LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

FOURTH SEMESTER – **APRIL 2013**

CH 4956 - ADVANCED COORDINATION CHEMISTRY

Date : 30/04/2013 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

Part-A

Answer all questions. Each question carries two mark: ***10x2=20***

1. What are excimers?
2. The coordination compounds of high-spin Mn(II) are feebly colored, whereas that of Mn(VII) are intensely colored. Explain.
3. What is transmetallation reaction. Cite an example.
4. What are internal electrochemical standard? Cite two such compounds.
5. How is the covalent character in transition metal complexes evaluated quantitatively?
6. Mention the different kinds of metallodendrimers.
7. Mention the roles of internal electrochemical standard. Cite two examples.
8. What are compartmental ligands? Give an example.
9. Mention the role of bridging ligands in the assembly of supramolecules. Cite an example.
10. In which of the compounds would you expect detectable Jahn Teller distortion:$[Mn(H_2O)]^{3+}$ or $[Mn(en)_2(NH_3)_2]^{3+}$? Justify your answer.

Part-B

Answer eight questions. Each question carries five marks: ***8x5=40***

11. Explain photoisomerization reaction with an example.
12. Highlight the spectroscopic and photochemical properties of polypyridylcomplexes of ruthenium(II).
13. Explain the electronic absorption spectral features of high spin octahedral and tetrahedral complexes of transition metal ions.
14. What is a molecular architecture? Explain the synthesis of a molecular square.
15. What are rotaxanes? Explain the construction of such an assembly.
16. Explain the template synthesis of 2- and 3-catenanes.
17. Define molecular machine. Explain the synthesis of one such molecule.
18. Explain the construction of a photochemically controlled molecular shuttle.
19. Explain acid/base driven threading and dethreading motions in supramolecular assemblies.
20. What are Tanabe Sugano diagrams? How are they constructed?
21. Illustrate the importance of cation cavity “best-fit” in the synthesis of macrocyclic complexes by coordination template effect with illustrative examples.
22. Explain the principle of cyclic voltammetry and the method of evaluating the electrochemical reversibility of a redox couple.

Part-C

Answer four questions. Each question carries ten marks ***4x10=40***

23a. According to MO theory, π-donation by ligands lowers the magnitudes of $10D_q$ values whereas π-back bonding increases its magnitude. Explain with a qualitative MO energy level diagrams.

b. Justify the position of π-donating and π-back bonding ligands in the spectrochemical series.

24. A six-coordinate low-spin cobalt(III) complex of a quadridentate ligand in the equatorial position with two monodentate ligands in the axial sites exhibits electronic transitions at 660 nm ($\in$ = 76.5 L mol^{-1} cm^{-1}), 525 nm ($\in$ = 1260 L mol^{-1} cm^{-1}), and 415 nm ($\in$ = 396 L mol^{-1} cm^{-1}). Assign these transitions, predict the geometry, and compute the field strength of the axial and equatorial ligands.

25a. What are contrast enhancing agents for MRI? Explain their role in accelerating water proton relaxivity.

b. Give the structure of the FDA-approved contrast agents for MRI.

26a. Explain the principle and methodology of constructing a dye sensitized solar cell.

b. Give an account of Ru(II) polypyridyl complexes used in the construction of solar cells.

27a. Explain the methods of synthesizing dendrimers.

b. Give an account of the application potential of dendrimers and metallodendrimers.

28. Explain template synthesis of macrocyclic and compartmental macrocyclic ligands and their complexes with illustrative examples.

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