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## Unit - 9

### CO-ORDINATION COMPOUNDS

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#### QUESTIONS

##### VSA QUESTIONS (1 - MARK QUESTIONS)

- Define the term coordination compound?
- Write the names of counter ions in  
(i)  $\text{Hg} [\text{Co} (\text{SCN})_4]$  and (ii)  $[\text{Pt}(\text{NH}_3)_4] \text{Cl}_2$ .
- Write the oxidation state of nickel in  $[\text{Ni}(\text{CO})_4]$
- \*4. What is the coordination number of central atom in  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ ?  
[Ans. : 6]
- What is the coordination number of iron in  $[\text{Fe} (\text{EDTA})]^-$  ? [Ans. : 6]
- Write the name of a complex compound used in chemotherapy.  
[Ans. : Cis-Platin.  $[\text{Pt}(\text{NH}_3)_2 \text{Cl}_2]$
- Name the compound used to estimate the hardness of water volumetrically.
- Give the IUPAC name of  $[\text{Pt} \text{Cl}_2 (\text{NH}_2\text{CH}_3) (\text{NH}_3)_2] \text{Cl}$ .
- \*9. How many geometrical isomers are possible for the tetrahedral complex  $[\text{Ni}(\text{CO})_4]$ .  
[Ans. : No isomer, as the relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other].
10. Arrange the following in the increasing order of conductivity in solution.  
 $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ ;  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and  $[\text{CoCl}_2(\text{en})_2] \text{Cl}$
11. Arrange the following ligands in increasing order of  $\Delta_o$  (Crystal field splitting energy) for octahedral complexes with a particular metal ion.  
 $\text{Cl}^-$ ,  $\text{NH}_3$ ,  $\text{I}^-$ ,  $\text{CO}$ ,  $\text{en}$ .

12. Write I.U.P.A.C. name of Tollens' reagent.
13. Which is more stable?  $K_3[Fe(CN)_6]$  or  $K_4[Fe(CN)_6]$
14. Calculate the overall dissociation equilibrium constant for the  $[Cu(NH_3)_4]^{2+}$  ion. Given that overall stability constant ( $\beta_4$ ) for this complex is  $2.1 \times 10^{13}$ .  
[Ans. :  $4.7 \times 10^{-14}$ ]
- \*15. What is a chelate ligand? Give one example.
16. Write the I.U.P.A.C. name of  $Li[AlH_4]$ .
17. Name one homogeneous catalyst used in hydrogenation of alkenes.
- \*18. Name the types of isomerism shown by coordination entity :  $[CrCl_2(Ox)_2]^{3-}$
- \*19.  $[Ti(H_2O)_6]Cl_3$  is coloured but on heating becomes colourless. Why?
- \*20. Write the IUPAC name of ionization isomer of  $[Co(NH_3)_5(SO_4)] Br$
- \*21. Write the formula and the name of the coordinate isomer of  $[Co(en)_3][Cr(CN)_6]$ .  
[Ans. :  $[Cr(en)_3][Co(CN)_6]$  Tris- (ethane -1, 2, diammine) chromium (III) hexacyanocobaltate (III)]

### SA(I) TYPE QUESTIONS (2 - MARK QUESTIONS)

- \*22. Write two differences between a double salt and a coordination compound with the help of an example of each.
23. Mention the main postulates of Werner's Theory.
24. Define (a) Homoleptic and (b) Heteroleptic complexes with the help of one example of each.
25. In the following coordination entity :  $[Cu(en)_2]^{2+}$   
(a) Identify the ligand involved and  
(b) Oxidation state of copper metal.
27. Calculate the magnetic moments of the following complexes :  
(i)  $[Fe(CN)_6]^{4-}$  (ii)  $[CoF_6]^{3-}$
28. Explain the following :  
(a)  $[Fe(CN)_6]^{3-}$  is an inner orbital complex whereas  $[FeF_6]^{3-}$  is an outer orbital complex.  
(b)  $NH_3$  acts as complexing agent but  $NH_4^+$  does not.

