

---

UNIVERSITI SAINS MALAYSIA

Kursus Semasa Cuti Panjang  
2009/2010 Academic Session

**KTT 212 – Inorganic Chemistry II**  
**[Kimia Takorganik II]**

Duration : 3 hours  
*[Masa : 3 jam]*

---

Please check that this examination paper consists of **TWELVE** pages of printed material 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.

In the event of any discrepancies, the English version shall be used.

...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  $\mu$  (spin-only) for this complex.
- (4 marks)
2. (a) Determine the oxidation state for the central metal atom and the crystal field stabilization energy for each of the following complexes:
- (i)  $[\text{Fe}(\text{ox})_3]^{3-}$
- (ii)  $[\text{Mn}(\text{acac})_3]^-$
- (iii)  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]^-$
- (iv)  $[\text{Co}(\text{CN})_5\text{CO}]^{3-}$
- (12 marks)

- 3 -

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

$$\log K_1 = 8.2 \quad \log K_2 = 7.3 \quad \log K_3 = 5.2$$

- (i) Write the equation for  $\beta_n$  in each step (where  $n = 1, 2$  and  $3$ ).  
(ii) Calculate the value of  $\log \beta$ .

(8 marks)

3. (a) The ligand-field splitting of the d-orbitals is typically larger in 2nd and 3rd row transition metals than in the first row.

- (i) Give a reason for this.  
(ii) Give three examples where this splitting influences the chemical properties of these elements.

(12marks)

- (b) Using the valence bond theory (VBT) and crystal field theory (CFT) approaches, consider the formation of  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{CN})_6]^{3+}$  complexes.

- (i) Based on each of the above theories, show the electronic arrangements and electronic configurations for both the complexes using appropriate graphical representations.

(4 marks)

- (ii) Explain the reasons for the expected magnetic properties for both the complexes. Calculate the  $\mu_B$  values for both the complexes.

(4 marks)

**SECTION B**

4. (a) Which of the following complexes would you expect to experience a Jahn-Teller distortion:

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

Give reasons for your answer.

(5 marks)

- (b) Briefly explain the principles involve in molecular orbital theory (MO).

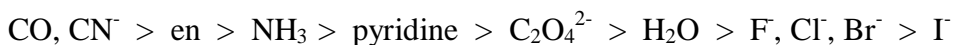
(7 marks)

- (c) For which member of the following pairs of complexes,  $\Delta_{\text{oct}}$  would be larger and state why:

- (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 marks)

5. (a) Explain the following order with respect to the ligands in the spectrochemical series:.



(10 marks)

- (b) By using iron and nickel coordination compounds as examples, describe the high-spin and low-spin complexes based on valence bond theory and crystal fields theory.

(10 marks)

6. (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  is a strong oxidizing agent that will oxidize water, but  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is stable in aqueous solution. Explain the differing reactivity of these two cobalt complexes using ligand-field stabilization energies and the following information:

- Both Co(III) complexes are low-spin; both Co(II) complexes are high-spin.
- $\Delta_o [\text{Co}(\text{NH}_3)_6]^{3+} = 24,000 \text{ cm}^{-1}$
- $\Delta_o [\text{Co}(\text{NH}_3)_6]^{2+} = 13,000 \text{ cm}^{-1}$
- $\Delta_o [\text{Co}(\text{H}_2\text{O})_6]^{3+} = 18,000 \text{ cm}^{-1}$
- $\Delta_o [\text{Co}(\text{H}_2\text{O})_6]^{2+} = 9,700 \text{ cm}^{-1}$

(14 marks)

(b) Explain why is it that  $\text{TiO}_2$  give a white color while  $\text{Fe}_2\text{O}_3$  gives a 'rusty' color.

(3 marks)

(c) Briefly describe the phenomena of conductivity, insulator and semiconductors using the Band theory.

