UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL-II (SEMESTER-II) EXAMINATION – JUNE / JULY 2022

SUBJECT: Chemistry **TIME**: **Two (02)** Hours

COURSE UNIT: CHE 2212 (Descriptive Inorganic Chemistry II)

*Answer **four (04)** questions only.*

Velocity of light, (c)	$= 2.998 \times 10^{8}$ m s^{-1}
Avogadro's number, (N_A)	$= 6.022 \times 10^{23}$ mol^{-1}
Planck's constant, (h)	$= 6.626 \times 10^{-34}$ J s
Electron charge, (e)	$= 1.602 \times 10^{-19}$ C
Proton mass, (m_p)	$= 1.673 \times 10^{-27}$ kg
Electron mass, (m_e)	$= 9.10 \times 10^{-31}$ kg

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(01) Answer **all** parts.

(a) Briefly explain the following statements.

(i) $[V(phen)_3]^{3+}$ is labile whereas $[V(H_2O)_6]^{2+}$ is inert.

(ii) Exchange rate of CN^- in $[Fe(CN)_6]^{4-}$ is relatively higher than that in $[Fe(CN)_6]^{3-}$.

(20 marks)

(b) Sketch a reaction profile for substitution in a square planar complex in which,

(i) a five-coordinate intermediate exists, but bond breaking is more difficult than bond making.

(ii) a five-coordinate intermediate exists, but bond making is more difficult than bond breaking.

(20 marks)

(c) Consider the following square-planar substitution reaction which is carried out in CH_3OH at 25 °C.

$$trans\text{-}Pt(py)_2Cl_2 + CN^- \longrightarrow Pt(py)_2Cl(CN) + Cl^-$$

(i) Write the rate law for this reaction and clearly define the terms associated with it.

(ii) Explain briefly what role CH_3OH plays in this reaction.

(iii) If the reaction is carried out in C_6H_6 what changes would you expect in the mechanism? Write a rate law that accounts for the changes in C_6H_6.

(iv) If 1 mol of *trans*-$Pt(py)_2Cl(CN)$ is treated with 1 mol of CN^-, what product would you expect? Clearly state the geometry of the product formed.

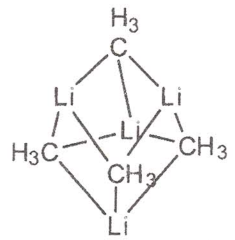
(v) What role(s) does platinum bound CN play in the reaction to reduce the activation energy?

(60 marks)

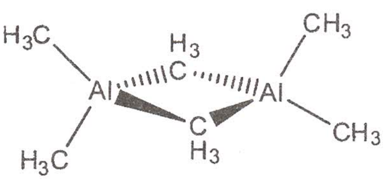
(02) Answer **all** parts.

(a) Which of the following complexes are organometallic complexes?

(i)



(ii)



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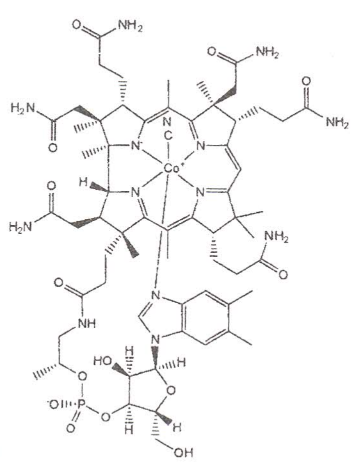

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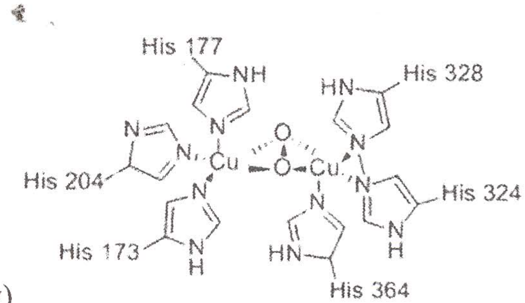


(12 marks)

(b) Sketch structures, with their proper geometries, for the following organometallic compounds.

