2009

M.Sc.

2nd Semester Examination

CHEMISTRY (INORGANIC)

PAPER—CH-1203

Full Marks : 40

Time : 2 Hours

The questions are of equal value.

The figures in the right-hand margin indicate full marks.

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

Illustrate the answers wherever necessary.

Answer *all* questions.

1. (a) What do you mean by stereochemical nonrigidity? Explain this with an example. 4

(b) Write down the different binding modes of a hydride ligand. 2

(c) Predict the products of the following reactions : 1×4

(i) $Mo(CO)_6 + \text{norboradiene} \xrightarrow[\text{reflux}]{\text{Octane}}$

(ii) $Cp_2Ti(CO)_2 + PhC \equiv CPh \xrightarrow[25°C,\ 3hrs.]{\text{heptane, vacuum}}$

(iii) $Fe_2(CO)_9 + 2\ CH_2 = C = CH_2 \longrightarrow$

(iv) $RhCl_3 + C_2H_4 \xrightarrow[H_2O]{EtOH}$

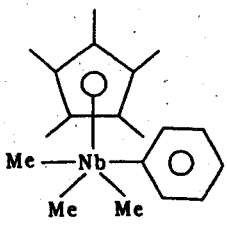
Or

(a) Why NMR technique is applied to detect fluxionality? 3

(b) What do you mean by Tollman's cone angle? 2

(c) Predict the products of the following reactions : 1×5

(i) $Fe(g) +$  $(g) \longrightarrow$

(ii) 

(iii) $Na[Mn(Co)_5] +$  $\xrightarrow{h\nu}$

(iv) $NiCl_2 +$  $+ AlR_3 \xrightarrow{C_2H_4}$

(v) $Cp_2Ni \xrightarrow[EtOH]{Na/Hg}$

2. (a) With the help of group theory proof that $\delta \rightarrow \delta^*$ transition in $Mo_2Cl_8^{4-}$ is electric-dipole allowed. What polarization of light is it necessary to use for this transition? 6+1

Character table for $Mo_2Cl_8^{4-}$ ion given below :

	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)	(xy,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)	

(b) Does the integral $\int(3dz^2)x(3dxy)d\tau$ vanish in a C_{2v} molecule? Explain. 3

Given below the character table for C_{2v} :

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

Or

(a) The ground state of NO_2 is A_1 in the group C_{2v}. To what excited states may it be excited by electric dipole transitions, and what polarization of light is it necessary to use? (the character table for C_{2v} is given above.) 4

(b) Is $P_x \longrightarrow P_y$ an allowed transition in a tetrahedral environment? Explain. Given below the character table for T_d : 4

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)	(xy, xz, yz)

(c) Deduce the following representation into its component species : 2

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ	15	0	−1	−1	3

(The character table for T_d is given above.)

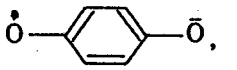
3. (a) Using valence bond theory deduce the expression for the energy of Symmetric and antisymmetric states of H_2 molecule. 7

(b) The centre of the EPR spectrum of atomic deuterium lies at 330·02 mT in a spectrometer operating at 9·2482 GHz. What is the g-value of the electron in the atom? 2

(c) Predict the intensity distribution in the hyperfine lines of the EPR spectra of $\dot{C}D_3$. 1

Or

(a) Draw the qualitative energy level diagram for the odd electron of the free radical ion,



in the presence of external magnetic field and find the possible transition with radiation of microwave region. Show the differential ESR spectral pattern of this radical indicating the intensity ratio. 3+1

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

(c) Discuss 'D' mechanism. 4

4. (a) Give a schematic representation of the experimental set up in atomic absorption spectrophotometry (AAs). How does flame photometry differ from AAs? 3+2

(b) Define diffusion current, residual current and half-wave potential in voltammetry. 1+1+1

(c) What are the advantages and disadvantages of using DME as the working electrode in polarography? 2

Or

(a) What is Coulometry? Mention the two types of coulometric methods used in analysis. 2+1

(b) Synthesize cis– and trans– isomer of $[PtCl_2(NO_2)(NH_3)]^-$ starting from $[PtCl_4]^{2-}$. Explain the reaction scheme. 2+2

(c) What do you mean by macrocyclic effect? 1

(d) What is a spectator ligand? 2