
UNIVERSITI SAINS MALAYSIA

Kursus Semasa Cuti Panjang
Sidang Akademik 2007/2008

June 2008

KTT 212 – Inorganic Chemistry II
[Kimia Takorganik II]

Duration : 3 hours
[Masa : 3 jam]

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

Instructions:

Answer **FIVE** (5) questions.

SECTION A, is **COMPULSORY** to answer all. **SECTION B**, select and answer **TWO** (2) questions only.

Begin the answers to each question on a new page.

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.

Appendix : Tanabe – Sugano diagram

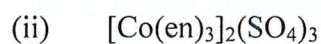
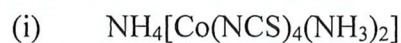
...2/-

SECTION A

1. (a) Write down the IUPAC name for each of the following complexes and indicate the oxidation state of the metal and its electronic configuration.
- (i) $\text{K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$
 - (ii) $\text{CrCl}_3(\text{py})_3$
 - (iii) $\text{K}_4[\text{Mn}(\text{CN})_6]$
- (6 marks)
- (b) The hexaaquamanganese(II) ion contains five unpaired electrons, while the hexacyanomanganese(II) ion contains only one unpaired electron. Explain this, using crystal field theory.
- (5 marks)
- (c) Outline how you would apply crystal field theory to explain why the five d orbitals in an octahedral complex are not degenerate.
- (5 marks)
- (d) The observed magnetic moment for $\text{K}_3[\text{TiF}_6]$ is $1.70 \mu_{\text{B}}$. Calculate μ (spin-only) for this complex.
- (4 marks)
2. (a) Explain briefly each of the following:
- (i) High spin complex.
 - (ii) Binuclear complex.
 - (iii) Five coordinate complex.
 - (iv) Metal chelate.
- (8 marks)

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(b) Describe the formation of the following complexes by based on Werner Theory.



(6 marks)

(c) The stepwise formation constants (K) for the reaction between Ni^{2+} and ethylenediamine in aqueous solution are given as follows:

$$\log K_1 = 7.5 \quad \log K_2 = 6.4 \quad \log K_3 = 4.4$$

(i) Write the equation for β_n in each step (where $n = 1, 2$ and 3).

(ii) Calculate the value of $\log \beta$.

(6 marks)

3. Consider the following substitution reaction between tungsten hexacarbonyl and triphenylphosphine:



(a) Give all the products.

(4 marks)

(b) Draw and name all the possible isomers of the tungsten complex formed in the reaction above.

(6 marks)

(c) Give two spectroscopic techniques and describe how these methods can be used to differentiate between these isomers.

(10 marks)

5. (a) The enthalpies of hydration, $-\Delta H$, at 25 °C for transition metal ions which form hexaaqua species are given as follows:

Ion	$-\Delta H$ (kJ mol ⁻¹)
Ca ²⁺	2467
V ²⁺	2776
Cr ²⁺	2794
Mn ²⁺	2735
Fe ²⁺	2884
Co ²⁺	2915
Ni ²⁺	2994
Cu ²⁺	2998
Zn ²⁺	2932

- (i) Plot the enthalpies of hydration, $-\Delta H$ (y axis) versus the number of d electrons (x axis).

- (ii) Explain the pattern of graph as obtained from (i).

(10 marks)

- (b) Draw the structure for each of the following compounds:

- (i) 1-chloro-3-bromoamminepyridineplatinum(II)
- (ii) anion bis(oxalato)cobalt(III)-di- μ -hydroxobis(oxalato)cobalt(III)
- (iii) bis(glicinato)cobalt(III)-di- μ -hydroxobis(glicinato)cobalt(III)
- (glicinato = NH₂CH₂CO₂⁻)

(6 marks)

- (c) How to differentiate the ionization isomer from the linkage isomer?

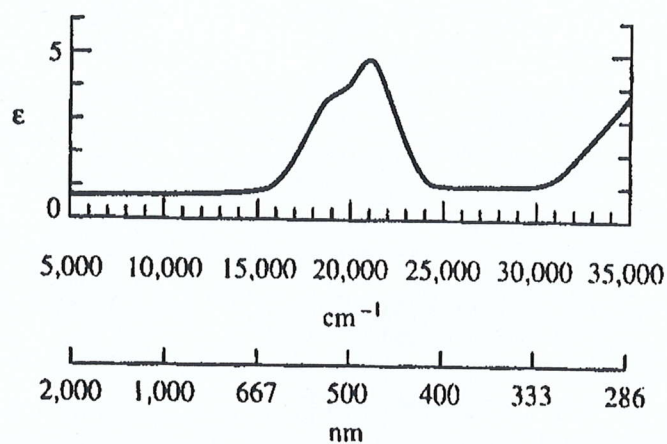
(4 marks)

-6-

6. (a) Explain why octahedral complexes of d^0 , d^1 , d^2 are considered labile while octahedral complexes of d^3 and d^6 (low spin) are inert.