(i) $CpRuCl(=CHCO_2Et)(PPh_3)$

(ii) $Co_2(\mu\text{-}CO)_2(CO)_6$ (Co-Co bond)

(iii) *trans*-$HRh(CO)(PPh_3)_2$

(iv) $Ir_2(\mu\text{-}Cl)_2(CO)_4$

(v) Cp_2TiCl_2

(15 marks)

(c) Provide the total electron count for each central metal of the following organometallic complexes

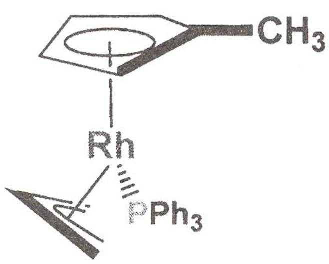
Note: Steps need to be shown to obtain full marks.

(i) $[CpCo(\eta^3\text{-}C_3H_5)]PF_6$

(ii) $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$

(iii) $[Mn(CO)_6]^+$

(iv)



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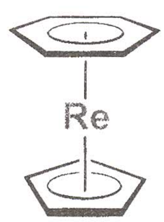
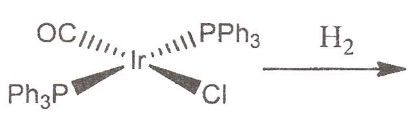


(35 marks)

(d) Predict the products of the following organometallic reactions:

(i) Ni + 4 CO →

(ii) 

(iii) $Cr(CO)_6$ + PPh_3 →

(iv) $Re(CO)_5Br$ + en →

(v) $Co_2(CO)_8$ + 2 Na →

Note : en: ethylenediamine

(25 marks)

(e) The iron carbonyl organometallic complex **A** ≡ $Na[Fe(CO)_3(NO)]$ has been synthesized in 1983 by a research group of University of Texas. Later on, it was found that compound **A** obeys the 18 electron rule. Determine the coordination mode of NO ligand in complex **A**.

(13 marks)

(03) Answer **all** parts.

(a) Molecular symmetry helps us understanding molecular properties of chemical entities.

(i) List the symmetry elements with their standard symbols.

(ii) Write down three applications of symmetry in chemistry.

(iii) Illustrate the following symmetry elements using the BCl_3 molecule.

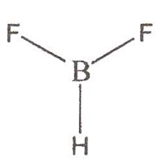
(I) Principal rotational axis

(II) Horizontal mirror plane

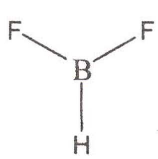
(III) Vertical mirror plane

(30 marks)

(b) Perform the operations shown and draw the new configurations for the following molecules/objects.

(i) 

Rotation by 120 ° → through B atom

(ii) 

Rotation by 180 ° → along B-H bond

(iii) 
Reflection along → the nodal plane

(iv) 
Reflection perpendicular → to the nodal plane

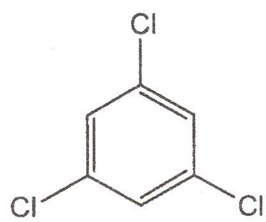
(20 marks)

(c) Distinguish the symmetry operations out of the above b(i)-b(iv).

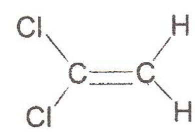
(10 marks)

(d) Giving the major symmetry elements derive the point groups of the following molecules.

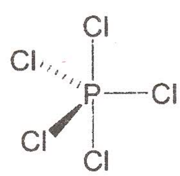
(i)



(iii)



(ii)



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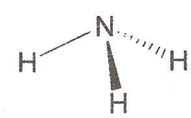


(40 marks)

(04) Answer **all** parts.

(a) Some properties of selected lanthanide elements are given in the following table.

