

2021

## CHEMISTRY — HONOURS

Paper : CC-10

[Inorganic Chemistry]

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer **question no. 1** and **any eight** from the rest.

1. Answer **any ten** questions : 1×10
- (a) Name a ligand which could effectively be used in chemical separation of *cis* and *trans* isomers of  $[\text{CrCl}_2(\text{NH}_3)_4]\text{Cl}$ .
  - (b)  $\text{TiCl}_3$  is easily oxidised in air.— Why?
  - (c) Name one eluting agent that could be used in separation of lanthanides in ion exchange method.
  - (d) What will be the ground state term for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ?
  - (e) Give one use of a lanthanide element or its compound.
  - (f) Arrange the following ligands in order of their increasing trans-effect :  
CO,  $\text{NH}_3$ ,  $\text{Cl}^-$
  - (g) Give an example of high spin cobalt (III) octahedral complex.
  - (h)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{MnCl}_4]^{2-}$  have  $\mu_{\text{eff}} \approx \mu_{\text{s}}$ . Why?
  - (i) Predict the sources of colour in  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{CrO}_4^{2-}$ .
  - (j) Write the ground state electronic configuration of Ce (At. No. – 58).
  - (k) Identify the complex with higher CFSE :  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  or  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
  - (l) Cite an example of dynamic Jahn-Teller distortion.
2. (a) Both  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$  are diamagnetic but they have different geometries. Explain. 3+2
- (b) Define lability and inertness with specific examples.
3. (a) Cu, Ag and Au are present in the same group but their most common oxidation states are different. Comment on their most common oxidation states and justify your answer with reason.
- (b) For  $[\text{Co X}_6]^{3-}$ , where X is a monodentate, uninegative ligand,  $\Delta_0 = 15000 \text{ cm}^{-1}$  and  $P = 18000 \text{ cm}^{-1}$ , calculate CFSE for the complex. 3+2

Please Turn Over

4. (a)  $K_2CuF_4$  forms crystal with two shortened bonds in an octahedron.— Explain.  
 (b)  $HgCl_2$  is white but  $HgI_2$  is red.— Justify. 3+2
5. (a) Calculate octahedral crystal field splitting energy in kJ/mol for  $[Fe(CN)_6]^{4-}$ , if the wavelength of the most intensely absorbed light is 305 nm.  
 (b) Using trans effect phenomenon, how would you chemically separate *cis* and *trans* isomers of diammine dichloro platinum (II)? 3+2
6. (a) Chloride substitution by water molecule in *trans*- $Co(AA)_2Cl_2$  complexes were studied (AA = ethylene diammine) and it was found that the rate is  $3.2 \times 10^5 \text{ sec}^{-1}$ . However, the rate gradually increases as we substitute one by one hydrogen of the ethylenic carbon atom of the ligand AA by a methyl group, and the rate becomes very high when AA is  $NH_2C(CH_3)_2 - C(CH_3)_2NH_2$ . Predict the mechanistic path with proper justification.  
 (b) It is easy to separate V from Nb in a mixture but difficult to separate Nb from Ta. Explain. 3+2
7. (a) In earlier actinides, electronic spectra show some resemblance with transition metals though the heavier actinides behave more lanthanide— like in this respect. Justify.  
 (b) Suggest the efficient routes to synthesize both *cis*- and *trans*- isomers of  $[PtCl_2(NH_3)(PPh_3)]$  starting from  $PtCl_4^{2-}$ . 3+2
8. (a) Comment on colour and discuss on magnetic properties of the following compounds :  
 (i)  $[FeF_6]^{3-}$  (ii)  $[Fe(CN)_6]^{3-}$   
 (b)  $[NiCl_4]^{2-}$  is tetrahedral but  $[PtCl_4]^{2-}$  is square planar.— Explain. 3+2
9. (a) What is tetragonal distortion? Which  $d^n$  configurations would lead to weak and strong Jahn-Teller distortion in octahedral complexes?  
 (b)  $MnO_4^-$  and  $CrO_4^{2-}$  are  $d^0$  systems. Which one will have higher  $\lambda$  value in the absorption spectra? 3+2
10. (a) How many electronic transitions are possible for an octahedral Ni(II) complex? Explain with Orgel diagram.  
 (b) What is the main difference in spectral output of 3d transition metal complexes and lanthanide complexes? 3+2
11. (a) Justify the following order of spectrochemical series :  
 $CO > H_2O > F^-$   
 (b)  $Au^{2+}$  is unstable towards disproportionation.— Explain. 3+2

12. (a) For isoelectronic series :  
 $V(CO)_6^-$ ,  $Cr(CO)_6$ ,  $Mn(CO)_6^+$ , predict and explain the change in MLCT band energies.
- (b) Predict the type of spinel structure for  $Fe_3O_4$  and  $Co_3O_4$ . 3+2
13. (a) Which  $d^n$  ion octahedral complexes show orbital contribution towards overall magnetic moment value?
- (b)  $Cu(II)$  acetate monohydrate shows lower  $\mu_s$  value than expected.— Justify. 3+2
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