

PSG COLLEGE OF ARTS & SCIENCE
(AUTONOMOUS)

MSc DEGREE EXAMINATION DECEMBER 2022
(First Semester)

Branch – CHEMISTRY

TRANSITION METAL CHEMISTRY

Time: Three Hours

Maximum: 50 Marks

SECTION-A (5 Marks)

Answer ALL questions

ALL questions carry EQUAL marks (5 x 1 = 5)

- The complex that has maximum CFSE value is
(i) $\text{Co}(\text{NH}_3)_6^{3+}$ (ii) $\text{Ir}(\text{NH}_3)_6^{3+}$ (iii) $\text{Ir}(\text{CN})_6^{3-}$ (iv) $\text{Rh}(\text{CN})_6^{3-}$
- The magnetic moment of an octahedral $\text{Co}(\text{II})$ complex is 4.0 BM. The electronic configuration of the complex is
(i) $t_{2g}^5 e_g^2$ (ii) $t_{2g}^6 e_g^1$ (iii) $t_{2g}^3 e_g^4$ (iv) $t_{2g}^4 e_g^3$
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+ + \text{Hg}^{2+} \longrightarrow [\text{Hg}(\text{NH}_3)_5\text{Cl}]^+ + \text{Co}^{2+}$ reaction is an example of
(i) Electrophilic substitution reaction (ii) Nucleophilic substitution reaction
(iii) Electrophilic addition reaction (iv) Nucleophilic addition reaction
- Which of the following complex is achiral?
(i) $[\text{Cr}(\text{ox})_3]^{3-}$ (ii) $\text{Cis-}[\text{PtCl}_2(\text{en})]$
(iii) $\text{Cis-}[\text{RhCl}_2(\text{NH}_3)_4]^+$ (iv) $[\text{Co}(\text{Elt})]$
- Identify the wrong pair in the following.
(i) Fenilin – Iron storage (ii) Hemoglobin – O_2 storage
(iii) Cytochrome – Electron transfer (iv) Myoglobin - O_2 storage

SECTION - B (15 Marks)

Answer ALL Questions

ALL questions carry EQUAL marks (5 x 3 = 15)

- a. Draw MO diagram of an octahedral complex containing lower energy π -orbitals and explain.
OR
b. Explain how MO theory supports the splitting of d-orbitals as indicated by the crystal field theory.
- a. Illustrate the utility of magnetic moment studies in understanding the structures of Cobalt(II) complexes.
OR
b. In the complex, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ three absorption bands at 17000, 24000 and 37000 cm^{-1} are obtained. Assign the transitions using Orgel Diagram.
- a. Discuss the mechanism of nucleophilic substitution reactions in square planar complexes.
OR
b. "Kinetically inert complexes are thermodynamically unstable and vice-versa". Justify this statement with suitable examples.

Cont...

9. a. Discuss in brief isomerization of octahedral complexes.
OR
b. Outline an account on non-complementary electron transfer reactions.
10. a. Discuss the dioxygen binding modes in hemerythrin and hemocyanin.
OR
b. Write a note on Xanthine oxidase.

SECTION -C (30 Marks)

Answer ALL questions

ALL questions carry EQUAL marks

(5 x 6 = 30)

11. a. Draw MO diagrams of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ and discuss the significance of Δ_0 values of the complexes.
OR
b. Using CFT, show the orbital occupancies for both weak and strong octahedral fields for Mn^{2+} , Zn^{2+} and Co^{2+} . Indicate the number of unpaired electron in each case.
12. a. Explain Jahn-Teller distortion observed in Cu(II) complexes with its consequences.
OR
b. What is the advantage of Tanabe-Sugano diagram over Orgel diagram. Sketch the Tanabe-Sugano diagram for Co^{3+} system.
13. a. Discuss $\text{S}_{\text{N}}1$ mechanism of substitution reaction in O_h complexes. How does the charge of the ion and steric effect alter the rate of the reaction?
OR
b. Differentiate between trans effect and trans influence. Give a synthetic route for the synthesis of $[\text{Pt}(\text{NH}_3)\text{PyBrCl}]$ where Cl and Br are trans to each other from PtCl_4^{2-} .
14. a. On addition of $\text{K}_3[\text{Cr}(\text{CN})_6]$ solution to Fe(II) ion solution, coloured precipitates is obtained at room temperature as well on heating at 100°C . Comment on the colour of the precipitates and type of isomers formed with structures.
OR
b. A compound $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Cl}$ exists in three isomeric forms (A), (B) and (C). (A) reacts neither with AgNO_3 nor with *en* and is optically inactive. (B) reacts with AgNO_3 and forms white precipitate but does not react with *en* and is optically inactive. (C) is optically active and reacts with both AgNO_3 and *en*. Identify each isomer, draw their structures and give suitable reasons.
15. a. Discuss the structure of carbonic anhydrase and the mechanism of the reversible hydration of carbon dioxide to carbonic acid involving carbonic anhydrase.
OR
b. Discuss in detail, the mechanism of drug action of *cis*-platin a anticancer drug.

Z-Z-Z

END