M.Sc 2nd Semester Examination, 2011

CHEMISTRY

(*Inorganic*)

PAPER—CEM - 203

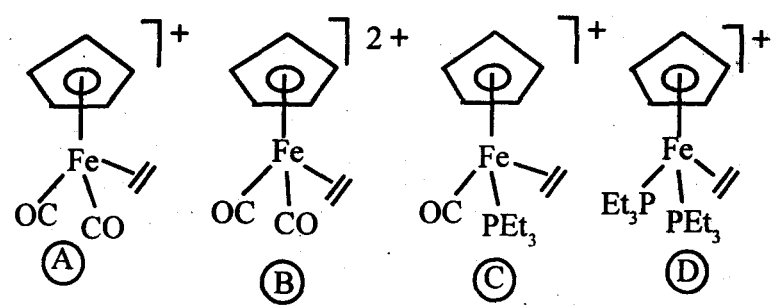
Full Marks : 40

Time : 2 hours

Answer any **four** questions

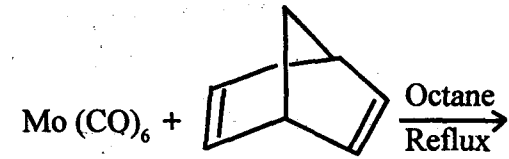
The figures in the right-hand margin indicate marks

1. (*a*) Arrange the following complexes in the order of ethylene C—C bond length with proper explanation : 3



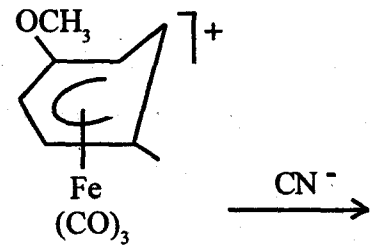
(*b*) Complete the following reaction : 5

(*i*)

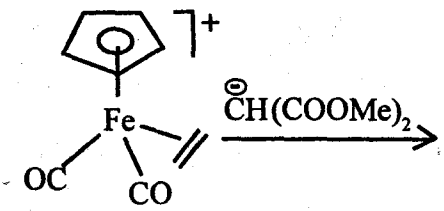


(*ii*) $ZrCl_4 + C_7H_8 \xrightarrow{Na\text{-}Hg}$

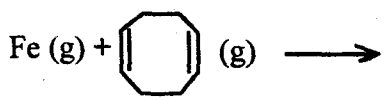
(*iii*)



(*iv*)

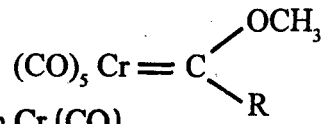


(*v*)



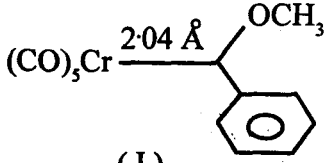
(*c*) Rationalise the observation "On forming $[IrBr(CO)(\eta^2\text{-}C_2(CN)_4)(PPh_3)_2]$, the C—C bond in $C_2(CN)_4$ lengthens from 135 to 151 pm. 2

2. (*a*) How will you synthesize

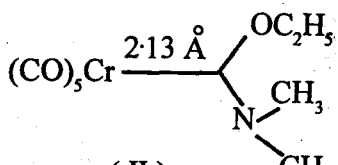


starting from $Cr(CO)_6$. 2

(*b*) Consider the following structures and explain why the C—C bond length is longer in 'II' compared to 'I' ? 2



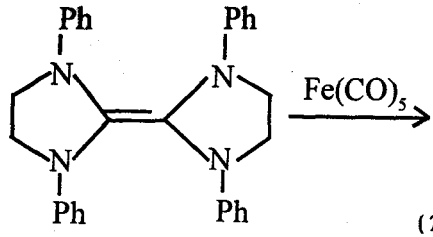
(I)



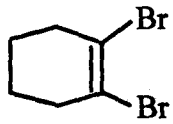
(II)

(*c*) Predict the product of the following reactions : 4

(*i*)



(*ii*) $Bu^t CH_2 TaCl_4 \xrightarrow[PMe_3]{Na\text{-}Hg}$

(*iii*)  $+ Pt(PPh_3)_3 \xrightarrow{Na\text{-}Hg}$

(*iv*) $Co_2(CO)_8 + PhC \equiv CPh \longrightarrow$

(*d*) Identify 'A' and 'B'. 2

$NiCl_2 +$  $+ AlR_3 \longrightarrow [A] \xrightarrow{\text{Cyclooctadiene}} [B]$

3. (*a*) Show that the p_x and p_y orbitals, as a pair, provide a basis for the E representation of C_{3v} point group. Given below the character table for C_{3v} point group. 4

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*) Investigate whether an A_1 electron in H_2O can make an electric dipole transition to a B_1 orbital. What polarized radiation will emitted (or absorbed) during this transition? Given below the character table for C_{2v} point group. 4

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

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

4. Using molecular orbital theory derive the expression for the energy of symmetric and antisymmetric states of H_2^+ ion. Deduce the expression for symmetric function and antisymmetric function of H_2^+ ion. Show the electron distribution of symmetric and antisymmetric states of this ion. (Derivation of secular determinant is not required). 4 + 4 + 2

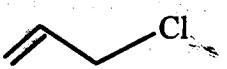
5. (*a*) Verify that the representation of a direct product, Γ_{AB}, will contain the totally symmetric representation only if the irreducible Γ_A = the irreducible Γ_B. 4

(*b*) Write short note on "spectral transition probabilities." 4

(*c*) He_2^+ and H_2^+ both have same bond order but differ in their stability. Explain. 2

6. (*a*) What do you mean by fluxionality ? Why NMR spectroscopy is used to detect fluxional behaviour. Explain. 1 + 2

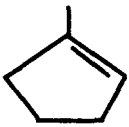
(*b*) What happens when $Na[Mn(CO)_5]$ is reacted with 2



(*c*) Draw the possible co-ordination modes of hydride ligand. 2

(*d*) Complete the following reaction. 2

(*i*) $NiBr_2 + 2C_3H_5MgBr \xrightarrow[-10°C]{Et_2O}$

(*ii*) $Na_2[PdCl_4] +$  $\xrightarrow{Na_2CO_3}$

(*e*) What do you mean by agostic interaction ? 1

7. (*a*) Write down the instrumental set-up of an atomic absorption spectrophotometer. 3

(*b*) Discuss "hollow cathode lamp". 3

(*c*) Write down the relationship between excitation spectra and fluorescence spectra. 2

(*d*) What do you mean by "Irving Williams Order" ? 2