

UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE LEVEL I (SEMESTER I)  
EXAMINATIONS- JULY-2016

SUBJECT: Chemistry

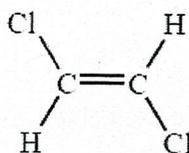
COURSE UNIT: CHE 4114

TIME: Three (03) hours

Answer all questions

(01) Answer all parts

(a) Consider the molecule given below.



- (i) List all the symmetry operations for this molecule.  
(ii) Assign the point group for the above molecule.

(iii) Write a set of transformation matrices that describe the effect of each symmetry operation listed in (a) (i) on a set of coordinates  $x, y, z$  for a point

(25 marks)

(b) Using the  $D_{2d}$  character table given below answer the questions (b) (i) and (ii).

$D_{2d}$	$E$	$2S_4$	$C_2$	$2C_2'$	$2\sigma_d$		
$A_1$	1	1	1	1	1	$R_z$ = ( $x, y$ ); ( $R_x, R_y$ )	$x^2 + y^2, z^2$
$A_2$	1	1	1	-1	-1		$x^2 - y^2$
$B_1$	1	-1	1	1	-1		$xy$
$B_2$	1	-1	1	-1	1		( $xz, yz$ )
$E$	2	0	-2	0	0		

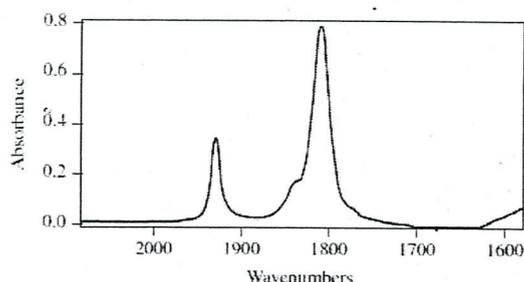
(i) Determine the order of the group.

(05 marks)

(ii) Verify that the  $E$  irreducible representation is orthogonal to the  $A_2$  irreducible representation.

(05 marks)

- (c) The reaction of  $[\text{Ti}(\text{CO})_6]^{2-}$  and chlorotriphenylmethane ( $\text{Ph}_3\text{CCl}$ ), results in rapid oxidation of  $[\text{Ti}(\text{CO})_6]^{2-}$  to afford a  $[\text{Ti}(\text{CO})_4]^-$  complex. The IR spectrum of  $[\text{Ti}(\text{CO})_4]^-$  in tetrahydrofuran solution is shown below.



- (i) Assign the point groups for the square planar and square pyramidal isomers of  $[\text{Ti}(\text{CO})_4]^-$  complex.
- (ii) Derive the basic set for reducible representation ( $\Gamma_{\text{str}}$ ) to obtain the normal CO stretching motion in above  $[\text{Ti}(\text{CO})_4]^-$  isomers.
- (iii) Show that the Ti complex expected to exhibit a square pyramidal arrangement of four CO ligands bound to Ti.

(30 marks)

- (d) Briefly explain the following statements pertaining to the intensity of the bands in UV-visible spectra.

(i) The aqueous solution of  $\text{Mn}^{2+}$  is pale pink but  $\text{MnO}_4^-$  is intense purple.

(07 Marks)

(ii) The colour of *trans*- $[\text{Co}(\text{en})_2\text{F}_2]^+$  is less intense than that of *cis*- $[\text{Co}(\text{en})_2\text{F}_2]^+$ .

(07 marks)

- (e) The electronic spectrum of  $[\text{V}(\text{NH}_3)_4](\text{NCS})_3$  displays three well resolved bands in the UV-visible region.

(i) Construct the Orgel diagram for the metal ion of the above complex.

(10 marks)

(ii) What are the possible electronic transitions for these three bands?

(06 marks)

(iii) What are the limitations of Orgel diagrams over the Tanabe-Sugano diagrams?