29. What type of structural isomerism is represented by the following complexes:
- (a)  $[\text{Mn}(\text{CO})_5(\text{SCN})]$  and  $[\text{Mn}(\text{CO})_5(\text{NCS})]$
- (b)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)] \text{SO}_4$
30. How are complex compounds applicable in (a) electroplating of silver, gold or other noble metals (b) in photography.
31. Explain on the basis of Valence Bond Theory that diamagnetic  $[\text{Ni}(\text{CN})_4]^{2-}$  has square planar structure and paramagnetic  $[\text{NiCl}_4]^{2-}$  ion has tetrahedral geometry.
23. Explain as to how the two complexes of nickel  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{Ni}(\text{CO})_4$  have different structures but do not differ in their magnetic behaviours. (At. no. of Ni = 28).
34. Draw the structures of geometrical isomers of the coordination complexes— $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  and  $[\text{CoCl}_2(\text{en})_2]^+$
35. Write the IUPAC name of the complexes :
- (a)  $[\text{NiCl}_2(\text{PPh}_3)_2]$  (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)] \text{Cl}$
- (c)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$
- [Hint. :** (a) Dichloridobis(triphenylphosphine)nickel (II);
36. Using IUPAC norms write the formulae for the following :
- (a) Terabromidocuprate (II)
- (b) Pentaamminenitrito-O- Cobalt (III)
- \*37. How does EDTA help as a cure for lead poisoning?
- [Ans. :** Calcium in Ca-EDTA complex is replaced by lead in the body. The more soluble complex lead-EDTA is eliminated in urine].
37. A complex is prepared by mixing  $\text{CoCl}_3$  and  $\text{NH}_3$  in the molar ratio of 1:4. 0.1 m solution of this complex was found to freeze at  $-0.372^\circ\text{C}$ . What is the formula of the complex?
- $K_f$  of water =  $1.86^\circ\text{C/m}$
- [Hint :**  $\Delta T_f = i K_f \times m = i \times 1.86 \times 0.1$
- $\Delta T_f(\text{obs}) = 0.373^\circ\text{C}$
- This means each molecule of complex dissociates into two ions. Hence the formula is  $i = 2$

- \*38. The  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  ion contains five unpaired electrons while  $[\text{Mn}(\text{CN})_6]^{4-}$  ion contains only one unpaired electron. Explain using Crystal Field Theory:

### SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

39. Account for the following —
- $[\text{NiCl}_4]^{2-}$  is paramagnetic while  $[\text{Ni}(\text{CO})_4]$  is diamagnetic though both are tetrahedral.
  - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic whereas  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  weakly paramagnetic.
  - $[\text{Co}(\text{NH}_3)_6]^{3+}$  is an inner orbital complex whereas  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is in outer orbital complex.
40. Compare the following complexes with respect to their shape, magnetic behaviours and the hybrid orbitals involved.
- $[\text{CoF}_6]^{3-}$
  - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
  - $[\text{Fe}(\text{CN})_6]^{4-}$
- [Atomic Number : Co = 27, Cr = 24, Fe = 26]
41. Draw the structure of
- cis-dichloridotetracyanochromate (II) ion
  - mer-triamminetrichloridocobalt (III)
  - fac-triaquatrininitrito-N-cobalt (III)
42. Name the central metal atom/ion present in (a) Chlorophyll (b) Haemoglobin (c) Vitamin B-12. [Ans. : (a) Mg (b) Fe; (c) Co.]
43. A metal complex having composition  $\text{Cr}(\text{NH}_3)_4 \text{Cl}_2 \text{Br}$  has been isolated in two forms 'A' and 'B'. The form 'A' reacts with  $\text{AgNO}_3$  solution to give white precipitate which is readily soluble in dilute aqueous ammonia, whereas 'B' gives a pale yellow precipitate which is soluble in concentrated ammonia solution. Write the formula of 'A' and 'B'. Also mention the isomerism which arises among 'A' and 'B'.
- [Hint : A =  $[\text{Cr}(\text{NH}_3)_4 \text{BrCl}] \text{Cl}$ ; B =  $[\text{Cr}(\text{NH}_3)_4 \text{Cl}_2] \text{Br}$  are ionisation isomers].
44. Write the limitations of Valence Bond Theory.
45. Draw a sketch to show the splitting of d-orbitals in an octahedral crystal field state for a  $d^4$  ion. How the actual electronic configuration of the split

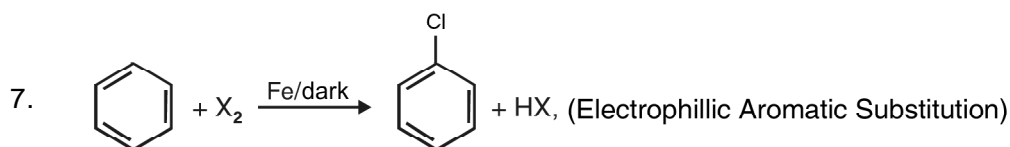
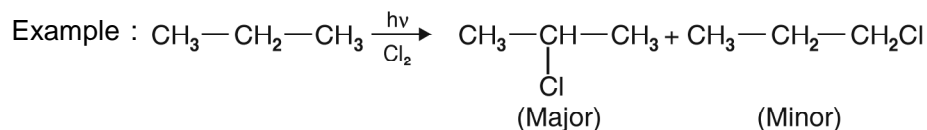
d-orbitals in an octahedral crystal field is decided by the relative values of  $\Delta_0$  and pairing energy (P)?