Element	Ionic Radius (M^{3+})	Number of unpaired electrons	Σm
Samarium (Sm)	96	1	0
Neodymium (Nd)	99	3	0
Praseodymium (Pr)	101	2	1
Gadolinium (Gd)	94	7	0

(i) Write the ground state electronic configuration of each of the following lanthanide atoms/ions;

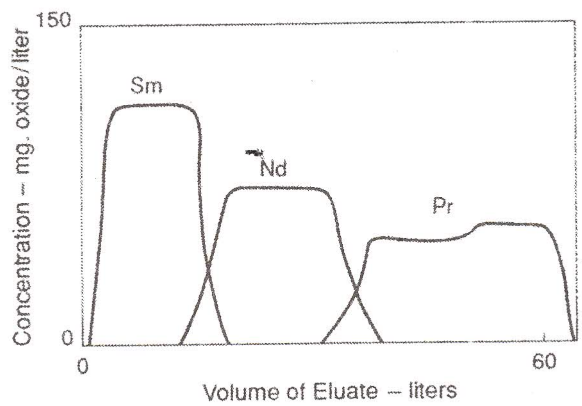
(I) Nd (II) Sm^{3+} (III) Gd^{3+} (IV) Pr

(ii) Calculate the magnetic moments of Gd^{3+}.

(iii) Briefly explain why the ionic radius of Nd^{3+} is greater than that of Gd^{3+}.

(iv) Explain how ion exchange chromatography could be used to separate mixtures of lanthanide elements.

(v) In a typical separation of a lanthanide mixture by ion exchange chromatography, the following chromatograph was obtained. Give reasons for the overlapping of these peaks and propose a method to overcome this poor separation.



(50 marks)

(b) Liquid SO_2 and liquid N_2O_4 are two non-aqueous solvents used in research and industry.

(i) Write equations for the self-ionization of the two solvents listed above.

(ii) From these self-ionized species, identify the acidic and basic species.

(iii) Show that NO_2 is not a product when Cu dissolves in liq. N_2O_4.

(iv) Predict the products of the following reactions and write balanced chemical equations.

(I) $SO_2Cl_2 + NH_3 \rightarrow$

(II) $BCl_3 + NH_3 \rightarrow$

(III) $SOCl_2 + Al_2(SO_3)_3 \rightarrow$

(IV) $[NO][ClO_4] + NaNO_3 \rightarrow$

(50 marks)

(05) Answer **all** parts.

(a) Aqueous solutions of transition metal complexes show various colours. The intensities of the absorption bands of such complexes are governed by two selection rules.

(i) Briefly explain why transition metal complexes show various colours in aqueous solutions.

(ii) State the selection rules pertaining to the electronic spectra of transition metal complexes.

(iii) Giving reasons briefly explain the following statements related to the colour intensities of transition metal complexes in aqueous solutions.

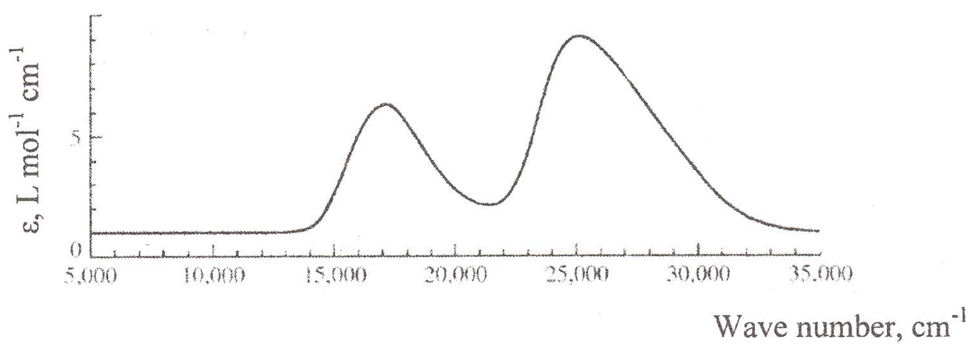
I. $[FeF_6]^{3-}$ is colourless whereas $]CoF_6]^{3-}$ is coloured.

