
UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

November 2008

KTT 313 – Inorganic Chemistry III
[Kimia Takorganik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **EIGHT** printed pages before you begin the examination.

Instructions:

Answer **FIVE** (5) questions.

The **FIRST QUESTION** is a compulsory question. Then answer **FOUR** (4) more questions by selecting **TWO** (2) questions from Section A and **TWO** (2) questions from Section B.

You may answer the questions either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

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1. (a) The cyclopentadienyl ligand forms η^1 , η^2 and η^5 complexes with main group elements. Give an example of each type of complex and draw their structures.

(10 marks)

- (b) $V(CO)_6$ and $[V(CO)_6]^-$ are octahedral complexes. However, the length of the V-C and C-O bonds of $V(CO)_6$ are different from that of $[V(CO)_6]^-$. Explain.

(10 marks)

SECTION A

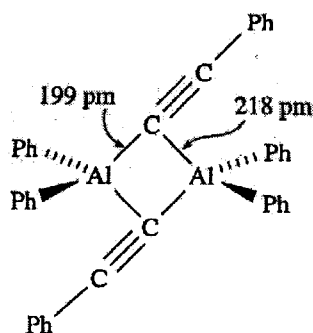
2. (a) The hydrolysis of the Si-Cl bond in $(CH_3)_3SiCl$ leading to the formation of siloxane, $(CH_3)_3SiOSi(CH_3)_3$ involves a two step reaction. Write an equation for each step of the reaction.

(6 marks)

- (b) Describe the tendency toward association through methyl bridges for the trimethyl compounds of boron, aluminium and gallium. Give reasons for the observed differences.

(7 marks)

- (c) The diagram below shows the structure of the alkynyl-bridged dimer of the organoaluminium compound, $Ph_2AlC\equiv CPh_2$. Explain why the alkynyl bridges tilt from the vertical position towards one of the aluminium centres.



(7 marks)

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3. Zinc plays an important role in enzymatic reactions in biological systems. Describe the mechanism of the enzymatic reaction of the metalloenzymes carbonic anhydrase II and carboxypeptidase A.

(20 marks)

4. Draw a schematic representation of an Fe^{3+} binding site in transferrin. Discuss the features in the structure that make transferrin an efficient transporter of iron in mammals. How does the uptake and transport of iron in aerobic microorganism differ from that in mammals?

(20 marks)

SECTION B

5. Rationalise the following observations.

- (a) On going from $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1} .

(6 marks)

- (b) During the photolysis of $\text{Mo}(\text{CO})_5(\text{THF})$ with PPh_3 , a signal in the ^{31}P NMR spectrum at $\delta -6$ disappears and is replaced by one at $\delta +37$.

(6 marks)

- (c) $\text{Fe}(\text{CO})_5$ loses CO very slowly, but the addition of aqueous acid greatly accelerates the loss of a CO ligand.

(8 marks)

6. (a) Explain why $\text{Os}_6(\text{CO})_{18}$ adopts a bicapped tetrahedral structure rather than an octahedral cage.

(6 marks)

- (b) Suggest and explain the change in cluster structure in the following reaction:



(6 marks)

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- (c) Provide an example and explain the mechanism for a ligand transformation at a metal centre of an organometallic compound via alkyl migration.

(8 marks)

7. (a) Reaction of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with $\text{Fe}(\text{CO})_5$ in tetrahydrofuran produces CO and a salt $\text{Na}_2[\text{Z}]$. The sodium ions can be easily replaced by tetraethylamine ions, $2[\text{Et}_4\text{N}]^+$. Analysis of the Raman spectrum of $[\text{Et}_4\text{N}]_2[\text{Z}]$ reveals the presence of an absorption at 160 cm^{-1} assignable to an unbridged Fe-Fe bond. Suggest an identity for $[\text{Z}]^{2-}$ and sketch its structure.

(8 marks)

- (b) Provide and sketch the structure for the main product in each of the following reactions:

- (i) $\text{Re}_2(\text{CO})_{10}$ with Na/Hg,
- (ii) $\text{Na}[\text{Mn}(\text{CO})_5]$ with H_3PO_4 ,
- (iii) $\text{Fe}(\text{CO})_5$ with $2\text{C}_2\text{H}_4$, and
- (iv) $(\eta^5\text{-Cp})_2\text{Fe}$ with toluene in the presence of Al and AlCl_3 .

(12 marks)

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TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan.

SOALAN PERTAMA adalah wajib. Kemudian jawab **EMPAT** (4) soalan lagi dengan memilih **DUA** (2) soalan dari Bahagian A dan **DUA** (2) soalan dari Bahagian B.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

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1. (a) Ligan siklopentadienil membentuk kompleks η^1 , η^2 dan η^5 dengan unsur kumpulan utama. Beri satu contoh bagi setiap jenis kompleks tersebut dan lukiskan strukturnya.