- \*46. For the complex  $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$  identify
- the oxidation number of iron.
  - the hybrid orbitals and the shape of the complex.
  - the magnetic behaviour of the complex.
  - the number of geometrical isomers.
  - whether there is an optical isomer also?
  - name of the complex. [At. no. of Fe = 26]
48. A chloride of fourth group cation in qualitative analysis gives a green coloured complex [A] in aqueous solution which when treated with ethane-1, 2-diamine (en) gives pale yellow solution [B] which on subsequent addition of ethane-1, 2-diamine turns to blue/purple [C] and finally to violet [D]. Identify [A], [B], [C] and [D] complexes,
- [Hint. : Nickel,  $[\text{A}] = [\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ;  $[\text{B}] = [\text{Ni}(\text{H}_2\text{O})_4(\text{en})]^{2+}$  ;  
 $[\text{C}] = [\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$  ;  $[\text{D}] = [\text{Ni}(\text{en})_3]^{2+}$ .

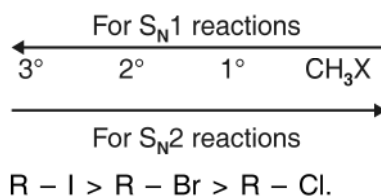
## ORGANIC CHEMISTRY

### SOME NOTEWORTHY POINTS

2. If there are two or more functional groups, the order of decreasing priority is :  $-\text{COOH} > -\text{SO}_3\text{H} > \text{anhydride} > \text{Ester} > \text{Acid halide} > \text{nitrile} > \text{aldehyde} > \text{ketone} > \text{alcohol} > \text{amine} \gg \text{C} = \text{C} < > - \text{C} \equiv \text{C} -$
3. Anti Markownikov's addition takes place only with HBr in presence of a peroxide.
4. Order of reactivity of hydrohalic acid :  $\text{HI} > \text{HBr} > \text{HCl}$ .
5. Order of reactivity of alcohols with Lucas reagent :  $3^\circ > 2^\circ > 1^\circ$ .
6.  $\text{R} - \text{H} + \text{X}_2 \xrightarrow{h\nu} \text{R} - \text{X} + \text{HX}$ . The order of reactivity of halogens  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$ . Order of reactivity of hydrogen atom abstracted is  $3^\circ > 2^\circ > 1^\circ$ .

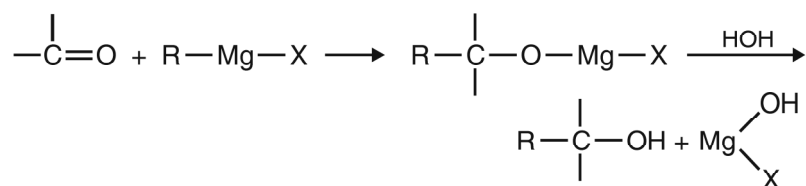


8. Order of reactivity in  $\text{S}_\text{N}1$  and  $\text{S}_\text{N}2$  mechanism are as follows :

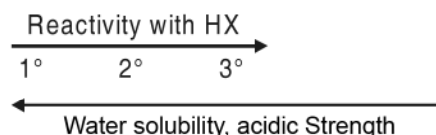


9. In case of optically active alkyl halide,  $\text{S}_\text{N}2$  mechanism results in the inversion of configuration while  $\text{S}_\text{N}1$  mechanism in racemisation.

10. Aryl halides are much less reactive towards nucleophilic substitution reactions. Presence of electron withdrawing groups (like  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{COOH}$  etc.) at  $o$ - and/or  $p$ -position to halogen increases the rate of reaction.
12. All the three types of monohydric alcohols ( $1^\circ$ ,  $2^\circ$  or  $3^\circ$ ) except methanol can be prepared from Grignard Reagent



13. Alcohols



14. Presence of electron withdrawing group increases the acid strength of alcohol, phenol and carboxylic acid while presence of electron donating group decreases the acid strength.  
E.W.G. :  $\text{NO}_2$ ,  $-\text{X}$ ,  $-\text{CN}$ ,  $-\text{COOH}$ , etc., E.D.G. :  $-\text{R}$ ,  $-\text{OR}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$  etc.
15. In electrophilic aromatic substitution reaction, ring activating groups like  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{OR}$ , are  $o$ - and  $p$ - directing whereas ring deactivating groups like  $-\text{CHO}$ ,  $>\text{C}=\text{O}$ ,  $-\text{COOH}$ ,  $-\text{NO}_2$ ,  $-\text{SO}_3\text{H}$  are  $m$ -directing. Halogens (F, Cl, Br and I) are deactivating but are  $o$ - and  $p$ - directing groups.
16.  $3^\circ$  alcohols are resistant to oxidation due to lack of  $\alpha$ -hydrogen.
17. Order of Acid strength : Alcohol < Phenol < Carboxylic acid, it is because of resonance stabilization of phenoxide and carboxylate ion. In carboxylate ion negative charge is delocalised over two oxygen atoms. while in phenoxide ion it is delocalised over one oxygen atom and the less electronegative C atom of benzene ring.
18. All organic compounds which form intermolecular H-bonds with water are soluble in water.
19. Intermolecular H-bonds of  $p$ - and  $m$ - nitrophenol increases water solubility/ Acid strength while intramolecular H-bonds in  $o$ -nitrophenol decreases

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