2022

CHEMISTRY

M.Sc. Second Semester End Examination - 2022

PAPER - CEM-203

(Inorganic Chemistry - II)

Full Marks : 40 ***Time : 2 hours***

The figures in the right-hand margin indicate marks.
Candidates are required to give their answers in their own words as far as practicable.
Illustrate the answers wherever necessary.

Group - A

1. Answer any four questions. **$2\frac{1}{2}\times4=10$**

(a) How metal-dioxygen complexes are prepared?

(b) Why heavier transition metals from more dinitrogen complexes than lighter elements?

(c) Determine the number of IR active vCO stretching mode of the following compounds.

(i) cis-$Mo(CO)_4(PMe_3)_2$ (ii) $Ni(CO)_3(PPh_3)$

(d) Briefly explain the term 'Agostic interaction'.

(e) $W(CO)_6$ reacts with MeLi to give an intermediate which upon treatment with CH_2N_2 gives compound X. Find X.

(f) The molecule $(CO)_5$=M=C(OMe)Ph obeys 18 electron rule. What are the two metals from 3d and 5d which satisfy the condition?

Group - B

Answer any four questions. **5×4=20**

2. (a) Give possible explanation of increased reactivity of dioxygen upon coordination with metal. Give examples of some reactions of metal-dioxygen complexes.
   (b) Draw the structure of Creutz-Taube complex and explain with reasoning of its high intense color. 2+3

3. (a) Write short notes on 'Vaska's complex'.
   (b) Give a scheme in which metal-dinitrogen complexes produce pyrrole and N-aminopyrrole. 3+2

4. Extend the concept of SALC to construct the MOS of cyclic H_3^+ using the character table of C_3 point group.

C_3	E	C_3^1	C_3^2	$\varepsilon=e^{2\pi i/3}$
A_1'	1	1	1	
E'	1 1	ε ε^*	ε^* ε	

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5. Decompose the following direct product in O point group.

   (1) T_1xT_2 (2) ExT_2

O	E	$8C_3$	$3C_2(=C_4^2)$	$6C_4$	$6C_2$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
T_1	3	0	−1	1	−1
T_2	3	0	−1	−1	1

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6. a) Discucss the bonding of metal-alkeni complexes with orbital diagram.

   (b) Comment on the major and minor product of the given reaction with explanation.

   $Cr(CO)_6 + 3PMe_3 \rightarrow$ 3+2

7. (a) Match the [Rh(CO)(Phosphine)$_2$Cl] complexes with their corresponding CO streching frequencies (ν_{co}cm^{-1}). Give explanation for selection.

Phosphine	[ν_{co}cm^{-1}]
(i) $P(C_6H_5)$	1923
(ii) $P(p\text{-}C_6H_4F)_3$	1965
(iii) $P(p\text{-}C_6H_4Me)_3$	1984
(iv) $P(t\text{-}C_4H_9)_3$	2004

(b) Explain why $Fe(CO)_5$ shows only one peak at room temperature while 2 peaks at low temperature in ^{13}C nmr spectroscopy. 3+2

Group - C

Answer any one question. **10×1=10**

8. (a) Determine the symmetry types of the genuine vibrations in furan (C_4H_4O, Point group : C_{2v}) by Cartesian coordinate method. How many of them are Raman active? The character table for C_{2v} point group is given below. 6

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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) Comment on the feasibility of following transitions in C_{3v} point group. [2+2=4]

$A_1 \rightarrow A_2$ and $E \rightarrow E$

The Character Table for C_{3v} is shown below :

C_{3V}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	Z
A_2	1	1	–1	R_z
E	2	–1	0	(x,y)
				(R_x,R_y)

9. (a) Calculate the styx numbers of B_6H_{10} and B_5H_{11}. Determine and draw the most probable structures of these compounds. Classify these compounds as closo, nido, arachano and hypho type. (2+2+1)

(b) Classify the following compounds by structural type

$C_2B_9H_{12}^-$, $[Ru_5(CO)_{16}C]$, $[Co_4(CO)_{12}]$ 3

(c) Complete the following reaction – 2

(i) $[R(H_2O)(NH_3)_5]^{3+}$ + $Aq.N_2H_4$

(ii) B_4H_{10} + $NaBH_4$