UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2007/08

October/November 2007

KTT 313 – Inorganic Chemistry III

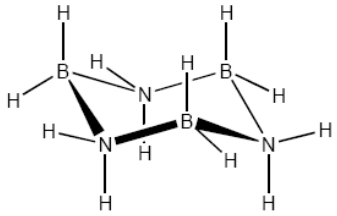
Time: 3 hours

Please make sure this paper consists of **TEN** printed pages before answering the questions.

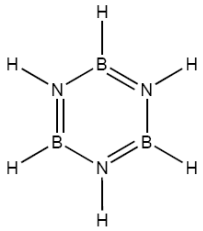
Answer **FIVE** questions.
The **FIRST QUESTION** is a compulsory question.
Then answer FOUR more questions by selecting TWO questions from **Section A** and TWO questions from **Section B.**

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

1. (a) Cyclotriborazane (an analogue of cyclohexane) and borazine (an analogue of benzene) have the following structures:



Cyclotriborazane



Borazine

Discuss the uses of cyclotriborazane as a hydrogen storage chemical based on the concept of intervonvertability between cyclotriborazane and borazine.

(10 marks)

(b) The substitution reaction of Cl^- with H_2O in $[PtCl\mathbf{L}(PEt_3)_2]$ was studied at 25 ^oC and the following data obtained:

L	$\mathbf{k_{obs}}$ **(M^{-1} s^{-1})**
2,6-dimethylpyridine	1.0×10^{-6}
2-methylpyridine	2.0×10^{-4}
pyridine	8.0×10^{-2}

Explain why the rate of the reaction ($\mathbf{k_{obs}}$) increased when **L** was changed from 2,6-dimethylpyridine to 2-methylpyridine and subsequently to pyridine.

(10 marks)

SECTION A

2. (a) $[Si_3O_9]^{6-}$, $[P_3O_9]^{3-}$ and $[S_3O_9]$ are isoelectronic and isostructural to one another. Draw the structure of the three species and account for their isoelectronic nature.

(6 marks)

(b) The dimeric complex, $Cr_2(CH_3COO)_4.2H_2O]$ is diamagnetic. The Cr-Cr bond length in the dimeric complex is 2.362 Å which is shorter than the Cr-Cr distance in the chromium metal which is 2.498 Å. Account for these observations.

(6 marks)

(c) State whether the cyclic compound $B_3N_3H_6$ is aromatic or non-aromatic. Give the physical and chemical properties to support your answer.

(8 marks)

3. (a) Draw the molecular orbital energy level diagram for $[B_6H_6]^{2-}$.

(3 marks)

(b) Draw the structure of the metalloborane product obtained from the following reaction:

$$[B_{11}H_{13}]^{2-} + Al_2(CH_3)_6 \xrightarrow[\Delta]{}$$

(3 marks)

(c) Classify B_4H_{10} according to Wade's rule as one of the following:
Closo, nido or *arachno*

(6 marks)

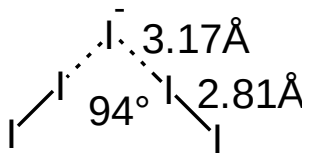
(d) Predict the products of the reaction between B_4H_{10} and NH_3. Give reasons for your answer. Write a complete and balanced equation for the reaction.

(8 marks)

4. (a) Explain why fluorine has one oxidation state (-1) but chlorine has multiple oxidation states (-1, 1, 3, 4, 5, 6 and 7).

(6 marks)

(b) Suggest explanatios for the difference in the I-I bond lengths for $[I_5]^-$ for which the structure is shown below:



(6 marks)

(c) Xenon fluoride can act as either an F^- acceptor or donor.
Predict the products of the following reactions:

(i) $XeF_4 + NaF \longrightarrow$

(ii) $XeF_2 + PtF_5 \longrightarrow$

Draw the structure of the products and state whether the xenon fluoride is acting as an F^- acceptor or donor.

(8 marks)

SECTION B

5. (a) What is the major difference between an $\mathbf{I_a}$ mechanism and an **A** mechanism?

(3 marks)

(b) Based on the stereochemical structures of the reactant and product, explain that it may be possible to predict the mechanism of ligand substitution reaction on a square planar complex: whether it occur via an associative mechanism (**A**) or an interchange mechanism ($\mathbf{I_a}$) or both.

(7 marks)

(c) Based on the following reaction,

$$[PtCl(py)_3]^{1+} + S=C(CH_3)_2 \longrightarrow [complex]^{m+} + Cl^-$$

draw the structure of the complex and explain why such a complex might formed when

(ii) **py** at the *trans* position with respect to the **Cl**$^-$ is replaced with **Cl**$^-$,
(iii) a **py** at the *cis* position with respect to the **Cl**$^-$ is replaced with **Cl**$^-$, and
(iv) **S=C(CH$_3$)$_2$** is replaced with <u>two</u> **CN**$^-$.

