

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 :
- (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

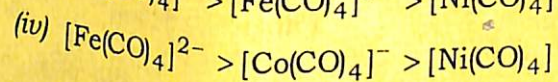
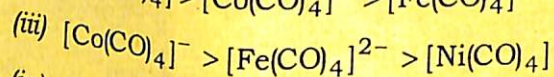
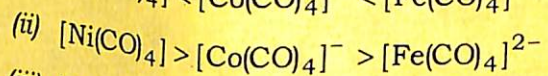
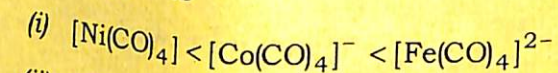
(iv) S_6 -molecule

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(2)

(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 (O_2), it is converted almost immediately to a dimer

(i) ferritin

(ii) ferryl complex

(iii) hematin

(iv) oxyhaemoglobin

(3)

(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

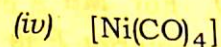
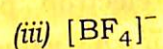
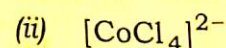
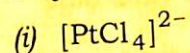
(i) 2

(ii) 4

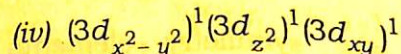
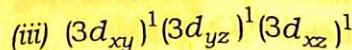
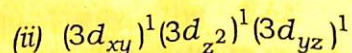
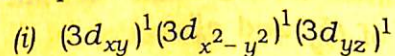
(iii) 3

(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



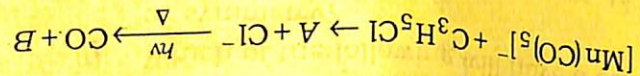
2. Answer the following very briefly :

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 BF_3 molecule possesses an S_3 axis of improper rotation but NF_3 does not.

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



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

3. Answer any three of the following short answer-type questions : $5 \times 3 = 15$

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

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

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- (c) (i) Discuss the factors which influence the magnitude of orbital splitting energy Δ in a complex.

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

- (d) (i) Discuss the mechanism of formation of heme in aqueous medium is exposed to dioxygen.

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

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

4. Answer any three of the following essay-type questions : $10 \times 3 = 30$

- (a) (i) 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.

(Turn Over)

(6)

(ii) What symmetry elements do BCl_3 and PCl_3 have in common? Also mention the point groups to which these molecules belong. 5

(iii) N_2 has molecular orbital rather similar to those of CO. Would you expect N_2 to be a stronger or weaker π -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 (σ) bonds only. Write the molecular electronic configuration of the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$. 5+4+1=10

(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 cm^{-1} and 1981 cm^{-1} respectively assigned to ν_{CO} and 460 cm^{-1} and 441 cm^{-1} assigned to ν_{MC} . 5