(10 markah)

- (b) $V(CO)_6$ dan $[V(CO)_6]^-$ adalah kompleks oktahedral. Namun, jarak ikatan V-C dan C-O bagi $V(CO)_6$ adalah berbeza berbanding dengan jarak ikatan V-C dan C-O bagi $[V(CO)_6]^-$. Jelaskan.

(10 markah)

BAHAGIAN A

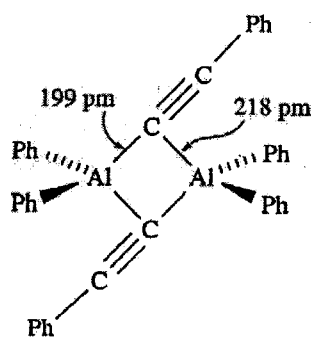
2. (a) Hidrolisis ikatan Si-Cl di dalam $(CH_3)_3SiCl$ yang membawa kepada pembentukan siloksan, $(CH_3)_3SiOSi(CH_3)_3$ melibatkan tindak balas dua langkah. Tuliskan persamaan bagi setiap langkah tindak balas tersebut.

(6 markah)

- (b) Huraikan kecenderungan terhadap pembentukan titian melalui metil bagi sebatian trimetil boron, aluminium dan galium. Beri penjelasan untuk perbezaan yang diperhatikan.

(7 markah)

- (c) Gambarajah di bawah menunjukkan struktur dimer bertitian alkinil bagi sebatian organoaluminium, $Ph_2AlC\equiv CPh_2$. Jelaskan mengapa titian alkinil condong dari posisi tegak terhadap salah satu pusat aluminium.



(7 markah)

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3. Zink memainkan peranan penting dalam tindak balas enzim sistem biologi. Huraikan mekanisme tindak balas enzim bagi metaloenzim karbonik anhidrasa II dan karboksipeptidasa A.

(20 markah)

4. Lukiskan perwakilan skema bagi suatu kawasan pengikatan Fe^{3+} di dalam transferrin. Bincangkan ciri-ciri di dalam struktur tersebut yang menyebabkan transferrin bertindak sebagai pengangkut ferum berkesan di dalam mamalia. Bagaimanakah proses pengambilan dan pengangkutan ferum di dalam mikroorganisma aerobik berbeza daripada proses tersebut di dalam mamalia?

(20 markah)

BAHAGIAN B

5. Terangkan pemerhatian berikut:

- (a) Perubahan daripada $\text{Fe}(\text{CO})_5$ kepada $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ memperlihatkan serapan dalam spektrum IR pada 2025 dan 2000 cm^{-1} ditukarganti dengan jalur pada 1944, 1886 dan 1881 cm^{-1} .

(6 markah)

- (b) Semasa fotolisis $\text{Mo}(\text{CO})_5(\text{THF})$ dengan PPh_3 , satu isyarat dalam spektrum ^{31}P NMR pada $\delta -6$ hilang dan diganti dengan satu isyarat pada $\delta +37$.

(6 markah)

- (c) $\text{Fe}(\text{CO})_5$ melepaskan CO dengan amat perlahan, tetapi kemasukan asid akues menyebabkan pelepasan satu ligan CO berlaku dengan ketara.

(8 markah)

6. (a) Jelaskan kenapa $\text{Os}_6(\text{CO})_{18}$ membentuk struktur tetrahedral bikap dan bukannya sangkar oktahedral.

(6 markah)

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- (b) Cadang dan jelaskan perubahan struktur kluster yang berlaku dalam tindak balas berikut:



(6 markah)

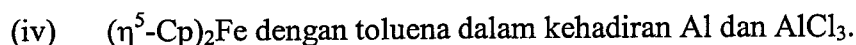
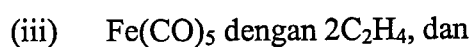
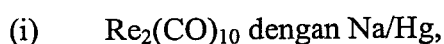
- (c) Berikan satu contoh dan jelaskan mekanisme transformasi ligan pada suatu logam pusat sebatian organologam yang berlaku melalui migrasi alkil.

(8 markah)

7. (a) Tindak balas $\text{Na}_2[\text{Fe}(\text{CO})_4]$ dengan $\text{Fe}(\text{CO})_5$ dalam tetrahidrofur menghasilkan CO dan satu garam $\text{Na}_2[\text{Z}]$. Ion natrium pada garam itu boleh dengan mudahnya ditukarganti dengan ion tetraetilamina $2[\text{Et}_4\text{N}]^+$. Analisis spektrum Raman $[\text{Et}_4\text{N}]_2[\text{Z}]$ menunjukkan kehadiran satu serapan pada 160 cm^{-1} yang boleh diperuntukkan kepada satu ikatan Fe-Fe tanpa jambatan. Cadangkan identiti $[\text{Z}]^{2-}$ dan lakarkan strukturnya.

(8 markah)

- (b) Beri dan lakarkan struktur bagi produk utama dalam setiap tindak balas berikut:



(12 markah)

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