## Registration Number:

Date \& session:

## ST JOSEPH'S UNIVERSITY, BENGALURU -27 <br> M.Sc (CHEMISTRY) - $2^{\text {nd }}$ SEMESTER <br> SEMESTER EXAMINATION: APRIL 2024 <br> (Examination conducted in May / June 2024) <br> CH 8122 - INORGANIC CHEMISTRY II <br> (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.

$8 \times 2=16$

1. Mention the coordination number and geometry of Re in $\mathrm{Ca}\left[\mathrm{ReH}_{9}\right]$.
2. Sketch the crystal field splitting diagram for $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$.
3. Which of the following complexes is more stable? Give reason.
$\left[\mathrm{Cu}(\text { trien })\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$ or $\left[\mathrm{Cu}(\text { cyclen })\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}$,
where trien: tri(ethylenediamine), cyclen: 1,4,7,10-Tetraazacyclododecane
4. Compare the IR spectra of fac- and mer- $\left[\mathrm{MA}_{3} \mathrm{~B}_{3}\right]$ isomers.
5. Calculate the number of microstates for $d^{4}$ 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- $\left[\mathrm{CoCl}\left(\mathrm{NH}_{3}\right)(\mathrm{en})_{2}\right]^{2+}$ complex ion.

## PART-B

## Answer any TWO of the following questions.

$2 \times 12=24$
11. a) Account for the higher lattice energy value of $\mathrm{NiF}_{2}\left(3060 \mathrm{kJmol}^{-1}\right)$ compared to $\mathrm{ZnF}_{2}$ ( $2985 \mathrm{kJmol}^{-1}$ ).
b) Sketch a qualitative molecular orbital energy level diagram for an octahedral $\mathrm{ML}_{6}$ complex with only $\sigma$ - bonding.
c) Which of the following ligands will form a more stable complex with a $\mathrm{M}(\mathrm{II})$ ion under basic conditions? Malonic acid $\mathrm{CH}_{2}(\mathrm{COOH})_{2}$ or acetylacetone $\mathrm{CH}_{2}\left(\mathrm{COCH}_{3}\right)_{2}$. Give reason.
d) Calculate the magnetic moment of $\mathrm{K}_{3}\left[\mathrm{FeF}_{6}\right]$ using the following data:
$\chi_{M}($ corrected $)=14.6 \times 10^{-3}$ (B.M. $)^{2} \mathrm{~K}^{-1}$ at 300 K . What is the calculated spin-only magnetic moment for this complex?
12. a) Identify the type of unidentate coordination mode of $\mathrm{NO}_{2}$ ligand in complexes (A) and (B) using the IR spectral data given below. Explain.

| Compound | $v(\mathrm{NO}), \mathrm{cm}^{-1}$ |
| :--- | :--- |
| $\mathrm{~K}_{3}\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)_{6}\right](\mathrm{A})$ | 1386,1332 |
| $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{NO}_{2}\right)\right] \mathrm{Cl}_{2}(\mathrm{~B})$ | 1468,1065 |

b) A solution of $\left[\mathrm{Cr}\left(\mathrm{OH}_{2}\right)_{6}\right]^{3+}$ is pale green-blue $\left(\varepsilon_{\max }=15 \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}\right)$, but a solution of $\left[\mathrm{CrO}_{4}\right]^{2-}$ is intense yellow ( $\varepsilon_{\max }=4500 \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}$ ). 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: ${ }^{1} \mathrm{G},{ }^{1} \mathrm{~S},{ }^{3} \mathrm{~F},{ }^{3} \mathrm{P}$. Give reasons for your answer.
d) Explain spin-crossover with an example.
13. a) Compare the $\mathrm{C}-\mathrm{O}$ and $\mathrm{M}-\mathrm{C}$ bond distances in $\left[\mathrm{V}(\mathrm{CO})_{6}\right]^{-}$and $\left[\mathrm{Mn}(\mathrm{CO})_{6}\right]^{+}$. Explain.
b) Deduce the total electron count and predict the skeletal structure of $\mathrm{HRu}_{4} \mathrm{~N}(\mathrm{CO})_{12}$.
c) What is Tolman cone angle? Between the following, identify the one with a larger Tolman cone angle.
i) $\mathrm{P}(n \text {-propyl })_{3}$ or ii) $\mathrm{P}(i \text {-propyl })_{3}$
d) Proton NMR spectra of titanocene, $\left[\mathrm{Ti}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{4}\right]$ shows a single peak at $62^{\circ} \mathrm{C}$ and two peaks at $-27^{\circ} \mathrm{C}$. Explain this on the basis of hapticity of the ligand.

## PART-C

Answer any TWO of the following questions.
$2 \times 5=10$
14. a) Predict the type of distortion in $\left[\mathrm{Ti}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ based on stabilization energy.
b) Which of the following conversions is accompanied by a larger change in metal-ligand bond distance? Justify.

$$
\begin{align*}
& \text { i) }\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-} \rightarrow\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{2-} \\
& \text { ii) }\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+} \rightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+} \tag{2+3}
\end{align*}
$$

15. Assign the electronic transitions in $\left[\mathrm{MCl}_{4}\right]^{-}$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. $\left(\mathrm{R}=8.314 \mathrm{kJmol}^{-1}\right)$ Justify.

| Compound | log K at 300 K |
| :---: | :---: |
| $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}(\mathrm{X})$ | 2.0 |
| $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}(\mathrm{Y})$ | 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) $\mathrm{Ce}^{3+}(\mathrm{L}=3, \mathrm{~S}=1 / 2, \mathrm{~g}=0.857)$
ii) $\mathrm{Ti}^{3+}(\mathrm{L}=2, \mathrm{~S}=1 / 2, \mathrm{~g}=2)$

