Reg. No. : .....

Code No. : 6353 Sub. Code : PCHM 32

## M.Sc. (CBCS) DEGREE EXAMINATION, NOVEMBER 2021

Third Semester

CHEMISTRY — CORE

# INORGANIC CHEMISTRY — III

(For those who joined in July 2017 onwards)

Time : Three hours

Maximum : 75 marks

PART A —  $(10 \times 1 = 10 \text{ marks})$ 

Answer ALL questions.

Choose the correct answers :

- 1. Which among the following metallocenes is easily oxidized?
  - (a)  $(\eta^5 C_5 H_5)_2 Ru$
  - (b)  $(\eta^{5} C_{5}H_{5})_{2}Fe$
  - (c)  $(\eta^5 C_5 H_5)_2 Co^+$
  - (d)  $(\eta^{5} C_{5}H_{5})_{2}Co$

(8 Pages)

- 2. The reaction of  $Mn_2(CO)_{10}$  with Na/Hg can be monitored by IR spectroscopy in the region 2100–  $1800 \,\mathrm{cm}^{-1}$ . The starting material show absorptions at 2046, 2015 and  $1984 \,\mathrm{cm}^{-1}$ , and whereas the product at 1896 and 1865 cm<sup>-1</sup>, respectively. Suggest a likely product of the reaction
  - (a)  $[Mn(CO)_6]^+$  (b)  $Na[Mn(CO)_5]$
  - (c)  $[Mn_2(CO)_8]$  (d) None of these
- 3. Reductive eliminations can sometimes be encouraged to take place by oxidizing the metal. Why do you think this is so?
  - (a) Oxidized complex is kinetically favourable
  - (b) It is easier to reduce a more oxidized complex
  - (c) Oxidized complex would be more stable
  - (d) None of the above
- 4. The two products obtained by oxidative addition of  $Cl_2$  to square planar complex [IrCl(Ph<sub>3</sub>P)<sub>3</sub>] are
  - (a) fac and mer (b) cis and trans
  - (c) enantiomers (d) linkage isomers

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- 5. How many lines are expected in the  $^{31}P$  NMR spectrum of  $PH_2H(^{15}NH_2)_2$ ?  $(J_{P-H}>J_{P-F}$   $>J_{P-N}>J_{P-H})$ 
  - (a) 15 (b) 30
  - (c) 45 (d) 90
- 6. The number of hyperfine lines in the EPR spectrum of a one electron reduced product of  $[Co_3(CO)_6Se]$  (I = 7/2 for Co nucleus) is
  - (a) 22 (b) 19
  - (c) 15 (d) 18
- 7. Several spectrophotometers have scales in optical density/percent transmittance. What would be transmittance reading at 0.25 optical density?
  - (a) 0.6989 (b) 0.7500
  - (c) 1.7780 (d) None of the these
- 8. Which of the following structural features in a molecule may make it fluorescent?
  - (a) The presence of benzene ring
  - (b) Fused ring system
  - (c) Rigidity in the molecule
  - (d) All of the above

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- TiO<sub>2</sub> is used as a green photocatalyst in removing pollutants from air and water. The band gaps in anatase and rutile are
  - (a) 5.2 eV and 5.1 eV
  - (b) 9.2 eV and 9.6 eV
  - (c) 3.2 eV and 3.0 eV
  - (d) 2.5 eV and 2.2 eV
- 10. The products of the aquation of the complex,  $[{\rm Cr}({\rm NH}_3)_5({\rm NCS})]^{2+}\,{\rm under}\qquad {\rm thermal}\qquad {\rm and}$  photochemical reactions are
  - (a)  $[Cr(NH_3)_5(H_2O)]^{3+}$  and  $[Cr(NH_3)_4(NCS)(H_2O)]^{2+}$
  - (b)  $[Cr(NH_3)_4(NCS)(H_2O)]^{2+}$  and  $[Cr(NH_3)_5(H_2O)]^{3+}$
  - (c)  $[Cr(NH_3)_4(H_2O_2)^{3+}$  and  $[Cr(NH_3)_4(H_2O_2)]^{3+}$
  - (d)  $[Cr(NH_3)_3(NCS)(H_2O_2)]^{2+}$  and  $[Cr(NH_3)_5(H_2O)]^{3+}$ 
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PART B —  $(5 \times 5 = 25 \text{ marks})$ 

Answer ALL questions, choosing either (a) or (b) Each answer should not exceed 250 words.

