2017

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 for the following : 1×7=7

(a) The point-group symmetry for a symmetrical human being is

(i) C_{2v}

(ii) C_s

(iii) $C_{\infty v}$

(iv) $D_{\infty h}$

(b) Carbon monoxide as a ligand is also known as π-acid because

(i) it has filled hybrid orbitals

(ii) it has vacant π-antibonding molecular orbitals

(iii) it has vacant π-bonding molecular orbitals

(iv) it has vacant hybrid orbitals

(c) An example of a molecule/object with point-group symmetry $D_{\alpha h}$ is

(i) pipette

(ii) CO_2

(iii) test tube

(iv) HCl

(d) The number of heme-groups present per haemoglobin molecule is

(i) 4 (ii) 3

(iii) 6 (iv) 2

(e) $Co_4(CO)_{12}$ is an organometallic compound of cobalt and carbon monoxide. The total number of M-M (metal-metal) in this cluster is

(i) 2 (ii) 6

(iii) 4 (iv) 3

(f) Of the five *d*-orbitals of a transition metal ion in a square planar complex, the orbital with highest energy will be

(i) d_{xy}

(ii) $d_{x^2-y^2}$

(iii) d_{z^2}

(iv) None of the above

(g) Dioxygen binds with iron atom of heme-group of haemoglobin to give oxyhaemoglobin. Find the correct statement.

(i) O_2 binds in nonlinear way and iron atom of heme-group comes to high spin state

(ii) O_2 binds in nonlinear way and iron atom of heme-group comes to low spin state

(iii) O_2 binds in linear way and iron atom of heme-group comes to high spin state

(iv) O_2 binds in linear way and iron atom of heme-group comes to low spin state

2. Answer the following very briefly : 2×4=8

(a) Draw the structure of $Fe_2(CO)_9$ and verify the EAN rule for this complex.

(b) Show all the symmetry elements present and assign the point-group symmetry of boric acid, $B(OH)_3$.

(c) For the complex $Cu_2(CH_3COO)_4 \cdot 2H_2O$ the effective magnetic moment (μ_{eff}) is 1·4 BM which is less than the effective magnetic moment (μ_{eff} = 1·87 BM) for free Cu(II) ion. Explain.

(d) Determine the configuration (in terms of $t_{2g}^x e_g^y$) and the number of unpaired electrons of the following complexes :

(i) $[Fe(CN)_6]^{3-}$

(ii) $[Co(NH_3)_6]^{3+}$

3. Answer the following questions (any *three*) : 5×3=15

(a) Determine the symmetry elements of (i) a *s*-orbital, (ii) a *p*-orbital and (iii) a d_{z^2}-orbital. 1+2+2=5

(b) What are successes and failures of EAN rule? Apply the rule to the following complexes : 2+3=5

(i) $[Mn(CO)_5(C_2H_4)]^+$

(ii) $[Mn(\eta^3\text{-}C_3H_5)(CO)_4]$

(iii) $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$

(c) Using CFSE account for the thermodynamic property, the oxides of formula MO which all have octahedral coordination of the metal ions have the following lattice enthalpies :

CaO	TiO	VO	MnO
3460 kJ	3878 kJ	3913 kJ	3810 kJ

Account for the trends in terms of CFSE. 5

(d) Describe the iron carriers in mammals and bacteria. Sketch their approximate structures and show the binding sites of iron atom. 2+2+1=5

(e) Explain the origin of Jahn-Teller distortion by crystal field theory. What are the conditions of Jahn-Teller distortion in an octahedral complex? How can you predict *z*-out and *z*-in distortion in an octahedral complex? 2+2+1=5

4. Answer the following questions (any *three*) : 10×3=30

(a) (i) In a metal ligand complex ML_6, the ligands are at the corners of a regular octahedron and if the following distortions are made,

then find the symmetry elements and point-group symmetry of the resultant configurations :

(1) If axial ligands along z-axis are pulled equally

(2) If two ligands along x- and y-axes are pulled equally

(3) If one set of three ligands are pulled along the triangular plane 2+1+2=5

(ii) Define symmetry elements and symmetry operations. What do you mean by point-group symmetry? Discuss the conditions under which a group of symmetry elements form a group. 1+1+3=5

(b) Draw the molecular orbital energy level diagram for the π-system of octahedral complexes with *(i)* π-donor ligand and *(ii)* π-acceptor ligand. How will you correlate the spectrochemical series with the π-bonding ability of ligands? 8+2=10

(c) What are the disadvantages and advantages of homogeneous and heterogeneous catalysts? Using Tolman's catalytic loop for homogeneous catalysis, discuss hydrogenation of alkenes with Wilkinson's catalyst. 5+5=10

(Continued)

(d) 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 σ-bonds only. 5+5=10

(e) *(i)* Give an account of synthetic dioxygen carriers. Write the structures and describe the nature of iron-oxygen bond in these molecules. 5

(ii) The C—O vibrational stretching frequencies (γ) values for the complexes $[Mn(CO)_6]^+$, $[Cr(CO)_6]$, $[V(CO)_6]^-$ and $[Ti(CO)_6]^{2-}$ are 2090 cm^{-1}, 2000 cm^{-1}, 1860 cm^{-1} and 1748 cm^{-1} respectively. Account for the trend. 5

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