PG/IIS/CEM-203/14

M.Sc. 2nd Semester Examination 2014

CHEMISTRY

(*Inorganic*)

PAPER – CEM-203

Full Marks : 40

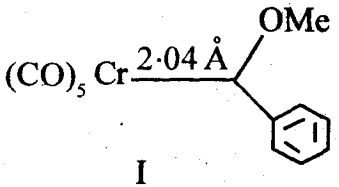
Time : 2 hours

Answer any **five** questions taking
at least **two** from each Group

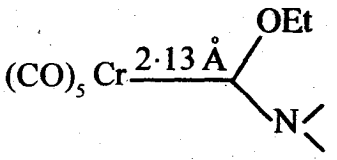
The figures in the right hand margin indicate marks

GROUP – A

1. (*a*) Consider the following structures and explain why the Cr—C bond length is longer in II compared to I ? 2



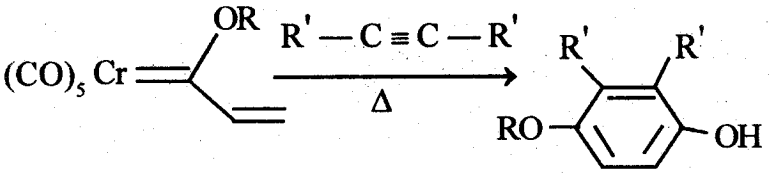
I



II

(*b*) How will you synthesize 'Tebbe's reagent' ? Write down the course of reaction when Tebbe's reagent in treated with  in pyridine. Mention the final product. 1 + 2

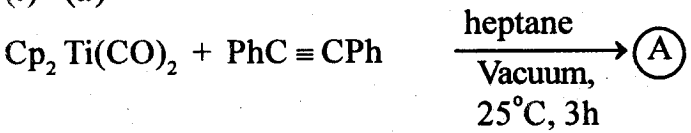
(*c*) Write down the mechanism of the following reaction. 2



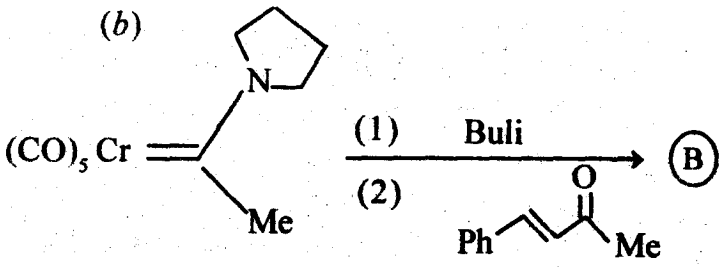
(*d*) Write down the coordination modes of 'hydride' as ligand. 1

2. Complete the following reaction— 1 + 1 + 2 + 1

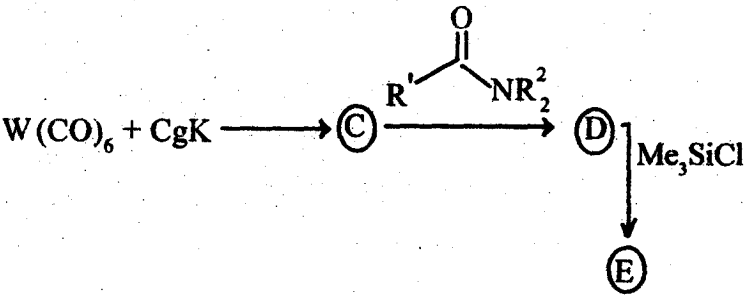
(*i*) (*a*)

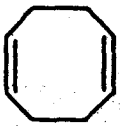


(*b*)



(*c*)



(*d*) Fe (g) +  (g) ⟶ F

(*ii*) Explain 'Agostic interaction'. 1

(*iii*) Draw the probable binding modes of 'alkyne' as ligand. 2

3. (*a*) Describe experimental determination of stability constant by mole ratio method.

(*b*) Stability of complexes increases in the following order : M (en) < M (trien) < M (EDTA). Explain.

(*c*) Discuss the factors affecting stability of complexes. 3 + 2 + 3

4. (*a*) Derive an expression for conditional stability constant of M-EDTA complex.

(*b*) Calculate $[Ni^{2+}]$ from a solution containing $[NiY^{2-}] = 0{\cdot}015$ M at pH 3·0 & pH 8·0 ($K_f = 4{\cdot}2 \times 10^{18}$ at pH = 3·0 and 8 ; $\alpha = 2{\cdot}5 \times 10^{-11}$ and $5{\cdot}4 \times 10^{-3}$)

(*c*) How can you derive the stability constant of ternary complexes by stepwise method ? 3 + 3 + 2

GROUP – B

5. (*a*) Use group theoretical principle to determine the symmetry of vibrational mode of CH_2Cl_2 molecule applying cartesian

co-ordinate method. Identify the symmetry of IR and Raman active mode in this molecule. Given below the character table for C_{2v} point group. 3 + 1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

(*b*) Explain why the polarization effect is not observed in cubic or higher symmetry molecule. 2

(*c*) Determine the characters of irreducible representations of D_4 point group. Write the appropriate Mulliken symbols for these irreducible representations. 2

6. (*a*) p_x and p_y orbitals provide basis for B_1 and B_2 representation, respectively, of C_{2v} point group. On the other hand p_x and p_y orbitals, as a pair, provide basis for the E representation of C_{3v} point group. Explain. Given below the character table for C_{3v} point group. (Use the character table of C_{2v} point group given in **Q.No.5**). 5

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	(x,y) (R_x, R_y)	$(x^2-y^2, xy)(xz, yz)$

(*b*) ClO_2 molecule is trapped in a solid. Its ground state is known to be B_1. Polarized light parallel to the y-axis excites the molecule to an upper state. What is the symmetry of that state ? (Use the character table of C_{2v} point group given in **Q.No.5**). 2

(*c*) The energy integral $\int \psi_i H \psi_j dY$ may be non-zero only if ψ_i and ψ_j belong to the same irreducible representation of the molecular point group. Explain. 1

7. (*a*) Using molecular orbital theory deduce the expression for symmetric and antisymmetric functions of H_2^+ ion. Show the electron distribution of symmetric and antisymmetric states of this ion. (Derivation of secular determinant is not required). 5

(*b*) Lattice structure of ZnS is tetrahedral whereas lattice structure of CsCl is body centred cubic. Explain. 3

8. (*a*) Deduce Born-Lande equation to estimate the lattice energy. 3

(*b*) Write short notes on : $2\frac{1}{2} \times 2$

(*i*) Thin layer chromatography

(*ii*) Ion-exchange chromatography.
