

Register Number:

Date:

**ST. JOSEPH’S COLLEGE (AUTONOMOUS), BANGALORE-27**

**M.Sc. CHEMISTRY– II SEMESTER**

**SEMESTER EXAMINATION: APRIL 2019**

**CH 8118 : INORGANIC CHEMISTRY**

Time- 2 ½ hrs Max Marks-70

**This paper contains TWO printed pages and THREE parts.**

**PART A**

**Answer any SIX questions. 2 x 6 =12**

1. High spin Cr(II) forms distorted octahedral complexes. Why?
2. Enthalpy of hydration of Mn2+ ion is less than that of Cr2+ ion. Explain.
3. The stability constants of the complex ions, [Fe(CN)6]3- and [Fe(CN)6]4- are about 1031 and 106 respectively. Explain.
4. Write the resonance structures to illustrate the bonding in metal nitrosyl complexes.
5. Distinguish between stepwise and overall stability constants.
6. What is the nature of bonding between a bridging hydride ion and a metal in dinuclar metal complexes?
7. Electronic absorption bands of the complex [NiCl4]2- show greater intensities than those of the octahedral complex [Ni(H2O)6]2+.
8. What are Pascal’s constants? What are they used for?

**PART B**

**Answer any FOUR questions. 12 x 4 =48**

1. a) Illustrate the metal d-orbital splitting in 5-coordinate complexes with square pyramidal and trigonal bipyramidal geometries.
2. [Fe(CN)6]3- is a low spin complex whereas [FeF6]3- is a high spin complex. Explain this observation using molecular orbital theory. (6+6)
3. a) Tris-chelates of Cu(II) are highly unstable. Explain this observation.

b) Metal ions can act as templates in the synthesis of supramolecular assemblies. Illustrate this statement with an example.

c) Explain ‘hole formalism’ using d1 and d9 configurations as examples. (4+4+4)

1. a) Discuss the determination of stability constant of a complex by ion-exchange method.

b) With proper reasoning explain the following: log K values of the complexes, [Co(NH3)4(H2O)2]2+ , [Co(en)2(H2O)2]2+ and [Co(trien)(H2O)2]2+ are 5.3, 10.9 and 12.8 respectively. Discuss the contribution of thermodynamic factor involved. (6+6)

1. a) What is optical rotatory dispersion (ORD)? Using an example explain how the absolute configuration of a complex is determined using this method.

b) Explain the bonding in transition metal complexes of tertiary phosphine(PR3). How does the nature of the substituent R affect the metal phosphine bond? (6+6)

1. a) Calculate the magnetic moment of Dy2(SO4)3.8H2O. Given, the outer electronic configuration of Dy is 4f106s2.

b) Explain the following observations: i) the observed μeff of spin-free octahedral Co2+ complexes are in the range 4.7-5.2 BM, while the calculated spin-only value is 3.89 BM ii) the observed μeff of spin-paired Co2+ complexes are in the range 1.8-1.85 BM whereas the calculated spin-only value is 1.73 BM. (6+6)

1. a) The complex [Ni(NH3)6]2+ shows three absorption maxima 10,750cm-1,17,500cm-1 and 28,200cm-1. Draw the appropriate Orgel diagram and assign the bands based on this diagram.
2. The lone absorption band in the visible spectrum of [Ti(H2O)6]3+ is of low intensity and is unsymmetrical. Explain each of these observations.
3. What is Tanabe-Sugano diagram? Explain its salient features. (4+4+4)

**PART C**

**Answer any TWO questions. 5 x 2 =10**

1. The hydration energies of Ca2+, Mn2+ and Zn2+ are plotted versus atomic number. A smooth curve passing through these points gave a value of 3000 kJ mol-1 for the hydration energy of Ni2+. If 3A2g →3T2g transition of [Ni(H2O)6]2+ ion occurs at 8600 cm-1, estimate the true hydration energy of Ni2+ ion.
2. The compound Fe(CO)2(η5-C5H5)2(η1-C5H5)2 gives two sharp proton NMR signals while Ti(η5-C5H5)2(η1-C5H5)2 gives only one signal at room temperature. Account for this observation. What is the nature of the spectrum you would expect for the titanium complex at very low temperatures?
3. In which among the following tetrahedral complexes would you expect orbital contribution towards magnetic moment? V3+, Cr3+, Mn2+? Explain your answer.