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Chem 370 - Spring, 2019
Hour Exam III - Part 1
May 13, 2019

1. (32 points; 4 points each) Fill in the blanks or circle the correct choice, as appropriate. 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.)

$[Ni(H_2O)_6]^{2+}$ (d^8, O_h) **3**

$[Cu(NH_3)_4]^{2+}$ (d^9, T_d) **1**

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

$[Ni(H_2O)_6]^{2+}$ (d^8, O_h) ^3E_g $^3T_{1g}$ $\boldsymbol{^3A_{2g}}$ $^3T_{2g}$

$[Cu(NH_3)_4]^{2+}$ (d^9, T_d) ^2E $^2T_1$ $^2A_2$ $\boldsymbol{^2T_2}$

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

$[Fe(H_2O)_6]^{2+}$ (d^6, O_h) **weak**

$[Fe(CN)_6]^{4-}$ (d^6, O_h) **no**

d. $[Cr(H_2O)_6]^{3+}$ (d^3, O_h) shows visible absorption bands at 17,400 cm^{-1}, 24,700 cm^{-1}, and 37,000 cm^{-1}. What is the value (cm^{-1}) of Δ_o 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_o? Be sure to include the correct spin states.

Δ_o = **17,400** cm^{-1}

transition $\boldsymbol{^4A_{2g} \rightarrow {}^4T_{2g}}$

e. The visible spectrum of $[Cu(H_2O)_6]^{2+}$ (d^9, O_h) shows a broad absorption band with a peak at ~12,500 cm^{-1}, but there is a pronounced shoulder on the band at ~11,000 cm^{-1}. Give the state-to-state assignment for the band and suggest a reason why it is partially split into two peaks.

One band is expected from the transition $\boldsymbol{^2E_g \rightarrow {}^2T_{2g}}$. But the $\boldsymbol{^2E_g}$ ground state is subject to a strong Jahn-Teller distortion, which lifts the double degeneracy of the ground state. Thus, two transitions from closely spaced lower states (possibly $\boldsymbol{^2A_{1g}}$ and $\boldsymbol{^2B_{1g}}$, if the distortion leads of $\boldsymbol{D_{4h}}$) to the weakly distorted $\boldsymbol{^2T_{2g}}$ excited state are possible, giving rise to the observed partial band splitting.

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f. The rates of substitution reactions of square planar complexes show a strong dependence on the identity of the entering ligand. Does this suggest a mechanism that is more ***associative*** ($S_{N}2$, A, I_a) or ***dissociative*** ($S_{N}1$, D, I_d)?

associative or dissociative? **associative**

g. The reaction, $^{*}Fe(CN)_6^{4-} + Fe(CN)_6^{3-} \rightarrow {}^{*}Fe(CN)_6^{3-} + Fe(CN)_6^{4-}$, in which *Fe is radioactive iron, is very rapid. Is this redox reaction likely to be an ***inner-sphere*** or an ***outer-sphere*** mechanism?

inner-sphere or outer-sphere? **outer-sphere**

h. Given:

$$[Ni(H_2O)_6]^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6\,H_2O \quad \log\beta_6 = 8.61$$

For the equilibrium,

$$[Ni(H_2O)_6]^{2+} + 3\,en \rightleftharpoons [Ni(en)_3]^{2+} + 6\,H_2O \qquad \log\beta_3 = ?$$

in which *en* = 1,2-diaminoethane (ethylenediamine), would you expect $\log\beta_3$ to be ***larger*** or ***smaller*** than 8.61?

Answer: $\log\beta_3$ is **larger** than 8.61.

Bonus Questions (4 points each)

a. CoF_6^{3-} has a single absorption band at ~14,300 cm^{-1}, resulting in a green color, but FeF_6^{3-} is colorless. Briefly explain the difference.

