3 SEM TDC CHM M 1 (N/O)

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(November)

CHEMISTRY
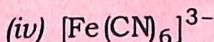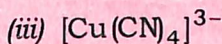
(Major)

Course : 301
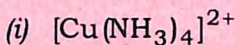
(Inorganic Chemistry—I)

(New Course)

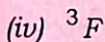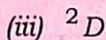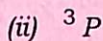_Full Marks : 48_
Pass Marks : 14

Time : 2 hours

The figures in the margin indicate full marks
for the questions

1. Select the correct answer :   1×5=5

(a) The complex ion which obeys the EAN
rule is

(i) $[Cu(NH_3)_4]^{2+}$

(ii) $[FeCl_4]^-$

(iii) $[Cu(CN)_4]^{3-}$

(iv) $[Fe(CN)_6]^{3-}$

(b) The spectroscopic free ion ground term for d^2 configuration is

   (i) ^1S

   (ii) ^3P

   (iii) ^2D

   (iv) ^3F

(c) Which of the following compounds exhibits optical isomerism?

   (i) $[Pt(NH_3)_2Cl_2]$

   (ii) $[Cr(gly)_3]$

   (iii) $[Co(NH_3)_3Cl_3]$

   (iv) $[Pt(gly)_2]$
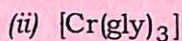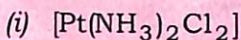
(d) Which of the following is labile?
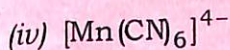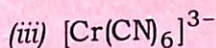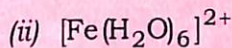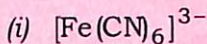
   (i) $[Fe(CN)_6]^{3-}$

   (ii) $[Fe(H_2O)_6]^{2+}$

   (iii) $[Cr(CN)_6]^{3-}$

   (iv) $[Mn(CN)_6]^{4-}$

(e) Which of the following does not belong to lanthanides?

　　(i) Am

　　(ii) Pm

　　(iii) Sm

　　(iv) Tm

2. Answer the following :　　　　　　　　$2 \times 5 = 10$

(a) What are macrocyclic ligands? Give an example.

(b) What do you understand by Mulliken's symbols A, B and E?

(c) What is magnetic moment? How is it related to paramagnetism and diamagnetism?

(d) Explain inert and labile complexes with examples.

(e) What are the causes of lanthanide contraction?

3. (a) Write the IUPAC names of the following compounds :
　　　　　　　　　　　　　　　　$1 \times 2 = 2$

　　(i) $Na[Co(CO)_4]$

　　(ii) $[(NH_3)_5 Cr-OH-Cr(NH_3)_5]Cl_5$

(4)

(b) Give the structural formulas of the following compounds : 1×2=2

  (i) Pentammineazidocobalt(III) sulphate

  (ii) Tetrafluorooxochromate(IV) ion

(c) What are chelating ligands? Discuss with a suitable example. 2

4. Answer any *three* questions : 5×3=15

  (a) (i) On the basis of crystal field theory, explain the splitting of d-orbitals in an octahedral complex. 3

     (ii) Discuss briefly why the d-orbital splitting is larger in octahedral complex than in tetrahedral one. 2

  (b) Predict the spin state and calculate CFSE for the following complex ions : 2½×2=5

     (i) $[Mn(CN)_6]^{3-}$, pairing energy $=$ 28800 cm^{-1} and $\Delta_0 = 38500$ cm^{-1}

     (ii) $[Fe(H_2O)_6]^{2+}$, pairing energy $=$ 17600 cm^{-1} and $\Delta_0 = 10400$ cm^{-1}

  (c) Calculate the value of L and S for a d^4 ion and write the ground term for it. Show how this state splits in an octahedral crystal field. 3+2=5

(Continued)

(d) How does valence bond theory account for the following? $2\frac{1}{2}\times2=5$

　(i) $[Ni(CN)_4]^{2-}$ is diamagnetic and square planar.

　(ii) $[MnCl_4]^{2-}$ is paramagnetic and tetrahedral.

(e) Discuss with suitable examples the stereoisomerism exhibited by the following types of complexes : $2\frac{1}{2}\times2=5$

　(i) $[Ma_4b_2]$

　(ii) $[M(AA)_2b_2]$

where a and b are monodentate ligands and AA is symmetrical bidentate ligand.

5. Answer any *three* questions : $3\times3=9$

(a) Discuss in detail the mechanism of acid hydrolysis of $[Co(NH_3)_5Cl]^{2+}$. 　3

(b) Discuss briefly the effect of the following factors on the rate of aquation of an octahedral complex : $1\frac{1}{2}\times2=3$

　(i) Charge on the complex

　(ii) Steric effect

　　　　　　　　　　　　(*Turn Over*)

(c) Explain S_N1 CB mechanism with a suitable example.

3

(d) What is *trans*-effect? Outline the synthesis of *cis*- and *trans*-dichloro-diammineplatinum(0). How will you distinguish between them?

3

6. Answer any *one* question :

3

(a) What are the consequences of lanthanide contraction?

