

2019

CHEMISTRY

( Major )

Paper : 5.4

( Inorganic Chemistry )

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks  
for the questions*

1. Choose the correct options for the following :

1×7=7

(a) Each of the following contains a six-membered ring. Which molecule will have a six-fold ( $C_6$ ) principal rotation axis?

(i) Borazine

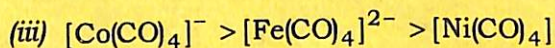
(ii) Pyridine

(iii) Benzene

(iv)  $S_6$ -molecule



(b) The correct C—O bond order in the complexes  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{Fe}(\text{CO})_4]^{2-}$  is



(c) The crystal field splitting energies for octahedral and tetrahedral complexes are related as

(i)  $\Delta_t = \frac{1}{2} \Delta_o$

(ii)  $\Delta_t = \frac{4}{9} \Delta_o$

(iii)  $\Delta_o = \frac{4}{9} \Delta_t$

(iv)  $\Delta_t = \frac{2}{5} \Delta_o$

(d) If free heme in aqueous solution is exposed to dioxygen ( $\text{O}_2$ ), it is converted almost immediately to a dimer

(i) ferritin

(ii) ferryl complex

(iii) hematin

(iv) oxyhaemoglobin

(e) The correct Cr—Cr bond order in the complex  $[\text{Cr}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{OH}_2)_2]$  is

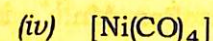
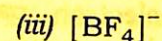
(i) 2

(ii) 4

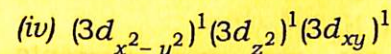
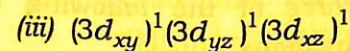
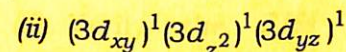
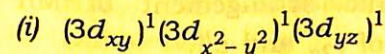
(iii) 3

(iv) 2.5

(f) Which of the following will have a centre of symmetry?



(g)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  has a magnetic moment of 3.83 BM. The correct distribution of 3d-electron in the chromium of the complex is



2. Answer the following very briefly :

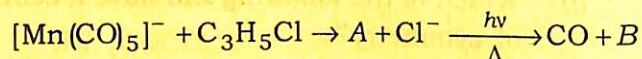
2×4=8

(a) Based on crystal field theory, show the d-orbital splitting pattern in square planar and trigonal bipyramidal geometry.



(b) Explain, why  $\text{BF}_3$  molecule possesses an  $S_3$  axis of improper rotation but  $\text{NF}_3$  does not.

(c) Identify the products A and B in the following reaction :



(d) For  $\text{Mn}^{3+}$  ions, the electron pairing energy  $P$  is  $28000 \text{ cm}^{-1}$ .  $\Delta_o$  values for complexes  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Mn}(\text{CN})_6]^{3-}$  are  $15800 \text{ cm}^{-1}$  and  $38500 \text{ cm}^{-1}$  respectively. Write the electronic arrangement of  $\text{Mn}^{3+}$  in terms of  $t_{2g}^x$  and  $e_g^y$ .

3. Answer any *three* of the following short answer-type questions : 5×3=15

(a) What are symmetry elements and symmetry operations? Assign the symmetry elements present in (i) a  $d_{x^2-y^2}$  orbital, (ii)  $\text{trans-N}_2\text{F}_2$  and (iii)  $\text{F}_2\text{C}=\text{O}$ . 5

(b) Discuss the Dewar-Chatt-Duncanson theory of bonding in metal olefin complexes. 5

(c) (i) Discuss the factors which influence the magnitude of orbital splitting energy  $\Delta$  in a complex. 3

(ii) Write the electronic arrangement in terms of  $e^x$  and  $t_2^y$  for tetrahedral complex  $[\text{FeCl}_4]^{2-}$ . Also find the spin only magnetic moment value. 2

(d) Discuss the mechanism of formation of hematin a  $\mu$ -oxodimer, when free heme in aqueous medium is exposed to dioxygen. 5

(e) (i) Explain the basis of 18-electron rule for octahedral organic complexes. 3

(ii) Verify the EAN rule for the organometallic compounds  $[\text{Mn}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_4]$  and  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)]$  2

4. Answer any *three* of the following essay-type questions : 10×3=30

(a) (i)  $\text{CH}_4$  molecule does not have a four-fold axis of rotation ( $C_4$ ) but it does have an  $S_4$  axis of improper rotation. Discuss the statement with a proper diagram. 3



( 6 )

(ii) What symmetry elements do  $\text{BCl}_3$  and  $\text{PCl}_3$  have in common? Also mention the point groups to which these molecules belong. 5

(iii)  $\text{N}_2$  has molecular orbital rather similar to those of CO. Would you expect  $\text{N}_2$  to be a stronger or weaker  $\pi$ -acceptor than CO? Explain. 2

(b) Discuss the catalytic cycle of hydroformylation reaction of alkenes by cobalt carbonyl catalyst. An increase in carbon monoxide (CO) partial pressure decreases the rate of cobalt catalyzed hydroformylation of 1-pentene. Suggest an interpretation of this observation. 6+4=10

(c) Give a brief description of molecular orbital theory as applied to coordination compounds. Construct a molecular orbital energy level diagram for an octahedral complex involving metal-ligand sigma ( $\sigma$ ) bonds only. Write the molecular electronic configuration of the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . 5+4+1=10

( Continued )

( 7 )

(d) (i) Discuss the physiology of haemoglobin and myoglobin. What do you mean by cooperativity binding of dioxygen with Hb? 5

(ii) How can you predict z-out and z-in distortion in an octahedral complex? 1

(iii) Why are transition metal aryls more stable than transition metal alkyls? 2

(iv) Write the IUPAC names for  $[(\text{Co})_3(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)\text{W}]$  and  $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2]$ . 2

(e) (i) What do you mean by normal and inverse spinels? With the help of CFSE calculation, verify the spinel nature of  $\text{Ni}[\text{Fe}_2]\text{O}_4$  and  $[\text{Co}_3\text{O}_4]$ . 5

(ii) Comment and discuss infrared spectra of  $[\text{V}(\text{CO})_6]^-$  and  $[\text{Cr}(\text{CO})_6]$ . Show absorptions at  $1859\text{ cm}^{-1}$  and  $1981\text{ cm}^{-1}$  respectively assigned to  $\nu_{\text{CO}}$  and  $460\text{ cm}^{-1}$  and  $441\text{ cm}^{-1}$  assigned to  $\nu_{\text{MC}}$ . 5

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