$	${}^{5}\!A_{2g}$	${}^{5}T_{2g}$

c. Indicate whether the following complexes in their ground states show *strong*, *weak*, or *no* Jahn-Teller distortion.

 $[Cr(H_2O)_6]^{3+}(d^3, O_h)$ _____ [Fe(H_2O)_6]^{2+}(d^6, O_h) _____

d. $[Ni(NH_3)_6]^{2+}$ (d^8, O_h) shows visible absorption bands at 10,750 cm⁻¹, 17,500 cm⁻¹, and 28,200 cm⁻¹. What is the value (cm⁻¹) of Δ_0 for this complex, and what is the state-to-state notation (e.g., ${}^2E_g \rightarrow {}^2T_{2g}$) for the transition that corresponds to Δ_0 ?

 $\Delta_{\rm o} = ___ cm^{-1}$

transition _____

e. The visible spectrum of $[Fe(H_2O)_6]^{2+}$ (d^6, O_h) shows a broad absorption band with two distinct peaks at about 10,000 cm⁻¹. Give the state-to-state assignment for this band and suggest a reason why it is spit into two peaks.

f. In the reaction, $[Pt(NH_3)Br_3]^- + NH_3 \rightarrow [Pt(NH_3)_2Br_2]$, which isomer, *cis* or *trans*, will be favored for the product?

Answer: _____

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g. Consider the redox reaction,

 $[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5Br]^{2+} + 5 H_3O^+ \rightarrow [Cr(H_2O)_5Br] + [Co(H_2O)_6]^{2+} + 5 NH_4^+$

which occurs slowly in acidic aqueous medium. Is this redox reaction likely to be an *inner-sphere* or an *outer-sphere* mechanism? Explain briefly.

h. For the hydrolysis reactions,

$$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + X^{-}$$

where X⁻ is a halide, the rates of reaction are found to increase in the order F⁻ < Cl⁻ < Br⁻ < I⁻. Does this suggest a mechanism that is more *associative* (S_{N^2} , A, I_a) or *dissociative* (S_{N^1} , D, I_d)? Explain briefly.

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2. (12 points) Consider the Tanabe-Sugano diagram for d^7 octahedral complexes shown below.

List the same-spin state-to-state transitions that are expected for both d^7 high-spin and d^7 low-spin ML₆ complexes, using the usual state-to-state notation (i.e., ground state \rightarrow excited state).

d^7 high-spin	d^7 low-spin	

What factors might lead to fewer observed bands in the visible spectrum from the number of possible transitions you have identified for each case?