(10 marks)

6. (a) Explain why the rate of the redox reaction between $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ is very slow, $k = 10^{-9}$ M^{-1} s^{-1}.

(10 marks)

(b) The products obtained when the inert complex $[Co(NH_3)_6]^{3+}$ was placed in an aqueous solution containing the labile complex $[Fe(CN)_5(H_2O)]^{3-}$ were Co^{2+} (aq) and $[Fe(CN)_5(H_2O)]^{2-}$. Explain whether the redox reaction between $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_5(H_2O)]^{3-}$ occurred via an outer-sphere mechanism or an inner-sphere mechanism.

(10 marks)

7. The redox reaction between $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ was studied and the following data obtained:

(i) It was found that the value of the activation energy and entropy for several redox reactions containing aqueous ions to be approximately 40 kJ mol^{-1} and -2.5 eu, respectively.

(ii) The rate of reaction of $Fe^{II}(H_2O)_6$ / $Fe^{III}(H_2O)_6$ decreased by a factor of 2 when H_2O is replaced with D_2O (solvent).

Suggest a mechanism for the redox reaction (between $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$) and explain how both data, (i) and (ii), support your suggestion.

(20 marks)

UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Pertama
Sidang Akademik 2007/08

Oktober/November 2007

KTT 313 – Kimia Takorganik III

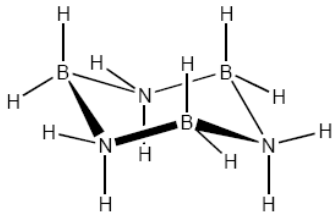
Masa: 3 jam

Sila pastikan bahawa kertas peperiksaan ini mengadungi **SEPULUH** muka surat yang bercetak sebelum anda memulakan peperiksaan ini.

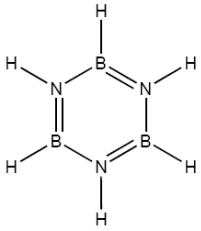
Jawab **LIMA** soalan.
SOALAN PERTAMA adalah WAJIB.
Kemudian jawab EMPAT soalan lagi dengan memilih DUA soalan dari **Bahagian A** dan DUA soalan dari **Bahagian B.**

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan yang diterima akan diperiksa.

1. (a) Siklotriborazana (analog sebatian sikloheksana) dan borazina (analog sebatian benzene) mempunyai struktur berikut:



Siklotriborazana



Borazina

Bincangkan kegunaan siklotriborazana sebagai bahan kimia penstoran hidrogen berdasarkan pada konsep saling tertukaran antara siklotriborazana dan borazina.

(10 markah)

(b) Tindak balas penukargantian Cl^- dengan H_2O dalam $[PtCl\mathbf{L}(PEt_3)_2]$ telah dikaji pada 25 ^oC dan maklumat berikut diperolehi.

L	$\mathbf{k_{obs}}$ **(M^{-1} s^{-1})**
2,6-dimetilpiridina	1.0×10^{-6}
2-metilpiridina	2.0×10^{-4}
piridina	8.0×10^{-2}

Jelaskan kenapa kadar tindak balas tersebut ($\mathbf{k_{obs}}$) meningkat apabila **L** ditukar daripada 2,6-dimetilpiridina ke 2-metilpiridina dan seterusnya ke piridina.

(10 markah)

2. (a) $[Si_3O_9]^{6-}$, $[P_3O_9]^{3-}$ dan $[S_3O_9]$ bersifat isoelektronik dan isostruktur. Lukiskan struktur bagi ketiga-tiga spesies dan beri penjelasan terhadap ciri isoelektronik bagi ketiga-tia spesies tersebut.

(6 markah)

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(b) Kompleks dimer, $[Cr_2(CH_3COO)_4.2H_2O]$ bersifat diamagnetik. Panjang ikatan Cr-Cr di dalam kompleks dimmer tersebut ialah 2.362 Å dan nilai ini kurang daripada panjang ikatan Cr-Cr di dalam logam kromium iaitu 2.498 Å. Jelaskan pemerhatian tersebut.

(6 markah)

(c) Nyatakan samada sebatian siklik $B_3N_3H_6$ merupakan aromatik atau bukan-aromatik. Beri sifat fizik atau sifat kimia untuk menyokong jawapan anda.

(8 markah)

3. (a) Lukiskan gambarajah paras tenaga orbital molekul bagi $[B_6H_6]^{2-}$.