(8 marks)

- (b) The UV spectrum for $[\text{Ti}(\text{NCS})_6]^{3-}$ is as follows:



- (i) Using the Tanabe-Sugano Diagram, determine the Δ_o value and the possible transitions for the complex.
- (ii) Explain the presence of splitting in the above spectrum.
- (iii) Describe the Tanabe-Sugano Diagram and briefly explain its application in determining the characteristics of electronic spectrum for transition metal complexes.

(12 marks)

7. (a) Define the following terms:

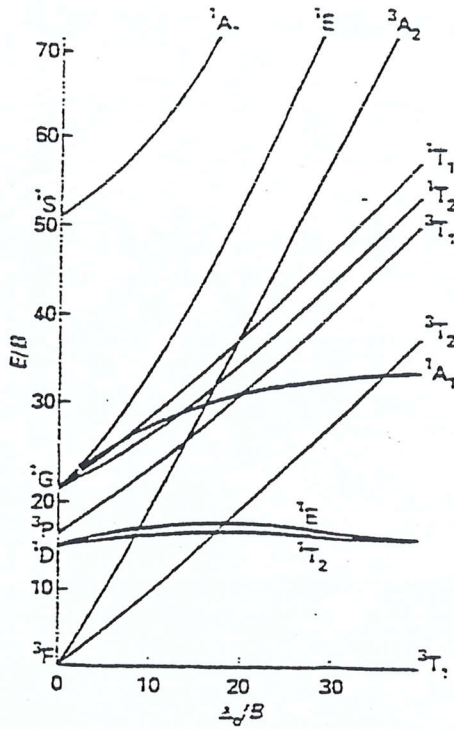
- (i) Coordination complex
- (ii) Coordination numbers
- (iii) Pauling electroneutrality principle

(7 marks)

