2018

M.Sc. 2nd Semester Examination

CHEMISTRY

PAPER—CEM-203

Subject Code—24

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(*Inorganic*)

Group—A

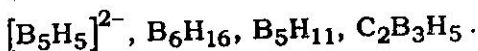Answer any *two* questions.   4×2

1. (a) Establish the relation

$$a_i = \frac{1}{h} \sum_R \chi(R)\, \chi_i(R)$$

where the terms have usual significance.

(b) Show that the representation of a direct product, ΓPQ, will contain the totally symmetric representation only if the irreducible ΓP = irreduciable ΓQ.

(c) Classify the following compounds as close, nido and hypo type

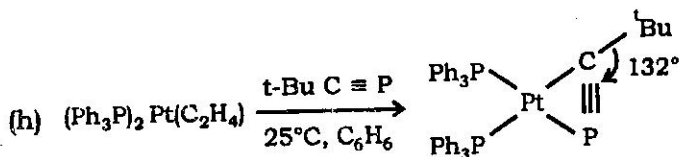$$[B_5H_5]^{2-}, \ B_6H_{16}, \ B_5H_{11}, \ C_2B_3H_5 .$$

(d) What is boron neutron capture therapy ? Give two examples of each for "first generation" and "second generation" BNCT agents.

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

(f) Predict the product(s) for the following reaction :

(i)

$$\xrightarrow{CF_3SO_3H}$$

(ii) $(C_5H_5)Mn(CO)_2THF \xrightarrow{CH_2N_2}$
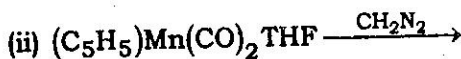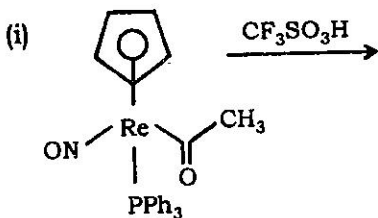
(g) What do you mean by metalloborane ? Give an example.

(h) $(Ph_3P)_2 Pt(C_2H_4)$ $\xrightarrow[\text{25°C, } C_6H_6]{\text{t-Bu } C \equiv P}$

Comment on the tBu — C — P bond angle.

Group—B

Answer any *one* question.   1×8

2. (a) Using group theoretical principle show that for formaldehyde the n → π^* electronic transition is not allowed, but $\pi → \pi^*$ transition is allowed.   5

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) Ground state of *cis*-N_2F_2 is A_1. To what excited states may it be excited by electric dipole transitions, and what polarization of light is necessary to use ?   3
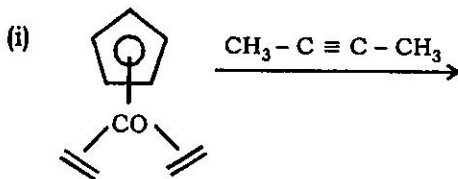
3. Use group theoretical principle determine the symmetry of vibrational modes of ClF_3 molecule applying both cartesian and internal coordinate method. Identify the symmetry of IR and Raman active modes in this molecule. Show possible modes of vibration for this molecule and indicate the nature of vibration. (*Use the character table of C2v point group given in Q. No. 2*)
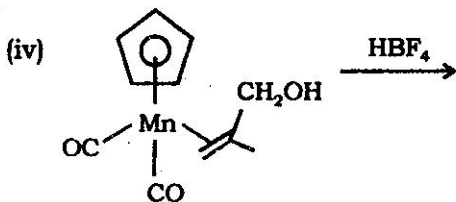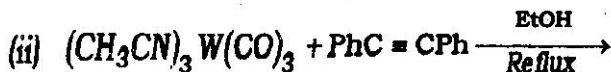
4+1+2+1

Group—C

Answer any *two* of the following questions. 2×4

4. What is the fundamental difference between the alkene and alkyne complexes while binding to transition metal ions. Draw the possible binding modes of alkyne to transition metal ions.

