

2018

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 option of the following : $1 \times 7 = 7$

(a) The point-group symmetry for boric acid $B(OH)_3$ is

(i) D_3h

(ii) C_3

(iii) C_3h

(iv) C_{3v}

(b) Three-fold axes of symmetry are present in

(i) octahedron

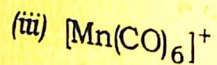
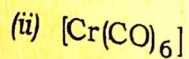
(ii) tetrahedron

(iii) pentagonal bipyramid

(iv) square planar

(Turn Over)

(c) Which of the following complexes has the shortest C—O bond?



(d) The metalloprotein which is involved in the storage of iron in living system is

(i) ferredoxin

(ii) haemoglobin

(iii) myoglobin

(iv) ferritin

(e) The crystal field stabilization energy for a d^6 -ion in a weak octahedral field is

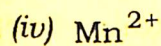
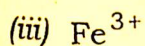
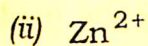
(i) $0.4\Delta_o$

(ii) $0.6\Delta_o$

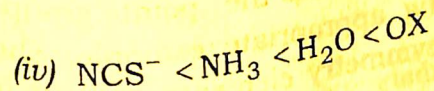
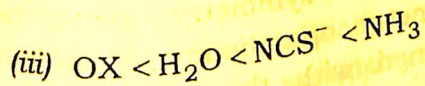
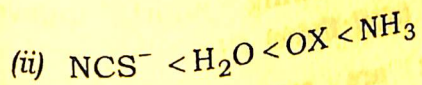
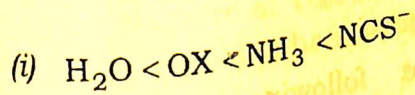
(iii) $0.8\Delta_o$

(iv) $1.2\Delta_o$

(f) In biological system, the metal ion present in the enzyme carbonic anhydrase is

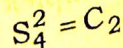


(g) Which of the following is the correct order of ligand strength?



2. Write the following very short answer-type questions : 2×4=8

(a) Taking suitable example, show that



(Turn Over)

- (b) Formulate neutral 18-electron complexes of chromium which contain only cyclopentadienyl and nitrosyl ligands.
- (c) The tetrahedral crystal field splitting Δ_t is roughly half $\left(\frac{4}{9}\Delta_o\right)$ of the octahedral splitting Δ_o . Explain.
- (d) Show by means of a diagram, how the pattern of d -orbital splitting changes as an octahedral complex undergoes tetragonal distortion and eventually becomes a square planar complex.
3. Write the following short answer-type questions (any three) : 5×3=15
- (a) What are symmetry elements and symmetry operations? A molecule is assigned with the point group D_{4h} . Taking appropriate example, show all the symmetry elements present in it.
- (b) Discuss different modes of coordination of allyl ligands. How are allyl organometallics prepared? Draw the structure and verify the 18-electron rule for the allyl complex $[\text{Mn}(\text{C}_3\text{H}_5)(\text{CO})_4]$.

- (c) What is crystal field stabilization energy? For each of the following pairs of complexes, identify the one that has the largest CFSE :
- (i) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- (ii) $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Ru}(\text{CN})_6]^{3-}$
- (d) Write briefly about Na/K pump in biology. Why is saline solution (e.g., ORS) prescribed to patient suffering from diarrhoea?
- (e) In the crystal structure of CuF_2 , the Cu^{2+} ion is six coordinates with four $\text{F}^{(-)}$ at a distance of 1.93 Å and two $\text{F}^{(-)}$ at 2.27 Å. Explain the reason for this.
4. Answer the following essay-type questions (any three) : 10×3=30
- (a) (i) Discuss the conditions under which a group of symmetry elements forms a group.
- (ii) Find the symmetry elements and respective point groups for the following molecules :
- (1) CO_2
- (2) $[\text{PtCl}_4]^{2-}$ 4+6=10
- (3) NH_3

- (e) The M—M bond lengths for the complexes $V_2(CO)_4Ph_2P(Bu)_2$ and $MO_2(CH_2Ph)_6$ are 2.92 and 2.17 Å respectively. Write what you know about M—M bonding and give the reason for this trend. Discuss the formation of a quadruple bond between Re atoms in $[ReCl_8]^{2-}$ showing overlap between orbitals involved in M—M bonding. 2+8=10

- (b) Taking the general formula $M^{II}M^{III}O_4$, discuss normal and inverse spinels (where M^{II} is the group IIA elements or transition metal in +2 oxidation state and M^{III} is the group IIIA metal or transition metal in +3 oxidation state). With the help of CFSE calculation, verify the spinel nature of Fe_3O_4 and Mn_3O_4 .

- (c) (i) Discuss the functions of haemoglobin and myoglobin. Explain the terms 'cooperative effect' and 'Bohr effect'.

- (ii) Give an account of toxicity arising from dioxygen in the living system. 6+4=

- (d) (i) What do you mean by hydroformylation reaction? Discuss the main features and the mechanism by taking a suitable example.

- (ii) Explain the preparation, structure and bonding in Zeise salt. The IR stretching frequency of the $C=C$ bond in metal ethylene complex is found to be 1576 cm^{-1} whereas the corresponding frequency for C_2H_4 is 1625 cm^{-1} . Explain. 5+5=