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 $[Ni(CO)_4]$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$ is

(i) $[Ni(CO)_4] < [Co(CO)_4]^- < [Fe(CO)_4]^{2-}$

(ii) $[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$

(iii) $[Co(CO)_4]^- > [Fe(CO)_4]^{2-} > [Ni(CO)_4]$

(iv) $[Fe(CO)_4]^{2-} > [Co(CO)_4]^- > [Ni(CO)_4]$

(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

(Continued)

(e) The correct Cr—Cr bond order in the complex $[Cr_2(\mu\text{-}O_2CCH_3)_4(OH_2)_2]$ is

(i) 2 (ii) 4

(iii) 3 (iv) 2·5

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

(i) $[PtCl_4]^{2-}$ (ii) $[CoCl_4]^{2-}$

(iii) $[BF_4]^-$ (iv) $[Ni(CO)_4]$

(g) $[Cr(H_2O)_6]Cl_3$ has a magnetic moment of 3·83 BM. The correct distribution of 3*d*-electron in the chromium of the complex is

(i) $(3d_{xy})^1(3d_{x^2-y^2})^1(3d_{yz})^1$

(ii) $(3d_{xy})^1(3d_{z^2})^1(3d_{yz})^1$

(iii) $(3d_{xy})^1(3d_{yz})^1(3d_{xz})^1$

(iv) $(3d_{x^2-y^2})^1(3d_{z^2})^1(3d_{xy})^1$

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.

(Turn Over)

(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 :

$$[Mn(CO)_5]^- + C_3H_5Cl \rightarrow A + Cl^- \xrightarrow[\Delta]{h\nu} CO + B$$

(d) For Mn^{3+} ions, the electron pairing energy P is 28000 cm^{-1}. Δ_o values for complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ 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 : 5×3=15

(a) What are symmetry elements and symmetry operations? Assign the symmetry elements present in *(i)* a $d_{x^2-y^2}$ orbital, *(ii)* *trans*-N_2F_2 and *(iii)* $F_2C{=}O$. 5

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

(Continued)

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

(ii) Write the electronic arrangement in terms of e^x and t_2^y for tetrahedral complex $[FeCl_4]^{2-}$. Also find the spin only magnetic moment value. 2

(d) Discuss the mechanism of formation of hematin a μ-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

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

$[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ 2

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

(Turn Over)

(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 $[Co(NH_3)_6]^{3+}$. 5+4+1=10

(Continued)

(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 $[(Co)_3(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)W]$ and $[Ni(\eta^3\text{-}C_3H_5)_2]$. 2

(e) (i) What do you mean by normal and inverse spinels? With the help of CFSE calculation, verify the spinel nature of $Ni[Fe_2]O_4$ and $[Co_3O_4]$. 5

(ii) Comment and discuss infrared spectra of $[V(CO)_6]^-$ and $[Cr(CO)_6]$. 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

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