

Birla Institute of Technology and Science, Pilani (Rajasthan)

Second Semester 2022-23, May 6, 2023

Comprehensive Examination (Open Book) Part -II

CHEM F241; Inorganic Chemistry II

Time: 2 hours 10 min

Max. Marks: 56

Q1. (a) (a) Two different complexes, one red-orange (A) and the other green (B), can be isolated from an aqueous solution of Co^{3+} containing excess HCl and en. The red-orange complex A has the empirical formula $\text{CoCl}_3(\text{en})_3$ while the green complex B has the empirical formula $\text{CoCl}_3(\text{en})_2$. Addition of excess AgNO_3 (aq) to an aqueous solution of A or B produces a white precipitate but A produces 3 times as much precipitate as B on a molar basis. The red orange complex A can be resolved into a pair of enantiomers while the green complex B is not optically active. Assume Co^{3+} has the same coordination number in both complexes. Propose reasonable structures for both complexes A and B consistent with these observations and the behavior of chelate ligands. [3]

(b) Write down the reducible representation for the symmetric stretching vibration for SO_2 molecule and comment on whether this particular mode is IR active or Raman active. [Hint: Draw the vectors to represent the symmetric stretching vibration of the molecule] [2+2]

(c) Predict which of the following complexes will show Jahn-Teller distortion with **short** explanation: $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Cu}(\text{NH}_3)_4(\text{OH}_2)_2]^{2+}$, $[\text{Ti}(\text{OH}_2)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$. [4]

(d) Refer the correlation diagram (**Fig 15.1**) of your text book and answer the followings:

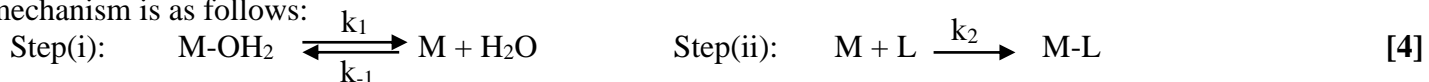
(i) Calculate the total number of microstates associated with t^2_{2g} electronic configuration at the ground state

(ii) Draw the microstates associated with 1E_g state appearing from e^2_g electronic configuration obtained as the highest excited state by applying strong ligand field. [1+2]

Q2. (a) Deduce the values of Δ_o and B for $[\text{Cr}(\text{NH}_3)_6]^{3+}$ from the Tanabe-Sugano diagram where the spectrum exhibits two lowest energy transitions at $21,550$ and $28,500 \text{ cm}^{-1}$. (Note: The final results may be approximated but the procedure should be clearly shown). [4]

(b) Formation of $[\text{Ni}(\text{en})_3]^{2+}$ is a three step process with the following stepwise formation constants $K_1=3.3 \times 10^7$, $K_2=1.9 \times 10^6$, and $K_3=1.8 \times 10^4$. Using this information find the overall formation constant and the formation constant for each of the intermediate steps. [2]

(c) Derive the rate law for the reaction in aqueous medium, $\text{M-OH}_2 + \text{L} \rightarrow \text{M-L} + \text{H}_2\text{O}$, where the proposed mechanism is as follows:

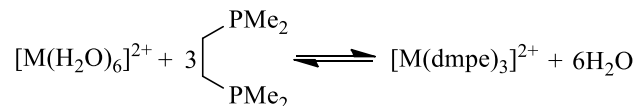


(d) How would you design a synthesis of the complex *trans*- $[\text{PtCl}_2(\text{NH}_3)(\text{tu})]$, (the *trans* descriptor refers to the pair of identical Cl⁻ ligands; Cl⁻ in this case, is mutually *trans*), given that the trans effect order is $\text{tu} > \text{Cl}^- > \text{NH}_3$ [$\text{tu} = (\text{H}_2\text{N})_2\text{CS}$]? Write down the steps involved. [4]

Q3. (a) Free N_2 has Raman stretching frequency at 2331 cm^{-1} and in $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ complex, N_2 shows the IR frequency at 2105 cm^{-1} . (i) Draw the structure of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and explain the reason behind the shift in stretching frequency observed? (ii) Why not the free N_2 molecule is IR active, whereas upon complexation it becomes IR active? [2+2]

(b) The organometallic compound, $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)(\text{CO})_2$ shows fluxional rearrangement. At room temperature, it shows two singlets in ^1H NMR one singlet of which at low temperature split further. Write down the structure of the molecule. Justify the ^1H NMR observations. [1+2]

(c) For the reaction,



(i) Would you expect the enthalpy contribution to be favourable ($\Delta H_0 < 0$) or unfavourable ($\Delta H_0 > 0$) if the metal is cobalt? In support of your answer, provide justification. [2]

(ii) Would you expect the entropy contribution to be favourable ($\Delta S_0 > 0$) or unfavourable ($\Delta S_0 < 0$) for the equilibrium shown in? Explain your answer. [1]

(d) What is Bohr Magneton? Calculate the spin-only magnetic moment of Co^{2+} ion in weak ligand field. The experimental magnetic moment ranges from 4.3 BM to 5.2 BM. Explain your observation. [1+1+2]

Q4. (a) With the help of a figure, explain the occupancy of electrons in the valence orbitals of C in a carbyne ligand and show its bonding with a metal. [3]

(b) How many total ligand group orbitals (LGO) are utilized from the ligand side to synthesize a metallocene molecule? Which atomic orbitals are used up to form those LGOs? Discuss the reason for the choice of the metal orbitals for the overlap with e_{1g} and e_{1u} LGO. [1+1+2]

(c) In the conversion of gasoline from synthesis gas, C-C bonds are generated to obtain $-(\text{CH}_2)_n-$ chain with appropriate number 'n'. Similarly, a typical carbide compound $\text{Fe}_6\text{C}(\text{CO})_{16}^{2-}$ creates C-C bond when it is oxidized and then is allowed to react with CO and then methanol. Show the newly formed C-C bond in the structure of the product and identify the driving force for the reaction to proceed to form this C-C bond. [1+2]

(d) Refer the catalytic loop for hydroformylation reaction (**Cycle 19.76**) in your text book and answer the following questions:

(i) What is the oxidation state of the metal present in the catalyst and how many valence electrons are there associated with the catalyst in the step where alkene is added to the catalyst? What type of addition reaction is that? [1+1]

(ii) Draw the structures of $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ with a proper justification mentioned, where C-O stretching frequencies observed in within the range of $1900\text{-}2050\text{ cm}^{-1}$. [1+1]

***** END *****