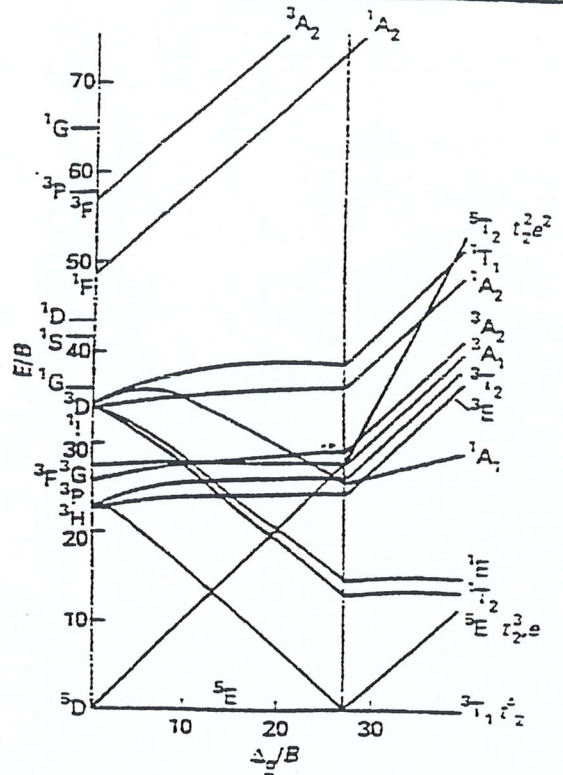
APPENDIX

TANABE-SUGANO DIAGRAM

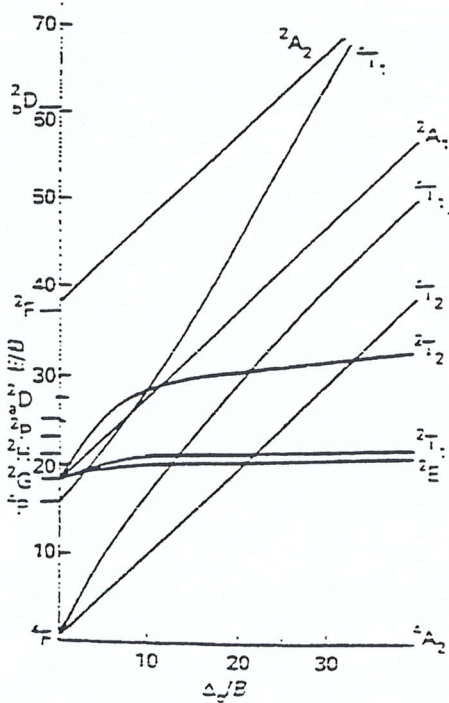
d^2 with $C = 4.42B$



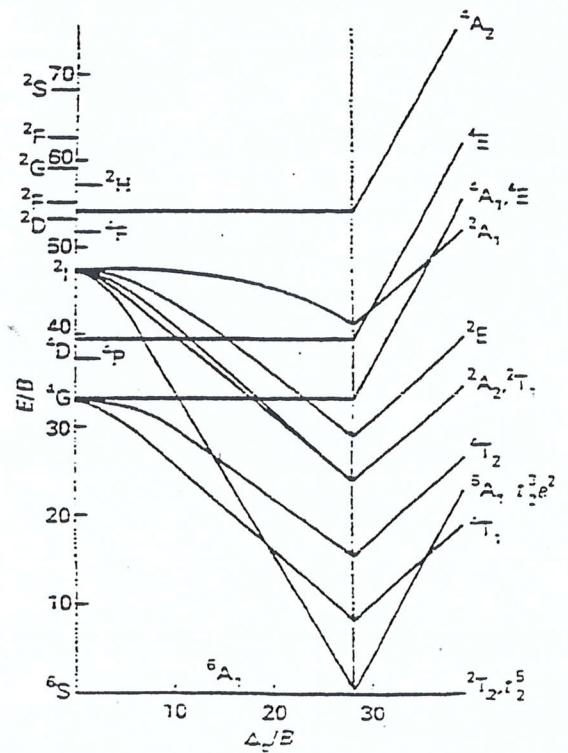
d^4 with $C = 4.61B$



d^3 with $C = 4.5B$



d^5 with $C = 4.4775B$



TERJEMAHAN

Arahan:

Jawab **LIMA (5)** soalan.

BAHAGIAN A, diwajibkan jawab **SEMUA** soalan. **BAHAGIAN B**, pilih dan jawab **DUA (2)** soalan sahaja.

Anda perlu mulakan setiap soalan pada muka surat baru.

Anda boleh menjawab 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.

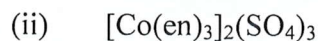
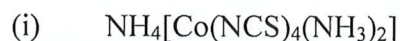
Lampiran : Gambarajah Tanabe - Sugano

BAHAGIAN A

1. (a) Tuliskan nama IUPAC untuk kompleks kompleks berikut dan nyatakan nombor pengoksidaan logam serta konfigurasi elektron logamnya.
- (i) $\text{K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$
- (ii) $\text{CrCl}_3(\text{py})_3$
- (iii) $\text{K}_4[\text{Mn}(\text{CN})_6]$ (6 markah)
- (b) Ion heksaakua-mangan(II) mengandungi lima elektron tak berpasangan manakala ion heksasiano- mengandungi hanya satu elektron tak berpasangan. Jelaskan hal ini berdasarkan teori medan hablur. (5 markah)
- (c) Gariskan bagaimana anda menggunakan teori medan hablur untuk menjelaskan kenapa kelima-lima orbital d dalam kompleks octahedral adalah tidak degenerat. (5 markah)
- (d) Momen magnet bagi $\text{K}_3[\text{TiF}_6]$ di ukur sebagai $1.70 \mu_{\text{B}}$. Kirakan μ (spin-sahaja) untuk kompleks ini. (4 markah)
2. (a) Huraikan dengan ringkas tiap-tiap perkara berikut:
- (i) Kompleks spin tinggi.
- (ii) Kompleks binuklear.
- (iii) Kompleks koordinat lima.
- (iv) Kelat logam. (8 markah)

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(b) Huraikan pembentukan bagi kompleks berikut dengan menggunakan teori Werner.



(6 markah)

(c) Pemalar pembentukan seselangkah (K) bagi tindak balas di antara Ni^{2+} dengan etilenadamina di dalam larutan akuas adalah seperti berikut:

$$\log K_1 = 7.5 \quad \log K_2 = 6.4 \quad \log K_3 = 4.4$$

(i) Tuliskan persamaan bagi β_n dalam setiap langkah (dengan $n = 1, 2$ and 3).

