Birla Institute of Technology and Science, Pilani (Rajasthan)

MID-SEM TEST, SEMESTER II (2015-16)

CHEM F241: Inorganic Chemistry II **Closed Book** **Marks: 60**

Time: 90 min **Date: 15th March, 2016**

Instructions: There has a total six questions in all. Attempt all the questions. Start answering each question on a fresh page and answer all parts in a question together

1. (a) Differentiate a paramagnetic nucleus with a ferromagnetic one with example.

(b) The magnetic moments of $[Fe(1,10\text{-Phen})_2(NCS)_2]$ (1,10-Phen = 1,10-phenanthroline) complex at high temperature (above 175K) show large magnetic susceptibility whereas at low temperature (below 175K) show small magnetic susceptibility — explain it with illustration.

3 + 4 = 7M

2. (a) Show the bonding picture of $[Cr(NH_3)_6]^{3+}$ based on VBT model (atomic no. of Cr = 24; mag. moment of the complex = 3.80 BM).

(b) The structure of Fe_3O_4 belongs to inverse spinel — justify it based on CFT model. **(c)** Experiment shows that H_2O stabilizes Co(II) and forms $[Co(H_2O)_6]^{2+}$ only, whereas NH_3 stabilizes Co(III) and forms $[Co(NH_3)_6]^{3+}$ — explain it

3 + 3 + 3 = 9M

3. (a) For the following reaction, $M + nL = ML_n$, show that $\beta_n = K_1 \times K_2 \times .....\times K_n$ where β_n = overall stability constant and K_1, K_2 ,..., K_n are respective stepwise stability constants (n = 1 , 2 , 3 ...etc).

(b) Mention the type of isomerism of the following complexes, $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. Write down any one chemical test which will distinguish these.

(c) In the following complex, $[Co(CN)_5X]^{3-}$, X = thiocyanate, state the mode of coordination of thiocyanate with explanation.

(d) Metal ions having d^0, d^1 and d^2, in general only results eight coordination complexes – justify it in the light of CFT model.

(e) The complex, $[Ti(H_2O)_6]^{+}$ undergoes tetragonal distortion. Will it be tetragonal elongation or tetragonal compression? Explain it with respect to your answer.

3 + 3 + 2 + 3 + 3 = 14M

4. (a) Rate of acid hydrolysis of trans-$[Co(en)_2Cl_2]^{+}$ at 25 ^{0}C and pH = 1 in aqueous solution is as follows:

$[Co(en)_2Cl_2] + H_2O \longrightarrow [Co(en)_2Cl(H_2O)]^{2+} + Cl^-$ [Rate (K) = 1.9×10^3 min^{-1}]

(i) What do you think if you vary the ligand from "ethylene diamine (en)" to "propylene diamine (NH_2-CH_2-$CH(CH_3)$-NH_2)" and *meso*-butylene diamine (meso-NH_2-$CH(CH_3)$-$CH(CH_3)$-NH_2) the rate of the reaction will vary or not? Justify your answer.

(ii) Identify what kind of Nucleophilic Substitution (S_N) reaction is possible for this acid hydrolysis reaction and show the outline mechanism of the reaction.

(b) Using the concept of trans effect draw an outline for the synthesis of trans-$[Pt(C_2H_4)(NH_3)Cl_2]$ from $[PtCl_4]^{2-}$

(c) Predict the geometry of the complex which result from the following reaction:

$[Pt(NO_2)Cl_3] + py \longrightarrow [Pt(NO_2)pyCl_2]^- + Cl^-$

(1 + 2 + 1 + 2) + 2 + 2 = 10M

5. (a) Arrange the following metal ions (increasing order) according to the water exchange capability by dissociation and justify your answer: Mg^{2+}, Be^{2+} and Pt^{2+}

(b) The following redox reaction proceeds rapidly ($K = 1.5 \times 10^6$ min^{-1}) by an electron transfer mechanism.

$[Co(NH_3)_5(NCS)]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_3O^+ \longrightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5(NCS)] + 5NH_4^+$

Write a mechanism for the above electron transfer reaction.

(c) What is ligand's hapticity? Justify the statement with an example "ligands with more extended π systems exhibit a greater number of binding modes".

(d) Using 18-electron rule calculate total number of electrons for a complex, $(\eta^6 - C_6H_6)_2Fe$ and identify the stability of the complex. (**NB:** Fe is a first row transition element and at. no. 26)

(1 + 2) + 2 + (1 + 2) + 2 = 10M

6. (a) Complete the following reaction

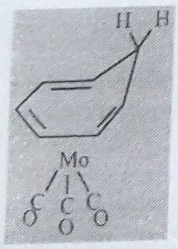
(i) $Co_2(CO)_8 + 2NO \longrightarrow$

(ii) $(OC)_5W = C(OMe)(Me) \xrightarrow{BCl_3}$

In the above question no (ii), describe the nature of metal-carbon bonding

(b) Describe with an example the nucleophilic nature of a Schrock carbene.

(c) Complete the following reaction



$\xrightarrow{(Ph_3C)^+(BF_4)^-}$

(2 + 2 + 2) + 2 + 2 = 10M