



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – NOVEMBER 2014

CH 3809 / 3813 - COORDINATION CHEMISTRY

Date : 30/10/2014

Dept. No.

Max. : 100 Marks

Time : 09:00-12:00

Part-A

Answer all questions. Each question carries two marks:

(10x2=20)

1. The thermodynamic stability of high-spin complexes of $d^{0,5,10}$ metal ions are lower than that of other d^n metal ions under identical ligand framework. Comment upon this observation.
2. It is exceedingly difficult to synthesize low-spin tetrahedral complexes of first row transition metals. Rationalize.
3. In the presence of moderate to strong field ligands Co(II) has a strong tendency to get oxidized to the Co(III) state in aqueous solution. Give reason.
4. The CN stretching vibration in cyano complexes occur at higher energy than that of free cyanide ion. Explain.
5. Differentiate *trans*-effect and *trans*-influence.
6. What is π -acceptor series? How is it constructed?
7. Transition metal complexes are invariably colored, while their carbonyls are mostly colorless. Give reason.
8. The complex $[\text{cpFe}(\text{CH}_2=\text{CH}_2)(\text{CO})_2]$ when reacted with a nucleophile, the coordinated cyclopentadienyl ligand remains a spectator, whereas ethylene reacts. Explain.
9. What are (i) exciflex and (ii) excimer?
10. What is intensity stealing?

Part-B

Answer eight questions. Each question carries five marks:

(8x5=40)

11. Explain linkage- and optical isomerism in coordination compounds.
12. d^6 Metal ions have a strong tendency to form octahedral complexes, while d^8 metal ions have a strong tendency to form square planar complexes with strong ligands. Explain with the aid of qualitative crystal field splitting energy level diagrams.
13. How are the following differentiated by IR spectroscopy: (a) nitro- and nitrito complexes and (b) thiocyanato- and isothiocyanatocomplexes.
14. State Jahn Teller theorem. Explain static dynamic Jahn Teller effect with an example.
15. What are Orgel diagrams? Construct the Orgel diagram for $d^{3,8}$ metal ions in O_h and T_d geometries.
16. Explain the mechanism of a photochemical reaction of a coordination compound when it is irradiated at its (a) charge transfer band (b) LF band.
17. Explain the electronic spectral features of high-spin octahedral and tetrahedral complexes of d^{1-9} metal ions.
18. Give an account of the reactivity of organometallic complexes of cyclobutadiene and benzene.
19. Explain oxidative addition and reductive elimination reactions with examples.
20. How is *cis*-platin synthesized? Explain the mechanism.
21. Explain the mechanism of Ziegler-Natta polymerization.
22. Explain the structure and functions of superoxide dismutase.

Part-C

Answer four questions. Each question carries ten marks:

(4x10=40)

- 23a. Identify the metal orbitals and LGOs suitable for σ - and π -bonding in octahedral complexes of transition metal ions. Construct a qualitative MO energy level diagram for σ -bonding.
b. Explain π -bonding by π -acceptor ligands with transition metal ions with the help of MO theory. (6+4)
24. Explain the principles of angular overlap model. Show that $\Delta_t = 4/9 \Delta_o$ with the help of this theory.
- 25a. What are electron transfer reactions? Differentiate complimentary and non-complimentary electron transfer reactions with examples. (3+7)
b. Explain the mechanisms of electron transfer reactions in coordination compounds with examples. Mention the various factors which affect these mechanisms.
26. Discuss the various mechanisms of substitution reactions of octahedral and tetrahedral complexes.
- 27a. Explain the structural features of hemoglobin and myoglobin. Explain the mechanism of oxygen transport and storage by these heme proteins. (6+4)
b. Write a note on copper proteins.
- 28a. The epr spectrum of bis(salicylalimine)copper(II) (spin of ^{63}Cu is 3/2) consists of four sets of eleven lines each. Interpret the spectrum and substantiate your result with the help of experimental evidences.
b. How would you differentiate isotropic and anisotropic systems by epr spectroscopy? Mention the causes of anisotropy in transition metal complexes.
