

**Birla Institute of Technology & Science, Pilani, Rajasthan 333031**  
**First Semester 2015-2016**

**Course Number: CHEM F111**

**Course Title: General Chemistry**

**Marks: 10**

**Tutorial Problem Set 4 (based on Lecture No.'s: 26-30 in the course hand out)**

**Instructions to the student:** *The following problems should be solved as home assignment within a week of display. Any one problem will be assigned as a closed book class test in the following tutorial hour.*

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Q. 1 Calculate the CFSE value for following complexes? Which of the following complexes is/are paramagnetic? [2 × 4 + 2]

(i)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$       (ii)  $[\text{RhF}_6]^{3-}$       (iii)  $[\text{Co}(\text{CN})_6]^{4-}$       (iv)  $[\text{Fe}(\text{CN})_6]^{4-}$

Q.2 a) Bis(ethylenediamine)copper(II) complex,  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  exists, whereas tris(ethylenediamine)copper(II) complex,  $[\text{Cu}(\text{en})_3]^{2+}$  is remarkably unstable. Justify the observations by showing the d-orbital splitting diagram. [6]

b) Tetrahedral complexes are always high-spin, while octahedral complexes can be either high- or low-spin depending on the metal and/or ligand. What is the most likely explanation of this experimental result? [4]

Q. 3 a) The structure of  $\text{Fe}_3\text{O}_4$  can be represented as  $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$  instead of  $\text{Fe}^{2+}[\text{Fe}^{3+}_2]\text{O}_4$  explain it using crystal field theory (the cationic species within “[ ]” is in octahedral lattice site while outside of “[ ]” is in tetrahedral lattice site of a close-packed cubic lattice of oxide). [6]

b) Explain, whether the ions  $\text{V}^{2+}$  and  $\text{Ti}^{2+}$  will undergo Jahn-Teller distortion or not? [4]

Q. 4 a) The complex ion  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  has an absorption peak at a wavelength of 410 nm. What is the ligand field splitting in the complex in joules, and in kJ/mol? When ammonia is added to the solution of this complex the colour changes to dark blue-purple and absorption peak moves to 350 nm. Has the ligand field splitting increased or decreased compared to the aqua complex? [4]

b) There are two isomers with formula  $\text{Pt}(\text{NH}_3)_4\text{Br}_2\text{SO}_4$ . In both isomers, the ammonia molecules are firmly bonded to the Pt ion. By measuring depression of freezing point of water it is found that 1 mol of one isomer has a depression corresponding to the presence of three moles of particles, while the other has a depression corresponding to the presence of two moles of particles. Explain the results and write formulae that show clearly the make-up of the coordination spheres. [6]

Q. 5 a) Explain, why in octahedral complex of Cu(II) fluoride, the  $\text{Cu}^{2+}$  ion has two  $\text{F}^-$  at 1.92 Å and four  $\text{F}^-$  at 2.22 Å distance? [4]

b) For Co(II) complexes, tetrahedral geometry is preferred over octahedral for bulky weak field ligands, whereas for Ni(II) complexes the reverse is true, explain. [6]

Q. 6 How many stereoisomers exist for  $[\text{CoBr}_2(\text{dipy})(\text{NH}_3)_2]^+$ . Draw the structures of all isomers and mention which are chiral. [10]

Q. 7 Write electronic configuration of metal ions in  $[\text{CoF}_6]^{3-}$  and  $[\text{CrF}_6]^{4-}$  (both paramagnetic) and predict hybridization of the metal ion and spin-only magnetic moment of the complex using VBT. [10]

Q. 8 Calculate the oxidation state of the metal and the number of d electrons in the following complexes. [10]

a)  $[\text{CoCl}_4]^{2-}$  b)  $[\text{Fe}(\text{bpy})_3]^{3+}$  c)  $[\text{Cu}(\text{ox})_2]^{2-}$  d)  $[\text{Cr}(\text{CO})_6]$  e) *cis*- $[\text{PtCl}_2(\text{en})]$

Q. 9 a) Identify the 3d metal (M) in the diamagnetic complex anion  $\text{M}(\text{CN})_6^{4-}$ . What is the oxidation state and d-electron count for this metal? [4]

b) What is the shape of an organometallic anion  $[\text{Cu}(\text{CF}_3)_4]^-$ ? Explain your reasoning. Do you expect this substance to be diamagnetic? [6]

Q. 10 For complexes  $\pi\text{-C}_6\text{H}_5\text{Mn}(\text{CO})_3$  and  $\text{Cr}(\text{acac})_3$ ; (a) calculate the formal oxidation state of the central metal, (b) give the d electron configuration, (c) deduce the coordination geometry, (d) predict the number of unpaired electrons and (e) give the number and types of stereoisomers, if any [10]

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