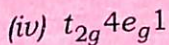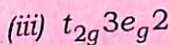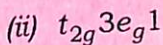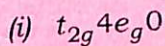(b) Give three points of differences between lanthanides and actinides.

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(Old Course)

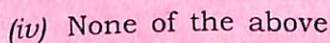<u>Full Marks : 48</u>
Pass Marks : 19

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

1. Select the correct answer :   1×5=5

   (a) The high-spin configuration of Cr(II) ion
       in octahedral crystal field is

      (i) $t_{2g}4e_g0$

     (ii) $t_{2g}3e_g1$

    (iii) $t_{2g}3e_g2$

    (iv) $t_{2g}4e_g1$

   (b) The ligand which does not form inner
       complexes is

      (i) acetylacetonato (acac)

     (ii) glycinato (gly)

    (iii) o-phenanthroline (o-phen)

    (iv) None of the above

(*Turn Over*)
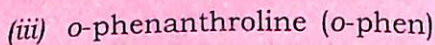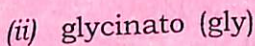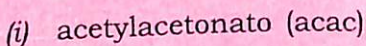
(c) The spectroscopic free ion ground term for d^2 configuration is

(i) ^1S

(ii) ^3P

(iii) ^2D

(iv) ^3F

(d) Which of the following has the highest lability?

(i) SF_6

(ii) $[PF_6]^-$

(iii) $[AlF_6]^{3-}$

(iv) $[SiF_6]^{2-}$

(e) Which of the following does not belong to lanthanides?

(i) Am

(ii) Pm

(iii) Sm

(iv) Tm

2. Answer the following : $2 \times 5 = 10$

(a) What are the L and S values of ^3P, ^1D, ^3F and ^2G?
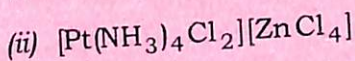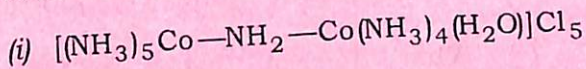
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(b) What is magnetic moment? How is it related to paramagnetism and diamagnetism?

(c) Write a note on coordination isomerism with suitable example.

(d) What are inert and labile complexes?

(e) Lanthanum exhibits only +3 oxidation states. Explain.

3. (a) Write the IUPAC names of the following :   2

 (i) $[(NH_3)_5 Co-NH_2-Co(NH_3)_4(H_2O)]Cl_5$

 (ii) $[Pt(NH_3)_4 Cl_2][ZnCl_4]$

(b) Write the formulas of the following compounds :   3

 (i) Ammonium hexa-isothiocyanatochromate(III)

 (ii) Amminebromo-*bis*-(ethylenediamine) cobalt(III) ion

 (iii) Octaquo-μ-dihydroxodiiron(III) nitrate

(*Turn Over*)

4. Answer any *four* questions : $4 \times 4 = 1$

 (a) How does the valence bond theory explain the shapes and magnetic properties of six coordinated complexes? Illustrate your answer by giving suitable example.

 (b) Predict the spin state and calculate crystal field stabilization energy for the following complexes :

  (i) $[Cr(H_2O)_6]^{3+}$, pairing energy = 23500 cm^{-1} and $\Delta = 13400$ cm^{-1}

  (ii) $[Co(NH_3)_6]^{3+}$, pairing energy = 21000 cm^{-1} and $\Delta = 23000$ cm^{-1}

 (c) What do you mean by the term 'spectroscopy'? Write the spectroscopic free ion ground terms for the following : 4

  (i) d^3

  (ii) d^6

 (d) What are 'spin' and 'laporte' selection rules?

  $2+2=4$

 (e) Explain the following properties of transition metal complexes in the light of crystal field theory :

  $2 \times 2 = 4$

  (i) Colour of the complex

  (ii) Magnetic property of the complex

(f) What is effective atomic number rule? Determine the effective atomic number of the central metal atom of the following compounds : 1+3=4

   (i) $K_4[Fe(CN)_6]$

   (ii) $[Cr(NH_3)_6]Cl_3$

   (iii) $Mn_2(CO)_{10}$
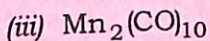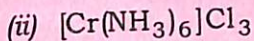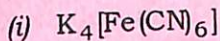
5. Answer any *three* questions : 3×3=9

   (a) What are associative and dissociative mechanisms in ligand substitution reaction? 3

   (b) Discuss the effect of the following factors on the rate of acid hydrolysis of octahedral complex : 1½×2=3

      (i) Charge on the substrate

      (ii) Steric effect

   (c) Write a note on acid hydrolysis of cobalt(III) compounds with suitable example. 3

   (d) What is *trans*-effect? Starting from $[PtCl_4]^{2-}$ and other ligands, outline the synthesis of *cis*- and *trans*-$[PtCl_2(NH_3)(NO_2)]$. 3

   (e) Discuss S_N1 CB mechanism with suitable example. 3

(*Turn Over*)

6. Answer any *one* question :   3

   (a) Give three points of differences between lanthanides and actinides.

   (b) What are the consequences of lanthanide contraction?

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