(ii) Hitungkan nilai bagi $\log \beta$.

(6 markah)

3. Pertimbangkan tindak balas penukargantian antara tungsten heksakarbonil dan trifenilfosfina berikut:



(a) Berikan semua hasil yang diperolehi daripada tindak balas tersebut.

(4 markah)

(b) Lakar dan berikan nama bagi semua isomer yang terdapat pada hasil tindak balas tersebut.

(6 markah)

(c) Nyatakan dua kaedah spektroskopi yang dapat digunakan untuk membezakan isomer yang terhasil. Berikan penjelasan bagaimana kedua kaedah tersebut dapat membezakan isomer yang terhasil.

(10 markah)

BAHAGIAN B

4. (a) Manakah di antara kompleks-kompleks berikut anda jangkakan untuk mengalami pengherotan Jahn-Teller:

- (i) $[\text{CrI}_6]^{4-}$
- (ii) $[\text{Cr}(\text{CN})_6]^{4-}$
- (iii) $[\text{CoF}_6]^{3-}$

Jelaskan pemilihan anda

(5 markah)

- (b) Secara ringkas, jelaskan prinsip yang di gunakan dalam pembentukan teori orbital molekul.

(7 markah)

- (c) Dalam setiap pasangan kompleks berikut, pilih satu yang mempunyai Δ_{oct} yang lebih besar dari pasangannya. Jelaskan pemilihan anda.

- (i) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- (ii) $[\text{CrF}_6]^{3-}$ and $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- (iii) $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$
- (iv) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$

(8 markah)

5. (a) Tenaga entalpi penghidratan, $-\Delta H$, pada 25 °C bagi ion logam peralihan yang membentuk spesies hexaakua diberikan sebagai berikut:

<u>Ion</u>	<u>$-\Delta H$ (kJ mol⁻¹)</u>
Ca ²⁺	2467
V ²⁺	2776
Cr ²⁺	2794
Mn ²⁺	2735
Fe ²⁺	2884
Co ²⁺	2915
Ni ²⁺	2994
Cu ²⁺	2998
Zn ²⁺	2932

- (i) Plotkan entalpi penghidratan, $-\Delta H$ (paksi y) melawan bilangan elektron d (paksi x).

- (ii) Terangkan corak graf yang diperoleh dari (i).

(10 markah)

- (b) Lakarkan struktur bagi setiap sebatian berikut:

- (i) 1-kloro-3-bromoamminapiridinaplatinum(II)

- (ii) anion bis(oksalato)kobalt(III)-di- μ -hidroksobis(oksalato)kobalt(III)

- (iii) bis(glisinato)kobalt(III)-di- μ -hidroksobis(glisinato)kobalt(III)

(glisinato = NH₂CH₂CO₂⁻)

(6 markah)

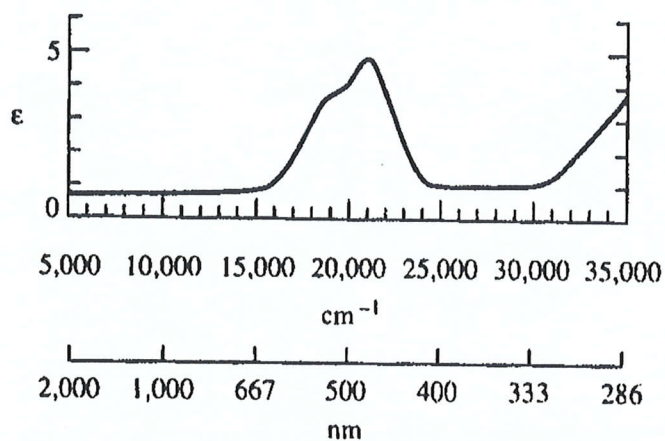
- (c) Bagaimana membezakan isomer pengionan daripada isomer linkej?

(4 markah)

6. (a) Berikan penjelasan kenapa kompleks oktahedral d^0 , d^1 , d^2 dianggap sebagai kompleks labil dan kompleks oktahedral d^3 dan d^6 (spin rendah) dianggap sebagai kompleks lengai.

