2022

M.Sc.

2nd Semester Examination

CHEMISTRY

PAPER—CEM-203

INORGANIC CHEMISTRY-II

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.

Group—A

Answer any *four* questions. 4×2

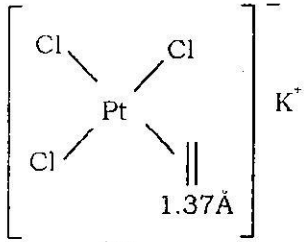
1. (a) Explain why polarization effect is not observed in cubic or higher symmetry molecule.

(b) The representation of a direct product, Γ_{AB}, will contain the totally symmetric representation only if the irreducible Γ_A = the irreducible Γ_B (where $\Gamma_{AB} = \Gamma_A \times \Gamma_B$). Explain.

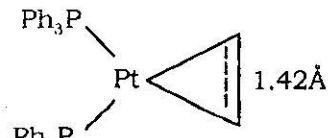
(c) Complete the following reaction :

$$[Cp\ Ni\ (CO)]_2 + RC \equiv CR \longrightarrow$$

(d)



[A]



[B]

Explain the observed C – C bond length in the above complexes. Show the related orbital diagram.

(e) Give at least two examples of each for 1st and 2nd and 3rd generation BNCT agents.

(f) Complete the following reactions : $4 \times \frac{1}{2}$

(i) $B_4H_{10} + C_2H_2 \longrightarrow$

(ii) $2B_4H_{10} + 2Na(Hg) + Et_2O \longrightarrow$

(iii) $B_5H_9 + CH_3Cl + AlCl_3 \longrightarrow$

(iv) $B_5H_9 + CH_3OH \longrightarrow$

Group—B

Answer any *one* question. 1×8

2. Justify that in $[Mo_2Cl_8]^{4-}$ the δ to δ^* transition is electric-dipole allowed with z-polarization and forbidden for radiation with its electric vector in the xy plane.

D_h	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
b_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

3. (a) Is p_x to p_y an allowed transition in a tetrahedral environment ? Explain.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z) (R_x, R_y)	(xy, xz, yz)

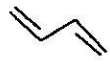
(b) Using group theoretical principle verify that n $\longrightarrow \pi^*$ electronic transition is forbidden whereas $\pi \longrightarrow \pi^*$ electronic transition is allowed in formaldehyde molecule.

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

3+5

Group—C

Answer any *one* question. 1×8

4. (a) $NiCl_2$ +  + AlR_3 ⟶

C_8H_{12} ⟶ [B]

[A]

C_2H_4 ⟶ [C]

Write down the structures of [A], [B] and [C] mentioning their geometries. Calculate the number of valence electrons in each complex.

(b) Complete the following reaction :

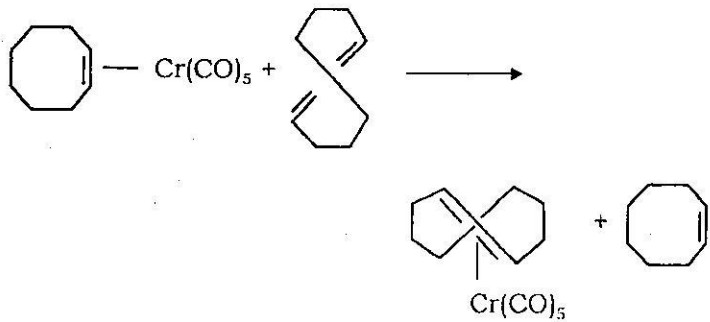
$$Cp_2Ti(CO)_2 + PhC \equiv CPh \xrightarrow[\text{vacuum}]{\text{heptane } 25^\circ C}$$

(2+2+2)+2

5. (a) "Halogen substituted acetylenes are highly explosive compounds in the uncomplexed state, however, it can be stabilized by complex formation" — justify the statement with a suitable example.

(b) Schematically present the bonding in Fischer's carbyne complex through the orbital diagram.

(c)



Discuss the reason behind the displacement of cis-cyclooctene by its trans-analogue.

(d) Write down the possible binding modes of alkyne ligand as 4 electron donors to metal atoms.

2+2+2+2

Group—D

Answer any *two* questions. 2×4

6. Categorize the following compounds as closo, nido, arachno and hypo boron hydrides :

$[CpCoC_2B_{10}H_{12})]$; $[Me_4(C_2B_7H_9]$; $[B_9H_{14}]^-$; $[C_2B_5H_7]$

7. Calculate the *styx* number of $[B_8H_{12}]^{2-}$. Established and draw the most probable structure of this anion.

8. For two boron hydrides the styx numbers are 3530 and 4320. Establish the probable structures of these boron hydrides. 2+2

Group—E

Answer any *two* questions. 2×4

9. Establish the equation

$$a_i = \frac{1}{h}\sum_R X_{AB}(R)\,X_i(R)$$

Where the terms have usual significance.

10. Complete the following reaction mentioning the structure, geometry and the valence electron count of the final product :

$$Mo(g) + 3C_4H_6 \longrightarrow$$

11. (a) Calculate the styx number of $[B_6H_{12}]$.

(b) Write the formation of possible product(s) when B_4H_{10} reacts with Me_2Hg. 2+2

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