(3 markah)

(b) Lukiskan struktur bagi hasil metaloborana daripada tindak balas berikut:

$$2[B_{11}H_{13}]^{2-} + Al_2(CH_3)_6 \xrightarrow[\Delta]{}$$

(3 markah)

(c) Klasifikasikan B_4H_{10} mengikut peraturan Wade sebagai satu daripada jenis yang berikut:
Kloso, nido atau *arakno*

(6 markah)

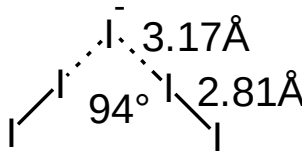
(d) Ramalkan hasil bagi tindak balas antara B_4H_{10} dan NH_3. Beri penjelasan untuk jawapan anda. Tulis persamaan yang lengkap dan seimbang bagi tindak balas tersebut.

(8 markah)

4. (a) Jelaskan mengapa fluorin mempunyai hanya satu keadaan pengoksidaan (-1) tetapi klorin mempunyai pelbagai keadaan pengoksidaan (-1, 1, 3, 4, 5, 6 dan 7).

(6 markah)

(b) Cadangkan penjelasan bagi perbezaan panjang ikatan I-I bagi $[I_5]^-$ seperti struktur di bawah:



(6 markah)

(c) Xenon fluorida boleh bertindak sebagai penerima atau penderma F^-. Ramalkan kesemua hasil tindak balas berikut:

(i) $XeF_4 + NaF \longrightarrow$

(ii) $XeF_2 + PtF_5 \longrightarrow$

Lukiskan sturktur hasil tindak balas di atas dan nyatakan samada xenon fluorida tersebut bertindak sebagai penerima atau penderma F^-.

(8 markah)

BAHAGIAN B

5. (a) Apakah perbezaan yang ketara antara mekanisme $\mathbf{I_a}$ dan mekanisme **A**?

(3 markah)

(b) Berdasarkan stereokimia struktur reaktan dan produk, terangkan bahawa mekanisme tindak balas penukargantian ligan pada sesuatu kompleks persegi empat sama mungkin dapat ditentukan: sama ada ianya berlaku melalui mekanisme (**A**) atau mekanisme ($\mathbf{I_a}$) atau kedua-duanya.

(7 markah)

(c) Berdasarkan tindak balas berikut,

$$[PtCl(py)_3]^{1+} + S{=}C(CH_3)_2 \longrightarrow [kompleks]^{m+} + Cl^-$$

Lukiskan struktur kompleks dan terangkan kenapa kompleks seumpama itu mungkin terbentuk apabila

(v) **py** yang berkedudukan *trans* kepada **Cl**$^-$ ditukarganti dengan **Cl**$^-$,
(vi) satu **py** yang berkedudukan *cis* kepada **Cl**$^-$ ditukarganti dengan **Cl**$^-$, dan
(vii) **S=C(CH$_3$)$_2$** ditukarganti dengan <u>dua</u> **CN**$^-$.

(10 markah)

6. (a) Jelaskan mengapa kadar tindak balas redoks antara $[Co(NH_3)_6]^{2+}$ dan $[Co(NH_3)_6]^{3+}$ adalah amat perlahan, $k = 10^{-9}$ M^{-1} s^{-1}.

(10 markah)

(b) Hasil yang diperolehi apabila kompleks lengai $[Co(NH_3)_6]^{3+}$ dimasukkan ke dalam larutan akueus yang mengandungi kompleks labil $[Fe(CN)_5(H_2O)]^{3-}$ ialah Co^{2+} (ak) dan $[Fe(CN)_5(H_2O)]^{2-}$. Jelaskan sama ada tindak balas redok antara $[Co(NH_3)_6]^{3+}$ dan $[Fe(CN)_5(H_2O)]^{3-}$ telah berlaku melalui mekanisme sfera-dalam atau mekanisme sfera-luar.

(10 markah)

7. Tindak balas redoks antara $[Fe(H_2O)_6]^{2+}$ dan $[Fe(H_2O)_6]^{3+}$ telah dikaji dan maklumat berikut diperolehi:

(i) Didapati nilai tenaga pengaktifan dan entropi bagi beberapa tindak balas redoks yang mengandungi ion akua adalah ≈ 40 kJ mol^{-1} dan ≈ -2.5 eu.

(ii) Kadarcepat tindak balas $Fe^{II}(H_2O)_6$ / $Fe^{III}(H_2O)_6$ berkurang dengan faktor 2 apabila H_2O digantikan dengan D_2O (pelarut).

Cadangkan satu mekanisme bagi tindak balas redoks tersebut (antara $[Fe(H_2O)_6]^{2+}$ dan $[Fe(H_2O)_6]^{3+}$) dan terangkan bagaimana kedua-dua maklumat, (i) dan (ii), menyokong cadangan anda.

(20 markah)

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