FeF_6^{3-} is high spin d^5 ($^6A_{1g}$), in contrast to CoF_6^{3-}, which is high spin d^6 ($^5T_{2g}$). For FeF_6^{3-} there are no excited states with the same spin, so no spin-allowed transitions are possible. The molar absorptivities for the spin-forbidden transitions are too low to give any noticeable color. In contrast, CoF_6^{3-} has one possible spin-allowed transition, $^5T_{2g} \rightarrow {}^5E_g$, which has a significant molar absorptivity. This gives rise to the band at ~14,300 cm^{-1}.

b. For the substitution reaction, $[PtClI_3]^{2-} + Cl^- \rightarrow [PtCl_2I_2]^{2-} + I^-$, which will be the principal isomer, *cis* or *trans*? Explain briefly.

The *cis* isomer will predominate, because I$^-$ is a better *trans*-directing ligand that Cl$^-$. Placing the attacking Cl$^-$ ligand *trans* to one of the existing I$^-$ ligands results in both Cl$^-$ ligands adjacent to each other and both I$^-$ ligands adjacent to each other, the *cis* isomer.

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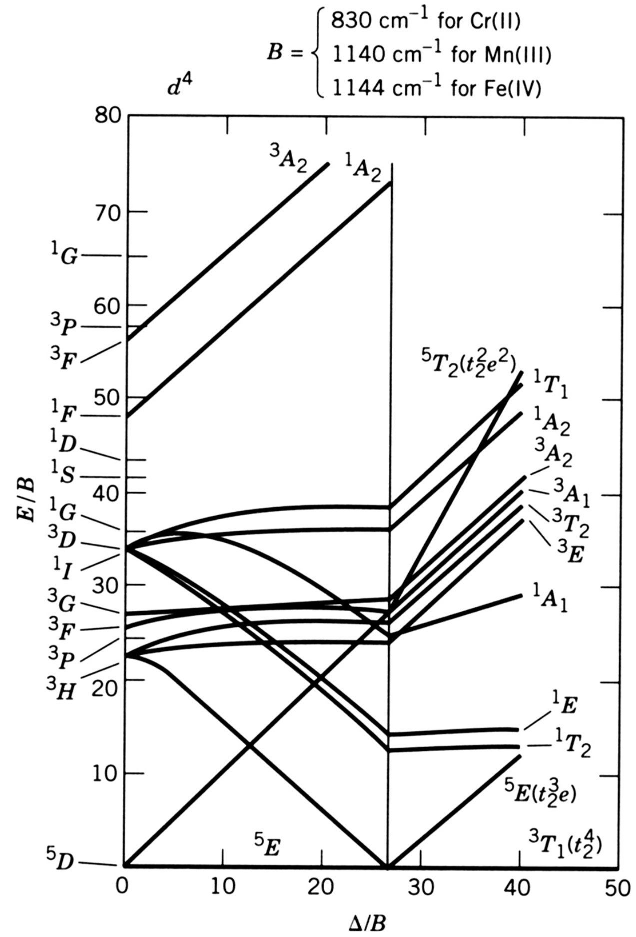
2. (12 points) Consider the Tanabe-Sugano diagram for d^4 octahedral complexes shown below.



List the same-spin state-to-state transitions that are expected for both d^4 high-spin and d^4 low-spin ML_6 complexes, using the usual state-to-state notation (i.e., ground state → excited state).

d^4 high-spin	d^4 low-spin
$^5E_g \rightarrow {}^5T_{2g}$	$^3T_{1g} \rightarrow {}^3E_g$
	$^3T_{1g} \rightarrow {}^3T_{2g}$
	$^3T_{1g} \rightarrow {}^3A_{1g}$
	$^3T_{1g} \rightarrow {}^3A_{2g}$

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

Both the ground state of the high-spin case and the first excited state of the low spin case have strong Jahn-Teller distortions, which could cause band splitting. For the low-spin case, the close spacing of all the excited states could result in incomplete resolution, making fewer bands apparent.