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End Semester Examination of Semester–III, 2015
Subject : CHEMISTRY (PG)
Paper : CEM–302 (Inorg Spl.) (Th)
Full Marks : 40
Time : 2 Hrs

The figures in the margin indicate the marks corresponding to the question

Candidates are requested to give their answers in their own word as far as practicable.

Illustrate the answers wherever necessary.

Attempt **one question** from each group

Group–A

1. a) How is $[(\eta^6\text{-arene})_2Cr]$ prepared from $CrCl_3$ by Fischer-Hafner synthesis? 3

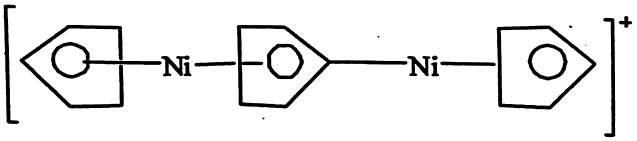
   b) Give the structure and function of Vitamin–C. 2+2

   c) Complete the reaction: 1

   $$C_pMn(CO)_3 \xrightarrow[AlCl_3]{MeCOCl} ?$$

   d) Why X-rays are used for crystal structure analysis? 2

2. a) How will you synthesize

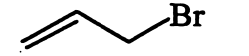


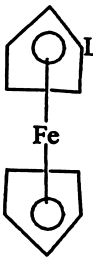
from nickelocene? 2

b) Define primitive cell with diagram. Is fcc structure primitive? Explain. 3

c) Give one example each of hall sandwich mixed sandwich and bent sandwich compound. 3

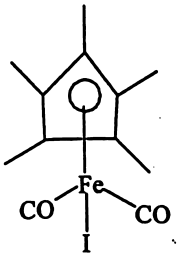
d) Complete the reactions: 2

i) Cp_2ReH  ?

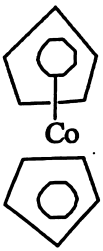
ii)  $B(OR)_3$?

Group–B

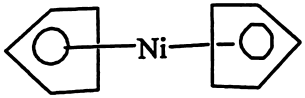
3. a) Complete the reactions: 1×4=4

i) 

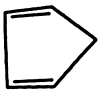
$\xrightarrow[C_5H_6]{AgBF_4}$? $\xrightarrow{Et_3N}$?

ii) 

$\xrightarrow{CF_2=CF_2}$?

iii) 

$\xrightarrow{C_3Ph_3Br}$?

iv) 

+ $Fe(CO)_5$ ⟶ ? $\xrightarrow[\Delta]{-CO}$?

b) What do you mean by symmetry operation? Prove that a crystal lattice can not have a five-fold symmetry. 1+3

c) Give the selection rules for d-d electronic transitions. 2

4. a) With specific examples of you choice explain how IR spectres copy helps to ascertain complex formation in carbonyls and nitrosyls. 5

b) The carbonyl stretching frequency for $[V(CO)_6]^-$, $G(CO)_6$ and $[Mn(CO)_6]^+$ are 1858 cm^{-1}, 1940 cm^{-1} and 2094 cm^{-1} respectively. Explain this trend with proper reasoning. 3

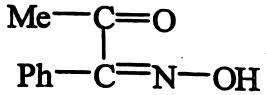
c) What is the fundamental criteria for the characterization of a compound by CD spectroscopy? 2

Group–C

5. a) With the help of suitable equations explain the creation of Stokes' radiation and Anti Stokes' radiation in Raman spectroscopy. 5

b) What is the basic difference pertaining to vibrational spectroscopy for IR and Raman active modes. 2

c) For the complex $[Ru^{III}(HK)(K)X_2]$, where HK is



explain the structure of the complex with regard to the ligand binding the metal from the data given below: 3

	Free ligand	*Ligand bound to Ru*
ν_{CO}	1645 cm^{-1}	~1500 cm^{-1}
ν_{CN}	1600 cm^{-1}	~1580 cm^{-1}
ν_{NO}	1000 cm^{-1}	1300 cm^{-1}
ν_{OH}	3600 cm^{-1} (Sharp)	Peak broading shifts to lower energy region
ν_{Ru-X}		~350 cm^{-1}

6. a) For the compound $[M(CN)_5(NO)]^{2-}$ the NO stretching frequencies are 1938 cm^{-1}, 1927 cm^{-1} and 1905 cm^{-1} as the metal changes from Fe, Ru to Os. Explain the trend with proper reasoning. 3

   b) What is cotton effect in CD spectroscopy. Explain its significance. 3

   c) Give the basic principles of UV-visible spectroscopy. 3

   d) How many atoms are there in the Primitive cell of diamond? 1

Group–D

7. a) Show that the spacing d of plane (hkl) in a simple cubic lattice of side 'a' is

$$d = \frac{a}{\left(h^2 + k^2 + l^2\right)^{\frac{1}{2}}}$$

and hence find $d_{100} : d_{110} : d_{111}$ 4+1

b) Nickelocene is more reactive than ferrocene. Justify. 2

c) The UV – Visible spectrum of $Ti(H_2O)_6^{3+}$ is broad and unsymmetrical. Why? 3

8. a) What is reciprocal lattice? Show that reciprocal lattice to the body centred cubic lattice is face centred cubic lattice. 1+3

b) What is analgesic? Give an example and its mode of action.

c) What are common properties of Vitamin A, C and E? From their structure explain their biomedical activity. 3