Registration Number:

Date & session:



ST JOSEPH'S UNIVERSITY, BENGALURU -27 M.Sc (CHEMISTRY) – 2<sup>nd</sup> SEMESTER SEMESTER EXAMINATION: APRIL 2024 (Examination conducted in May / June 2024) <u>CH 8122 – INORGANIC CHEMISTRY II</u> (For current batch students only)

Time: 2 Hours

Max Marks: 50

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

# PART-A

#### Answer any EIGHT of the following questions.

8 X 2 = 16

- 1. Mention the coordination number and geometry of Re in Ca[ReH<sub>9</sub>].
- 2. Sketch the crystal field splitting diagram for [Ni(CN)<sub>4</sub>]<sup>2-</sup>.
- Which of the following complexes is more stable? Give reason. [Cu(trien)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> or [Cu(cyclen)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, where trien: tri(ethylenediamine), cyclen: 1,4,7,10-Tetraazacyclododecane
- 4. Compare the IR spectra of *fac* and *mer*-[MA<sub>3</sub>B<sub>3</sub>] isomers.
- 5. Calculate the number of microstates for d<sup>4</sup> configuration.
- 6. Many lanthanide complexes display weak but sharp absorption spectra. Give reasons.
- 7. List the factors contributing to the bandwidth of electronic absorption spectra.
- 8. With a suitable diagram, illustrate the super exchange mechanism of antiferromagnetic coupling between two metal centers by a bridging ligand.
- 9. Depict the binding modes of hydride ligands in metal hydrides showing i) 3*c*-2*e* and ii) 4*c*-2*e* interactions.
- 10. Draw the optical isomers of *cis*- $[CoCl(NH_3)(en)_2]^{2+}$  complex ion.

### PART-B

#### Answer any TWO of the following questions.

# 2 X 12 = 24

11. a) Account for the higher lattice energy value of NiF<sub>2</sub> (3060 kJmol<sup>-1</sup>) compared to  $ZnF_2$  (2985 kJmol<sup>-1</sup>).

b) Sketch a qualitative molecular orbital energy level diagram for an octahedral  $ML_6$  complex with only  $\sigma$ - bonding.

c) Which of the following ligands will form a more stable complex with a M(II) ion under basic conditions? Malonic acid  $CH_2(COOH)_2$  or acetylacetone  $CH_2(COCH_3)_2$ . Give reason. d) Calculate the magnetic moment of  $K_3[FeF_6]$  using the following data:

 $\chi_{M}$  (corrected) =14.6 x 10<sup>-3</sup> (B.M.)<sup>2</sup>K<sup>-1</sup> at 300 K. What is the calculated spin-only magnetic moment for this complex? (3+3+3+3)

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12. a) Identify the type of unidentate coordination mode of NO<sub>2</sub> ligand in complexes (A) and (B) using the IR spectral data given below. Explain.

Compound	ν(NO), cm <sup>-1</sup>
$K_{3}[Co(NO_{2})_{6}](A)$	1386, 1332
$[Co(NH_3)_5(NO_2)]Cl_2(B)$	1468, 1065

b) A solution of  $[Cr(OH_2)_6]^{3+}$  is pale green-blue ( $\epsilon_{max} = 15 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ), but a solution of  $[CrO_4]^{2-1}$  is intense yellow ( $\epsilon_{max} = 4500 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ). Identify the origins of electronic transitions in these complexes and explain their relative intensities.

c) Arrange the following terms in the order of increasing energy: <sup>1</sup>G, <sup>1</sup>S, <sup>3</sup>F, <sup>3</sup>P. Give reasons for your answer.

d) Explain spin-crossover with an example. (3+3+3+3)

13. a) Compare the C-O and M-C bond distances in  $[V(CO)_6]^-$  and  $[Mn(CO)_6]^+$ . Explain.

b) Deduce the total electron count and predict the skeletal structure of HRu<sub>4</sub>N(CO)<sub>12</sub>.

c) What is Tolman cone angle? Between the following, identify the one with a larger Tolman cone angle.

i) P(*n*-propyl)<sub>3</sub> or ii) P(*i*-propyl)<sub>3</sub>

d) Proton NMR spectra of titanocene,  $[Ti(C_5H_5)_4]$  shows a single peak at 62°C and two peaks at -27°C. Explain this on the basis of hapticity of the ligand. (3+3+3+3)

# PART-CAnswer any TWO of the following questions.2 X 5 = 10

- 14. a) Predict the type of distortion in  $[Ti(H_2O)_6]^{3+}$  based on stabilization energy.
  - b) Which of the following conversions is accompanied by a larger change in metal-ligand bond distance? Justify.

i) 
$$[Fe(CN)_6]^{3-}$$
 →  $[Fe(CN)_6]^{2-}$   
ii)  $[Co(NH_3)_6]^{3+}$  →  $[Co(NH_3)_6]^{2+}$  (2+3)

- 15. Assign the electronic transitions in [MCl<sub>4</sub>]<sup>-</sup> ion using an Orgel diagram, where M is a firstrow transition metal ion with two unpaired electrons in 'e' orbitals.
- 16. a) Predict the feasibility of formation of the following complexes (X and Y) using the log K values given below. (R = 8.314 kJmol<sup>-1</sup>) Justify.

Compound	log K at 300 K
[Cu(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup> (X)	2.0
[Cu(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O)] <sup>2+</sup> (Y)	0.5

b) Identify the one with a higher magnetic moment among the following based on the given data. (Hint: Both ions have a single unpaired electron each)

i) 
$$Ce^{3+}$$
 (L = 3, S =  $\frac{1}{2}$ , g = 0.857)  
ii)  $Ti^{3+}$  (L = 2, S =  $\frac{1}{2}$ , g = 2) (2+3)

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