(8 markah)

- (b) Spektrum kompleks $[\text{Ti}(\text{NCS})_6]^{3-}$ adalah seperti berikut:



- (i) Berpandukan Gambarajah Tanabe-Sugano, berikan nilai Δ_o dan jenis peralihan yang berkemungkinan bagi kompleks tersebut.
- (ii) Berikan penjelasan ringkas tentang kewujudan spektrum yang menunjukkan sifat pemecahan (*splitting*).
- (iii) Berikan penjelasan tentang Gambarajah Tanabe-Sugano dan penggunaannya dalam pencerian spektrum elektronik kompleks logam peralihan.

(12 markah)

7. (a) Berikan definasi istilah istilah berikut:

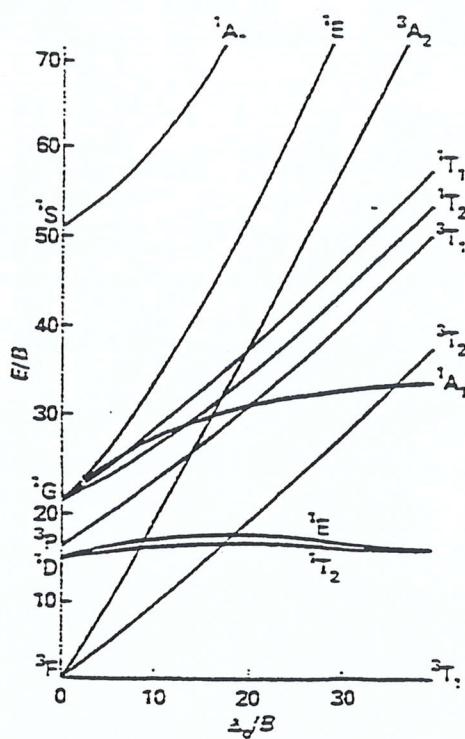
- (i) Kompleks koordinatan
- (ii) Nombor koordinatan
- (iii) Prinsip keelektroneutralan Pauli

(7 markah)

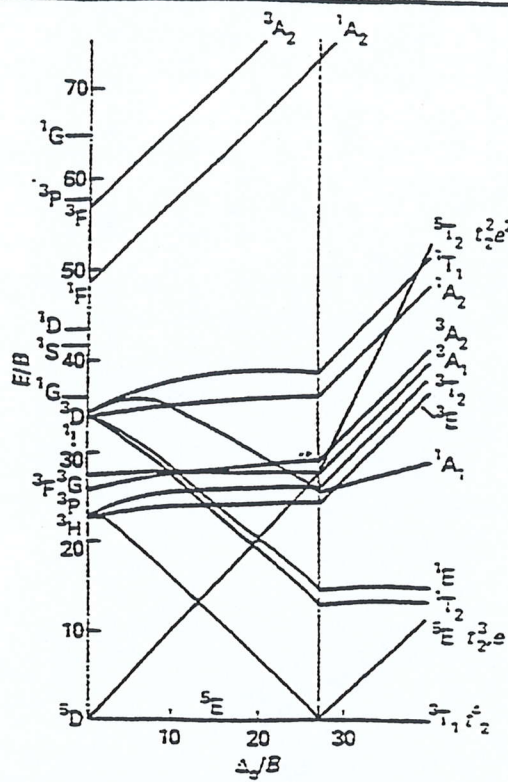
LAMPIRAN

GAMBARAJAH TANABE-SUGANO

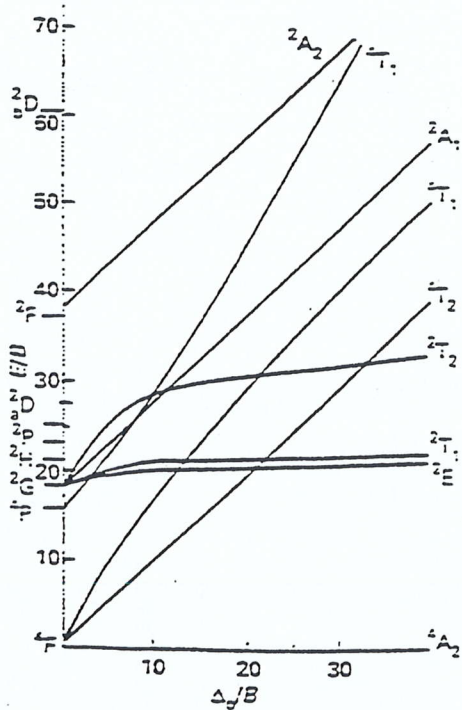
d^2 with $C = 4.42B$



d^4 with $C = 4.61B$



d^3 with $C = 4.5B$



d^5 with $C = 4.4775B$