5. How Cyclohexyne can be stabilized by reacting with $Pt(PPh_3)_3$ in presence of Na/Hg ? Write down the reaction with structure of the complex.

6. Predict the product for the following reaction :

(i)

$$CH_3 - C \equiv C - CH_3$$

(*Continued*)

(ii) $(CH_3CN)_3 W(CO)_3 + PhC \equiv CPh \xrightarrow[\text{Reflux}]{\text{EtOH}}$

(iii) $H CO(CO)_4 +$ $\longrightarrow$

(iv)

$\xrightarrow{HBF_4}$

7. (a) Which among the following alkenes with bind most strongly to a metal ? Give reasons

   (i) cyclooctadiene

   (ii) ethylene

   (iii) norborene

   (iv) cyclohexene   2

   (b) Which of the following metal alkene complex do you think will look most like a metalla cyclopropane ? Explain your answer.

   (i) $(CH_2 = CH_2) Ni(PPh_3)_2$
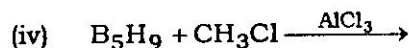
   (ii) $(CH_2 = CH_2) Fe(CO)_4$ 2

Group—D

Answer any *two* questions. $\frac{1}{2} \times 8$

8. Complete the following reactions :

(i) $B_4H_{10} + N(CH_3)_3 \longrightarrow$

(ii) $B_5H_9 + Li(CH_3) \longrightarrow$

(iii) $5K[B_9H_{14}] + 2B_5H_9 \longrightarrow$

(iv) $B_5H_9 + CH_3Cl \xrightarrow{\text{AlCl}_3}$

(v) $B_{10}C_2H_{12} + 2LiC_4H_9 \longrightarrow$

(vi) $Al_2(CH_3)_6 + 2[B_{11}H_{13}]^{2-} \xrightarrow{\Delta}$

(vii) $2C_4H_9Li + C_2H_2B_{10}H_{10} \longrightarrow$

(viii) $2RMgBr + C_2H_2B_{10}H_{10} \longrightarrow$

(Continued)
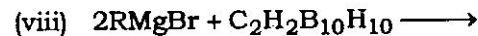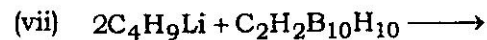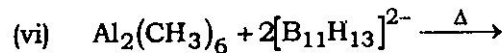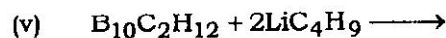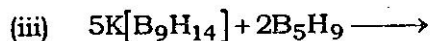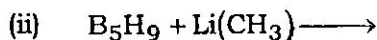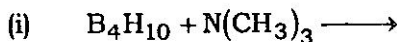
9. Calculate the synx numbers of $[B_5H_5]^{2-}$ and $[B_4H_8]$. Determine the most probable structures of these anion/compound. 4

10. Styx numbers of boron hydride A and boron hydride B are given below. Establish the most probable structures of these boron hydrides.

| Boron hydride	Styx number
A	2102
B	3120

11. Describe the synthetic procedure for the synthesis of different types of closo carboranes. 4

Group—E

Answer any *one* question. 1×8

12. (a) Determine the characters of irreducible representation of D_4 point group. Write the appropriate Multiken symbols for these irreducible representations. 2+2

(b) What do you mean by fluxional behaviour ? Explain with a proper example. 2

(c) Complete the following reactions :

(i) $Ph_3PAuCl + C_2RLiB_{10}H_{10} \longrightarrow$
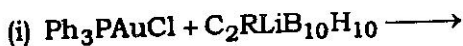
(ii) $RC_2LiB_{10}H_{10} \xrightarrow{HgCl_2}$ 2

13. (a) The energy integral $\int \psi_i H \psi_j dr$ may be non-zero only if

ψ_i and ψ_j belong to same irreducible representation of the molecular point group. Explain. 2

(b) Why NMR spectroscopy is applied to detect fluxionality in compounds ? 2

(c) An unexpected product is formed in the reaction of diphenylacetylene with tris-(acetonitrile) tricarbonyl tungsten. Write down the product. 2

(d) Write short note on "spectral transition probabilities". 2

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