



# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

## M.Sc. DEGREE EXAMINATION - CHEMISTRY

THIRD SEMESTER – NOVEMBER 2011

### CH 3809 - COORDINATION CHEMISTRY

Date : 02-11-2011  
Time : 9:00 - 12:00

Dept. No.

Max. : 100 Marks

#### Part-A

*Answer all questions. Each question carries two marks.*

1. It is exceedingly difficult to synthesize tetrahedral complexes of  $d^6$  metal ions with strong ligands. Rationalize.
2. Both Mn(II) and Fe(III) are  $d^5$  metal ions, but the tendency of Fe(III) to form low-spin complexes is much higher than that of Mn(II). Offer a reasonable explanation.
3. The reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with ethylenediamine and HCl in a 1:2:2 mole ratio affords a green complex, which on heating becomes purple. Explain this observation.
4. For which of the following would you expect the molar extinction coefficient to be greater: high-spin Fe(II) or high-spin Mn(II)? Justify your answer.
5. In which of the compounds would you expect detectable Jahn Teller distortion:  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  or  $[\text{Mn}(\text{en})_2(\text{NH}_3)_2]^{3+}$ ? Justify your answer.
6. What is  $\pi$ -acceptor series? How is it constructed?
7. Cobaltocene is more susceptible for oxidation than ferrocene. Give reason.
8. What is *trans*-directing series? How is it constructed?
9. What is insertion reaction? Cite an example.
10. Mention the biological role of superoxide dismutase.

#### Part-B

*Answer eight questions. Each question carries five marks.*

11. Crystal field theory treats square planar geometry as an extreme case of Jahn Teller distortion arising by the elongation of the axial ligands. Explain with the help of crystal field splitting energy level diagram.
12. Define constitutional isomerism.  
Write the structures of possible isomers of (a)  $[\text{Co}(\text{en})_2(\text{SCN})_2]^+$  and (b)  $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2\text{Cl}_2]$ .
13. Justify the position of  $\text{F}^-$  in the spectrochemical series with the help of MO theory.
14. Construct the Orgel diagram for the electronic transitions of high spin octahedral complexes of  $d^2$  and  $d^8$  metal ions.
15. How are Zeigler Natta catalysts prepared? Explain the mechanism of polymerization of olefins by this catalyst.
16. Illustrate the influence of coordination on the reactivity coordinated of ligands with examples.
17. Explain the mechanism of alkene hydrogenation by Wilkinson's catalyst.
18. Define *trans*-effect. Explain the synthesis of coordination compounds by exploiting this effect.
19. Explain photoisomerization and photosubstitution reactions in transition metal complexes with examples.

20. Give an account of the synthesis and structural features of  $\pi$ -complexes of cyclooctatetraene and cycloheptatriene with transition metals.
21. Explain the structure and functions of carboxypeptidase A.
22. Explain the mechanism of oxygen transport in mammalian systems.

### Part-C

*Answer four questions. Each question carries ten marks.*

- 23a. What are LGOs? How are they constructed? Identify the LGOs and transition metal orbitals suitable for  $\sigma$ - and  $\pi$ -bonding. (3)
- b. Construct a qualitative MO energy level diagram for an octahedral complex of a transition metal ion with a ligand which is both a  $\sigma$ - and  $\pi$ -donor. (7)
- 24a. Explain the principle of angular overlap model. (4)
- b. Show that  $\Delta_t = 4/9 \Delta_o$ . (6)
- 25a. State Jahn Teller theorem. Explain the crystal field splitting pattern in a tetragonally distorted octahedral geometry as a consequence of Jahn teller distortion. (6)
- b. Show that Jahn Teller distortion in octahedral complexes of  $d^1$  metal ions by the compression of the axial ligands is energetically more favorable than the distortion taking place by the elongation of the axial ligands. (4)
- 26a. What are electron transfer reactions? Differentiate complimentary and noncomplimentary electron transfer reactions with examples. (3)
- b. Explain the inner- and outer-sphere mechanisms of electron transfer reactions in coordination compounds with examples. Mention the various factors which affect these mechanisms.
- 27a. What is molecular recognition? Give an account of recognition of neutral molecules by molecular receptors. (5)
- b. Explain supramolecular assemblies formed by self assembly methods. (5)
- 28a. The solid state epr spectrum of  $[\text{Cu}^{\text{II}}(\text{salen})]$  doped onto a diamagnetic host consists of four sets of four lines. Interpret the spectrum and justify your interpretation with experimental evidences. (7)
- b. How do you differentiate isotropic and anisotropic systems by epr spectroscopy? (3)

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