11. (a) Provide plausible reasons for the differences in IR stretching frequencies between each of the following pairs : (i)  $[Mo(CO)_3(PF_3)_3]$  2040, 1991 cm<sup>-1</sup> versus  $[Mo(CO)_3(PMe_3)_3]$  1945, 1851 cm<sup>-1</sup>, (ii)  $[Mn(\eta^5 - C_5H_5)(CO)_3]$  2023, 1939 cm<sup>-1</sup> versus  $[Mn(\eta^5 - C_5Me_5)(CO)_3]$  2017, 1928 cm<sup>-1</sup>.

#### Or

- (b) Metal-metal bonding in multinuclear species is not always clear-cut. Solely on the basis of the 18-electron rule, suggest whether  $(\eta^5 - \text{Cp})\text{Ni}(\mu - \text{PPh}_2)_2\text{Ni}(\eta^5 - \text{Cp})$  might be expected to contain a metal-metal bond.
- 12. (a) With suitable examples explain nucleophilic and electrophilic attack of coordinated ligands in organometalic compounds.

#### Or

- (b) Write short note on Zeigler-Natta catalysis.
- 13. (a) Sketch and explain  ${}^{31}P$  NMR of  $P_4S_3$ .

Or

(b) Explain the terms zero field splitting and Kramer's degeneracy. Applying these two phenomena, predict the number of EPR spectral lines for [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>.

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14. (a) Explain thermometric titrations with example.

### Or

- (b) Describe the applications of TGA/DTA in the analysis of minerals.
- 15. (a) Discuss the photochemical reactions that are useful in the solar energy conversion.

Or

(b) Discuss the two principal mechanisms of energy transfer in excited states.

PART C —  $(5 \times 8 = 40 \text{ marks})$ 

Answer ALL questions, choosing either (a) or (b) Each answer should not exceed 600 words.

16. (a) Draw the MO diagram for metallocene. Using the diagram, predict the stability and magnetic properties of manganocene, ferrocene and cobaltocene. What would dhappen to the M-L bond length if an electron is removed from [Co(η<sup>5</sup>-Cp<sub>2</sub>] to form [Co(η<sup>5</sup>-Cp<sub>2</sub>]<sup>+</sup>. Justify your answer.

 $\mathbf{Or}$ 

- (b) (i) What are metal metal bonds? With Illustrative examples discuss the structures of carbonyls containing metalmetal bonds.
  - (ii) Beryllocene has interesting sandwich structure with a strong shorter covalent bond and a longer weaker ionic bond. Substantiate the statement.

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17. (a) What is Wilkinson catalyst? Describe the mechanism of homogenous hydrogenation of alkene using Tolman cycle. What modifications are to be made in the catalyst to bring about enentioselective hydrogenation of prochiral alkenes?

Or

- (b) (i) Describe the mechanistic aspect involved in the hydroformylation of olefins by CO<sub>2</sub>(CO)<sub>8</sub>.
  - (ii) Explain the role of organometallic compounds in carbonylation of alcohols.
- 18. (a) (i) The <sup>31</sup>P-NMR spectrum of mer-[Rh(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] is given below. Explain the features of the basis of its structure. How this spectrum differ from that of fac-[Rh(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]?(for Rh, I =  $\frac{1}{2}$ )



(ii) What are fluxional molecules? How is NMR useful in the study of fluxionality in organometalic compounds?

Or

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- (b) (i) Enumerate different factors affecting the magnitude of 'g' values.
  - (ii) V(IV) system (<sup>51</sup>V, I = 7/2), is expected to give eight line pattern in EPR but two overlapping eight line patterns are obtained at low temperature. Give reason.
- 19. (a) (i) Discuss inductively coupled Argon plasma source used in atomic emission spectroscopy.
  - (ii) Describe spectral and chemical interferences in atomic absorption spectroscopic analysis.
    - $\mathbf{Or}$
  - (b) (i) Bring out the relationship between fluorescence intensity and concentration.
    - (ii) How will you estimate  $Al^{3+}$  and  $F^{-}$  ions in polluted water by fluorimetric method?
- 20. (a) Discuss the applications of semiconductor based photoelectrochemical cells in the storage of solar energy.

 $\mathbf{Or}$ 

(b) Discuss in detail the photochemical reactions of Co(III) complexes enumerating the role of different excited states involved in these reactions.

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