

Date:

Registration number:

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

**M.Sc. Chemistry - II SEMESTER**

 **SEMESTER EXAMINATION: April 2022**

 (Examination conducted in July 2022)

 **CH 8121 – Inorganic Chemistry- II**

**Time- 2 ½ hrs Max. Marks-70**

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

**PART-A**

**Answer any SIX out of the following EIGHT questions: 6 X 2 = 12 Marks**

1. Mention any four geometries exhibited by eight coordinated transition metal ions.
2. Write the expression for nephelauxetic ratio and explain the terms.
3. Represent the modes of coordination of NO2- ligand with transition metal ions.
4. Write the selection rules for electronic transitions.
5. Arrive at the free ion term for d2 configuration.
6. Write the expression for Curie-Weiss law. What does Weiss constant signify?
7. What is Tolman cone angle? Give its significance.
8. Explain the following statement: The complex, [Ni(CN)4]2-, although thermodynamically stable, is kinetically labile. .

**PART-B**

**Answer any FOUR out of the following SIX questions: 4 X 12 = 48 Marks**

1. (a) Sketch the crystal field splitting pattern of metal d orbitals in i) square pyramidal and ii) trigonal bipyramidal ligand fields.

(b) The lattice energy of CrCl2 is greater than that of MnCl2 but less than that of VCl2. Explain.

(c) Complexes of Cu(II) and high spin Cr(II) ions exhibit distorted octahedral geometry. Explain. (4+4+4)

1. (a) Describe the charge transfer transitions LMCT and MLCT, with the help of a qualitative partial molecular orbital diagram.

(b) [Mn(OH2)6]2+ is pale pink in colour whereas [MnBr4]2- show yellowish green colour which is more intense than the former. Explain.

(c) What is Tanabe-Sugano diagram? Draw a qualitative Tanabe-Sugano diagram for a transition metal with d2 configuration. (4+4+4)

1. a) Differentiate between stepwise and overall stability constants taking the formation of [Co(en)3]2+ as an example. Arrange the stepwise formation constants in the order of decreasing magnitude and give a reason for this order.

b) Discuss the Job’s spectrophotometric method of determining the stability constant and composition of coordination complexes. (6+6)

1. (a) Sketch different modes of coordination of sulphate ion in metal complexes. Predict the number of IR active ν(S-O) bands based on the symmetry of each mode of coordination.

(b) Discuss the bonding in metal nitrosyl complexes on the basis of MO theory. (6+6)

1. (a) Deduce the total electron count and predict the skeletal structure of the following carbonyl clusters. (i) HRu4N(CO)12 (ii) Fe5(CO)15C

(b) Which complex will have a higher CO absorption frequency, [(Me3P)Ni(CO)3] or [(F3P)Ni(CO)3]? Give reason.

(c) Explain the fluxional behaviour of Fe(CO)5 based on 13C NMR spectroscopy.

 (6+3+3)

1. (a) Sketch the qualitative molecular orbital energy level diagram for an octahedral complex containing only six sigma donor ligands.

(b) Explain the following observations:

i) The observed *μ*eff of spin-free octahedral Co2+ complexes are in the range 4.7-5.2 BM, while the calculated *μ*(spin-only) is 3.89 BM.

 ii) The observed *μ*eff ofoctahedral Cr3+ complexes are generally lower than that of *μ*(spin-only) value.

(c) What is the condition for an electron to have orbital contribution to magnetic moment? Explain why an electron present in a dz2 orbital does not contribute to magnetic moment. (4+5+3)

**PART-C**

**Answer any TWO out of the following THREE questions: 2X 5 = 10 Marks**

1. Give reason/s for the following observations.

(a) The UV-Vis spectrum of an aqueous solution containing Cr(III) ion shows only two bands.

(b) The aqueous solution of Ce(IV) is bright yellow in colour (explain based on the nature of electronic transitions). (3+2)

1. Account for the following:

(a) Almost all complexes of Co(III) are octahedral and low spin while with Fe(III) both high spin and low spin octahedral complexes are observed.

(b) Two transition metal ions that consistently form a large number of normal spinels are Zn2+ and Cr3+. (3+2)

1. Red crystalline [NiCl2(PPh2CH2Ph)2] is diamagnetic. On heating to 387K for 2 hours, a blue-green form of the complex is obtained, which has a magnetic moment of 3.18 BM at 295 K. Suggest an explanation for these observations and draw structures for the complexes.

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