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 :

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

(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=

(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)* $F_2C{=}O$.

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

(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

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

(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.

(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=1

(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=1

(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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