

D 6814

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Name.....

Reg. No.....

THIRD SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2016

(CUCSS)

Chemistry

CH 3C 08—INORGANIC CHEMISTRY—II

(2010 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Part A

Answer all questions.

Each question carries 1 weightage.

1. The LMCT bands increases in energy in the series $\text{CoI}_4 < \text{CoBr}_4 < \text{CoCl}_4$. Explain.
2. Name two substances used in Gouy method as standard.
3. Calculate the spin only magnetic moments of the following complexes : (a) $[\text{Mn}(\text{H}_2\text{O})_6] \text{SO}_4$; and (b) $\text{K}_4 [\text{Mn} (\text{CN})_6]$.
4. Explain Curie and Curie-Weiss laws.
5. What do you mean by *cis* effect ?
6. Derive the ground state terms of d^2 and d^3 configurations.
7. Describe the photosubstitution and photoaquation reactions with examples.
8. What changes take place in the ligand vibrations in IR spectra on co-ordination with metals ?
9. What are the limitations of Mössbauer spectroscopy ?
10. Represent the structures of $\text{Mn}_2\text{CO}_{10}$, CO_2CO_8 , Fe_2CO_9 and $\text{Fe}_3\text{CO}_{12}$.
11. How carbonyl groups stabilize low positive oxidation states of transition metals ?
12. Free cyclobutadiene (C_4H_4) is unstable whereas complexes such as $[\text{Fe} (\text{CO})_3 (\eta^4 - \text{C}_4\text{H}_4)]$ are stable. Explain why ?
13. What are nitrogenases ? Give the functions of nitrogenases.
14. What are cytochromes ? Give the active site structure of cytochrome P -450.

(14 × 1 = 14 weightage)

Turn over

Part B

Answer any seven questions.
Each question carries 2 weightage.

15. Calculate $10 Dq$ and β value for the complex $[\text{Ni}(\text{CH}_3\text{NH}_2)_6]^{2+}$ from the following data :

$$\nu_1 = 10000 \text{ cm}^{-1}, \nu_2 = 16780 \text{ cm}^{-1}, \nu_3 = 27320 \text{ cm}^{-1} \text{ and } B = 1030 \text{ cm}^{-1} \text{ for } \text{Ni}^{2+} \text{ ion.}$$

16. Discuss the magnetic properties of lanthanides.
17. Describe the associative and dissociative mechanisms of substitution reactions involving co-ordination complexes. How can you distinguish between them ?
18. How *cis* and *trans* isomers of $[\text{PtCl}_2(\text{NH}_3)\text{NO}_2]^-$ are prepared from $\text{K}_2[\text{PtCl}_4]$?
19. Why are Cr(III) and Co(III) ions important from photochemical point of view ?
20. Draw the structures of $\text{Co}_2(\text{CO})_8$, $\text{Ru}_3(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$. Show that 18-electron rule is satisfied in each case.
21. Account for the following variations in CO stretching vibrations :
- | | |
|---------------------------------|------------------------|
| $\text{CO}(\text{g})$ | 2143 cm^{-1} |
| $[\text{Mn}(\text{CO})_6]^+$ | 2090 cm^{-1} |
| $\text{Cr}(\text{CO})_6$ | 2000 cm^{-1} |
| $[\text{V}(\text{CO})_6]^-$ | 1860 cm^{-1} |
| $[\text{Ti}(\text{CO})_6]^{2+}$ | 1750 cm^{-1} |
22. Explain the synthesis of dibenzene chromium. Describe its structure.
23. What metal ions are present in superoxide dismutase ? How are they linked ?
24. Give the co-ordination environment of the metal ion in vitamin B_{12} and mention any two biochemical reactions catalysed by vitamin B_{12} .

(7 × 2 = 14 weightage)

Part C

Answer any two questions.
Each question carries 4 weightage.

25. Explain the significance of Pascals constants. How it is possible to distinguish octahedral, tetrahedral and square planar complexes of nickel(II) using magnetic susceptibility measurements ?

26. What is Marcus theory of electron transfer ? Give its significance with suitable examples.
27. The EPR spectrum of bis(salicylalimine) copper (II) shows four groups of lines which result from the coupling of ^{63}Cu ($I = 3/2$) nucleus ; the hyperfine structure in each of the four groups consists of eleven peaks with intensity ratio of 1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1. Explain the two types of splitting observed.
28. Describe the synthesis, structure and MO diagram of ferrocene.

(2 × 4 = 8 weightage)