

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

(2)

(c) An example of a molecule/object with point-group symmetry D_{oh} 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

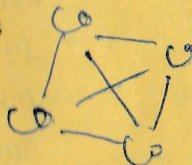
(e) $Co_4(CO)_{12}$ is an organometallic compound of cobalt and carbon monoxide. The total number of M-M (metal-metal) in this cluster is

~~(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

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(Continued)

$16 + 12 + 6$
 n

(3)

(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

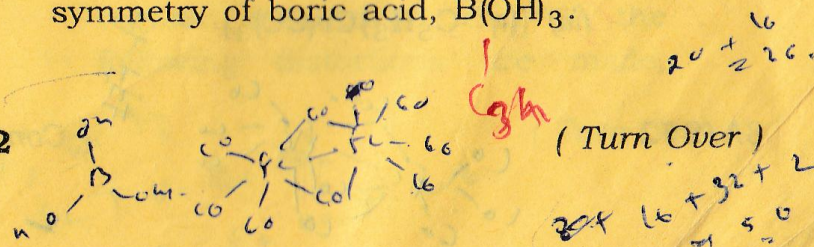
(iv) O_2 binds in linear way and iron atom of heme-group comes to low spin state

2. Answer the following very briefly : $2 \times 4 = 8$

(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, $B(OH)_3$.

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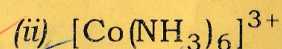
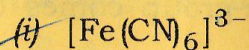
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$20 + 16 = 36$
 $20 + 12 + 2 = 34$
 n

(4)

(c) For the complex $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ the effective magnetic moment (μ_{eff}) is 1.4 BM which is less than the effective magnetic moment ($\mu_{\text{eff}} = 1.87 \text{ BM}$) 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 :



3. Answer the following questions (any three) :

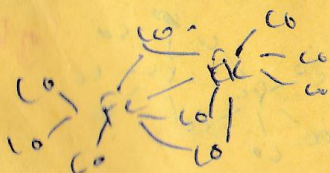
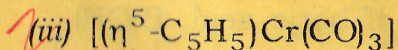
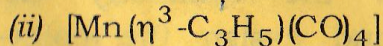
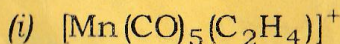
$5 \times 3 = 15$

(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 :

$2 + 3 = 5$



(Continued)

(5)

(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) :

$10 \times 3 = 30$

(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,

(6)

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

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

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

trigonal (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. $5+5=10$

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(Continued)

(7)

(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 (ν) values for the complexes $[\text{Mn}(\text{CO})_6]^+$, $[\text{Cr}(\text{CO})_6]$, $[\text{V}(\text{CO})_6]^-$ and $[\text{Ti}(\text{CO})_6]^{2-}$ are 2090 cm^{-1} , 2000 cm^{-1} , 1860 cm^{-1} and 1748 cm^{-1} respectively. Account for the trend. 5

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3 (Sem-5) CHM M 4