(05 marks)

Note: en = ethylenediamine

(2) Answer **all** parts

- (a) Using a group theoretical approach, construct a molecular orbital (MO) energy level diagram for  $\text{BH}_3$ . Include appropriate symmetry labels and clearly indicate major steps you follow to construct the MO diagram.

(25 marks)

- (b) Draw an orbital correlation (Walsh) diagram that illustrates what happens to each of the bonding molecular orbitals of  $\text{BH}_3$  upon distortion to a trigonal pyramidal geometry. Explain your reasoning. **Hint:** first construct a MO energy level diagram for “trigonal pyramidal”  $\text{BH}_3$ .

(25 marks)

- (c) Indicate which MO are involved in the formation of  $\text{NH}_3 \cdot \text{BH}_3$  adduct. Draw the shape of the molecular orbitals involved in bonding

(15 marks)

- (d) Consider that tetrakis(triphenylphosphine)palladium is having a tetrahedral structure.

- (i) Deduce the irreducible representation of tetrakis(triphenylphosphine)palladium complex considering  $\sigma$  only interaction

(14 marks)

- (ii) What are the atomic orbitals of Pd involved in bonding? State their symmetry labels.

(05 marks)

- (iii) What are the non-bonding atomic orbitals of Pd?

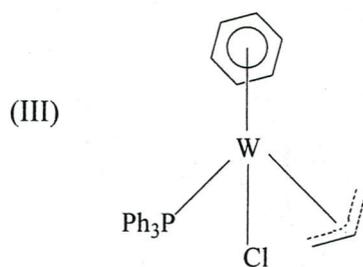
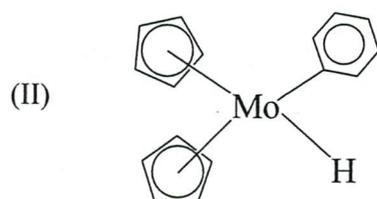
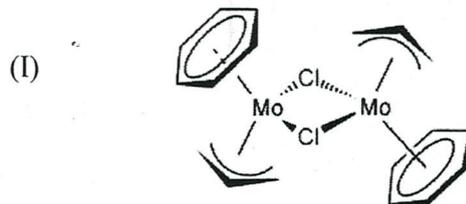
(02 marks)

- (iv) Draw MO diagram for the valence shell of above complex and clearly indicate HOMO and LUMO.

(14 marks)

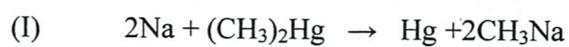
(3) Answer all parts.

(a) (i) Calculate the total number of electrons at the metal center in each of the following complexes.

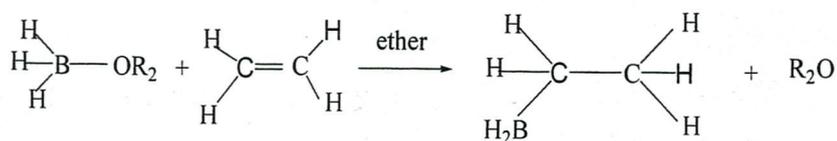


(15 marks)

(ii) State the type of reaction involved in each of the following.



(III)



(15 marks)

(b) (i) What are the factors that facilitate oxidative addition reactions?

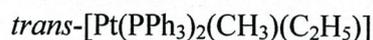
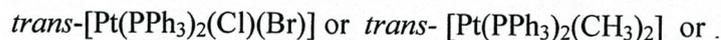
(08 marks)

(ii) Out of each of the following sets of complexes, select the complex showing the given property. Give reasons for your answer.

(I) more reactive towards oxidative addition of  $H_2$ :



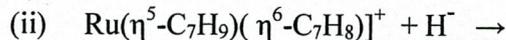
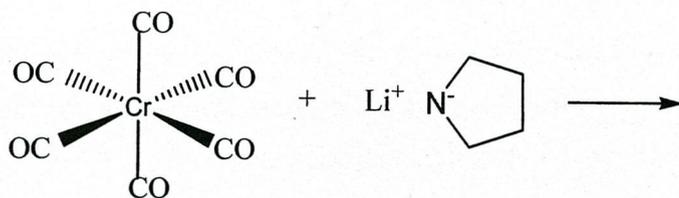
(II) most unstable



(12 marks)

(c) Predict possible products of following nucleophilic reactions.