II. The colour of *trans*-$[Co(en)_2F_2]^+$ is less intense than that of *cis*-$[Co(en)_2F_2]^+$. (en –ethylenediamine)

III. $KMnO_4$ is dark purple whereas $[Mn(H_2O)_6]^{2+}$ is pale pink.

(50 marks)

b) The UV – visible spectrum of $[V(H_2O)_6]^{3+}$ is given below.



(i) Calculate the number of possible microstates of the metal ion in the above complex.

(ii) Derive all possible term symbols for the above metal ion.

(iii) Giving reasons, identify the ground and first excited state term symbols from the term symbols you derived in (ii) above.

(iv) Construct the Orgel diagram for the complex.

(v) Label the electronic transitions corresponding to the absorption peaks in the above spectrum, on the Orgel diagram constructed (iv) above.

(50 marks)

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PERIODIC TABLE OF THE ELEMENTS

Atomic Number → 1
Symbol → H
1.008 ← Atomic Mass
Hydrogen ← Name

1 H 1.008 Hydrogen																	2 He 4.002602 Helium
3 Li 6.94 Lithium	4 Be 9.012182 Beryllium											5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.9984032 Fluorine	10 Ne 20.1797 Neon
11 Na 22.98976928 Sodium	12 Mg 24.305 Magnesium											13 Al 26.9815385 Aluminium	14 Si 28.085 Silicon	15 P 30.973761998 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.948 Argon
19 K 39.0983 Potassium	20 Ca 40.078 Calcium	21 Sc 44.955908 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938044 Manganese	26 Fe 55.845 Iron	27 Co 58.933194 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.630 Germanium	33 As 74.921595 Arsenic	34 Se 78.971 Selenium	35 Br 79.904 Bromine	36 Kr 83.798 Krypton
37 Rb 85.4678 Rubidium	38 Sr 87.62 Strontium	39 Y 88.90584 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.90637 Niobium	42 Mo 95.95 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.90550 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.414 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.90447 Iodine	54 Xe 131.293 Xenon
55 Cs 132.90545196 Caesium	56 Ba 137.327 Barium	57 / 71	72 Hf 178.49 Hafnium	73 Ta 180.94788 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.084 Platinum	79 Au 196.966569 Gold	80 Hg 200.592 Mercury	81 Tl 204.38 Thallium	82 Pb 207.2 Lead	83 Bi 208.98040 Bismuth	84 Po 209 Polonium	85 At 210 Astatine	86 Rn 222 Radon
87 Fr 223 Francium	88 Ra 226 Radium	89 / 103	104 Rf 267 Rutherfordium	105 Db 268 Dubnium	106 Sg 269 Seaborgium	107 Bh 270 Bohrium	108 Hs 269 Hassium	109 Mt 278 Meitnerium	110 Ds 281 Darmstadtium	111 Rg 281 Roentgenium	112 Cn 285 Copernicium	113 Uut 286 Ununtrium	114 Fl 289 Flerovium	115 Uup 289 Ununpentium	116 Lv 293 Livermorium	117 Uus 294 Ununseptium	118 Uuo 294 Ununoctium

Lanthanide Series	57 La 138.90547 Lanthanum	58 Ce 140.116 Cerium	59 Pr 140.90766 Praseodymium	60 Nd 144.242 Neodymium	61 Pm 145 Promethium	62 Sm 150.36 Samarium	63 Eu 151.964 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.92535 Terbium	66 Dy 162.500 Dysprosium	67 Ho 164.93033 Holmium	68 Er 167.259 Erbium	69 Tm 168.93422 Thulium	70 Yb 173.054 Ytterbium	71 Lu 174.9668 Lutetium
Actinide Series	89 Ac 227 Actinium	90 Th 232.0377 Thorium	91 Pa 231.03588 Protactinium	92 U 238.02891 Uranium	93 Np 237 Neptunium	94 Pu 244 Plutonium	95 Am 243 Americium	96 Cm 247 Curium	97 Bk 247 Berkelium	98 Cf 251 Californium	99 Es 252 Einsteinium	100 Fm 257 Fermium	101 Md 258 Mendelevium	102 No 259 Nobelium	103 Lr 266 Lawrencium