First Semester Examination
2020/2021 Academic Session

February 2021

KTT313 – Inorganic Chemistry III

Duration: 2 hours

Please check that this examination paper consists of **SEVEN (7)** pages of printed material before you begin the examination.

Answer **Four (4)** questions only.

SECTION A : Answer all the questions.

SECTION B : Select and answer only **ONE (1)** question.

Answer each question on a new page.

If a candidate answered more than four questions, only the first four questions in order of the arrangement in the received answer scripts will be marked.

SECTION A : ANSWER ALL THE QUESTIONS.

1. (a) For the organometallic complex ion $[(\eta^3\text{-}C_3H_3)(\eta^5\text{-}C_5H_5)M(CO)]^-$

(i) assign a suitable first row transition metal for M based on 18 electron rule. Show your calculation.

(ii) name and draw the complex ion.

(8 marks)

(b) The equation below shows the reaction of dimerization of iridium complex.

$$2[Ir(CO)_2Cp] \xrightarrow{\Delta} [Ir_2(CO)_2(\mu\text{-}CO)Cp_2] + CO$$

The infrared spectrum of the dimer shows two peaks in CO region at 2010 cm^{-1} and 1870 cm^{-1}.

(i) Assign the peaks to the terminal and bridging carbonyl.

(ii) Justify your answer in (i) and draw the dimer to support your justification.

(7 marks)

(c) Application of organometallic compounds as catalyst has revolutionized chemical industries. A well known organometallic catalyst is Wilkinson's catalyst.

(i) State organic reaction gets catalysed by the Wilkinson's catalyst.

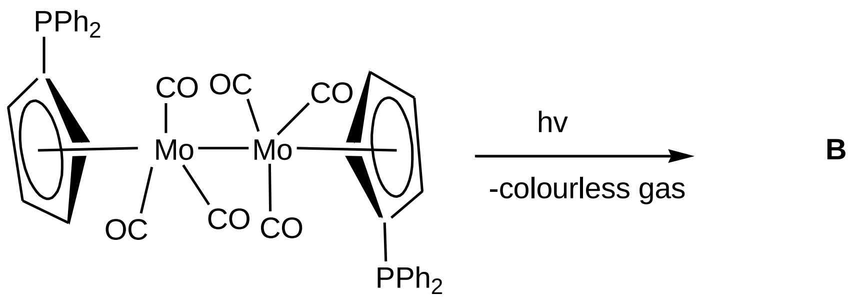
(ii) Taking 1-butene as an example, propose an appropriate cyclic diagram to illustrate the mechanism of catalyst in the reaction.

(10 marks)

2. (a) The IR frequency of NO for $[Mn(CN)_5(NO)]^{3-}$ (ν(NO) = 1725 cm^{-1}) is lower than that in $[Fe(CN)_5(NO)]^{2-}$ (ν(NO) = 1939 cm^{-1}). Explain.

(5 marks)

(b) The molybdenum compound **A** under UV irradiation liberates two moles of a gas giving a new compound **B**.



A

The infrared spectrum of compound **B** shows four C-O stretching bands. The ^{31}P-NMR spectrum of compound **A** gave a singlet at –17.0 ppm while for **B** a singlet was observed at +68.2 ppm which suggests the new coordination mode of Mo-P.

(i) Determine the effective atomic number (EAN) for Mo in compound **A**.

(ii) The ^{31}P-NMR chemical shift for compound **B** is found to be higher than that in compound **A**. Provide a reason.

(iii) Given that compound **B** has a symmetrical structure and obeys 18-electron rule, provide the structure of compound **B**.

(iv) Name the colourless gas liberated from the reaction.

(20 marks)

3. (a) Define the following terms.

(i) Amino acid

(ii) Peptide bond

(iii) Protein

(iv) Metalloprotein

(4 marks)

(b) Aspartate, Asp is the anionic form of aspartic acid that occurs in the body under physiological conditions.

(i) Draw the structure of aspartate.

(ii) Explain the bonding of aspartate to two different metals.

(6 marks)

(c) Describe with diagrams the α-helix and β–pleated sheet of the secondary protein structure.

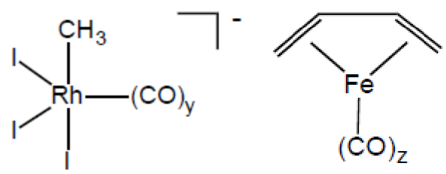
(10 marks)

(d) Describe the conformation changes of deoxymyoglobin upon binding with O_2.

(5 marks)

SECTION B: Select and answer only **ONE (1)** question.

4. (a) For the following complexes **I** and **II**:



I **II**

(i) Given both complexes obey 18-electron rule, determine the values of y and z.

(ii) Propose the organic fragments isolobal with complexes **I** and **II**.

(8 marks)

(b) Discuss the cooperative binding by haemoglobin.

(5 marks)

(c) Discuss why carbon monoxide (CO) binds to haemoglobin and myoglobin with affinities of 25 and 200 times those of O_2, respectively.

(4 marks)

(d) Describe the catalytic cycle of Cativa process as an industrial method for the manufacturing of acetic acid by catalytic carbonylation of methanol.

(8 marks)

5. (a) The molecular formula of the iridium compounds (**A-D**) are shown below:

Compound	**Molecular Formula**
A	$IrCl(CO)(PPh_3)_2$
B	$IrCl(CO)(PMe_3)_2$
C	$IrMe(CO)(PMe_3)_2$
D	$IrPh(CO)(PMe_3)_2$

(i) Predict the change in the ν(CO) frequencies of compounds **A-D** in going to the oxidative addition products.

(ii) Explain your answer in (i).

(8 marks)

(b) The ultimate molecular basis of chemotherapeutic action of cisplatin is the formation of a complex between Pt(II) and DNA. Explain the changes that takes place to the cisplatin upon the complexation.

(4 marks)

(c) Tc is used as an imaging agent in a hospital technique known as single-photon emission computed tomography (SPECT). Briefly describe the preparation of ^{99m}Tc from ^{98}Mo for the application in the diagnostic medicine.

(4 marks)

(d) Reaction I : $[Cr(CO)_6] + PH_3 \longrightarrow [Cr(CO)_5(PH_3)] + CO$

Reaction II : $[Mo(CO)_6] + Cl^- \longrightarrow [Mo(CO)_5Cl] + CO$

(i) Choose the reaction that likely to proceed via associative mechanism.

(ii) Explain your answer by elaborating the factors that favour the mechanism.

(5 marks)

(e) Suggest a possibility of the complex with empirical formula $[Cr(CO)_3(C_6H_5)_2]$ that will attain the 18-electron rule.

(4 marks)

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