(i)



(15 marks)

(d) (i) Draw structure of each of the following complexes.

(I)  $\mu$ -oxo-bis[pentamminemolybdenum(III)] ion

(II) *cis*-diaquabis(oxalato)manganese(III) ion

(06 marks)

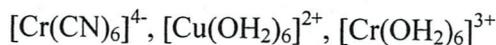
(ii) Identify whether above complexes are chiral or not.

(04 marks)

(e) (i) The complex  $[PdBr_4]^{2-}$  is paramagnetic with two unpaired electrons whereas the complex  $[Pd(CN)_4]^{2-}$  is diamagnetic. Deduce the geometries of the two complexes using the Crystal Field Theory.

(15 marks)

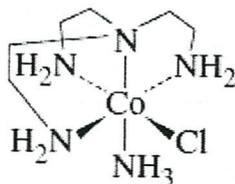
- (ii) Which of the following octahedral complexes would undergo Jahn Teller distortion? Arrange them in the increasing order of Jahn Teller distortion. Give a reason(s) for your answer.



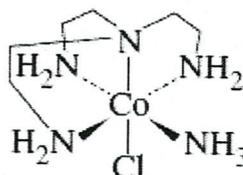
(10 marks)

(4). Answer all parts

- (a) Consider the base hydrolysis of the following two isomers of  $[\text{Co}(\text{tren})(\text{NH}_3)\text{Cl}]^{2+}$ .



Isomer I



Isomer II

Note: tren =  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$

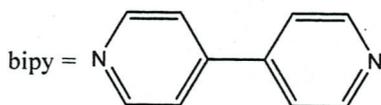
- (i) Assuming that the nitrogen atom *trans* to the leaving group in isomer I is most likely to be deprotonated by base hydrolysis, give the detailed mechanism for the formation of the final product *via* a trigonal bipyramidal transition state.
- (ii) The base hydrolysis of isomer I is  $10^4$  times faster than that of isomer II when the two reactions take place *via* a trigonal bipyramidal transition state. Give reasons for this observation.

(30 marks)

- (b) The following reaction occurs via an inner sphere mechanism.



Note:



Answer the following questions based on the above reaction.

- (i) Predict the product of the above reaction indicating the sequence of elementary steps involved.
- (ii) What would be the electron transfer mechanism if  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is used instead of  $[\text{Co}(\text{NH}_3)_5(\text{bipy})]^{3+}$ ? Give reasons for your answer.

- (iii) When bipy is replaced by OH<sup>-</sup>, the reaction proceeds by an inner sphere mechanism with a rate constant  $1.5 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . However, when bipy is replaced by H<sub>2</sub>O in the [Co(NH<sub>3</sub>)<sub>5</sub>(bipy)], the rate constant is  $0.1 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . Explain the above observation.

(35 marks)

- (c) The UV-visible spectrum of green [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> solution gives three absorption bands in the visible and near IR region with molar absorption coefficients,  $\epsilon$ , below  $10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The lowest energy band appears at  $8,600 \text{ cm}^{-1}$  while the highest energy band appears at  $25,300 \text{ cm}^{-1}$ . The energy of the middle band has not been assigned, because it appears as a shoulder type band.

- (i) Derive possible terms for d<sup>2</sup> electronic configuration. Giving reasons, identify the ground state term and the first excited state term.

(08 marks)

- (ii) How could you use above terms to derive the ground state and the first excited state terms of [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>?

(05 marks)

- (iii) Using the appropriate Tanabe-Sugano diagram, estimate the energy of spin allowed transition which should be appeared in the shoulder type middle band.

(15 marks)

- (iv) Indicating possible electronic transitions, briefly explain the origin and the intensity of the shoulder type middle band.

(07 marks)

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