(3 marks)

7. (a) Define the following terms:

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

(7 marks)

(b) Explain why both Pd(II) and Pt(II) form complexes with square planar geometry but Ni(II) complex can adopt both square planar and tetrahedral geometries.

(7 marks)

- (c) Briefly describe:
- (i) The importance and role of organometallic complexes as catalysts, using one example, **or**
  - (ii) The role of transition metal complexes as therapeutic drugs, citing one example.
- (6 marks)

### TANABE-SUGANO DIAGRAMS

**BAHAGIAN A**

1. (a) Tuliskan nama IUPAC bagi setiap 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  $1.70 \mu_B$ . Kirakan  $\mu$  (spin-sahaja) untuk kompleks ini.
- (4 markah)
2. (a) Tentukan keadaan pengoksidaan bagi atom logam pusat dan tenaga penstabilan medan hablur bagi setiap kompleks berikut:
- (i)  $[\text{Fe}(\text{ox})_3]^{3-}$
  - (ii)  $[\text{Mn}(\text{acac})_3]^-$
  - (iii)  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]^-$
  - (iv)  $[\text{Co}(\text{CN})_5\text{CO}]^{3-}$
- (12 markah)

- (b) Pemalar pembentukan seselangkah ( $K$ ) bagi tindak balas di antara  $\text{Ni}^{2+}$  dengan etilenadiamina di dalam larutan akuas adalah seperti berikut:

$$\log K_1 = 8.2 \quad \log K_2 = 7.3 \quad \log K_3 = 4.2$$

- (i) Tuliskan persamaan bagi  $\beta_n$  dalam setiap langkah (dengan  $n = 1, 2$  and  $3$ ).  
 (i) Hitungkan nilai bagi  $\log \beta$ .

(8 markah)

3. (a) Pemecahan medan ligan bagi orbital-d kebiasaannya adalah lebih besar untuk logam peralihan dalam baris kedua dan ketiga berbanding dengan baris pertama.

- (i) Berikan penjelasan.  
 (ii) Berikan tiga contoh di mana pemecahan ini memberi kesan terhadap sifat kimia bagi unsur tersebut.

(12 markah)

- (b) Pertimbangkan pembentukan kompleks  $[\text{CoF}_6]^{3-}$  dan  $[\text{Co}(\text{CN})_6]^{3+}$  mengikut teori ikatan valens dan teori medan hablur.

- (i) Berdasarkan setiap teori di atas, tunjukkan susunan elektron dan konfigurasi elektron bagi kedua kompleks tersebut dengan menggunakan gambarajah.

(4 markah)

- (ii) Berikan penjelasan mengenai sifat magnet yang dijangkakan bagi kedua-dua kompleks tersebut. Seterusnya kirakan nilai  $\mu_B$  bagi kedua-dua kompleks.

(4 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)  $[\text{CoF}_6]^{3-}$

Beri alasan bagi jawapan anda

(5 markah)

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

(7 markah)

- (c) Dalam setiap pasangan kompleks berikut, pilih satu yang mempunyai  $\Delta_{\text{oct}}$  yang lebih besar dari pasangannya. Jelaskan pilihan 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) Berikan penjelasan mengenai turutan am berikut bagi ligan dalam siri spektrokimia.

$\text{CO}, \text{CN}^- > \text{en} > \text{NH}_3 > \text{piridina} > \text{C}_2\text{O}_4^{2-} > \text{H}_2\text{O} > \text{F}, \text{Cl}, \text{Br}^- > \text{I}^-$

(10 markah)

- (b) Dengan menggunakan contoh sebatian koordinatan ferum dan nikel, terangkan kompleks spin-tinggi dan spin-rendah dengan berpandukan kepada teori ikatan valens dan teori medan hablur.

(10 markah)

6. (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  adalah suatu agen pengoksidaan yang sangat kuat dan mengoksidakan air, tetapi tidak pula  $[\text{Co}(\text{NH}_3)_6]^{3+}$  dan ia stabil di dalam air. Jelaskan perbezaan keaktifan kedua-dua kompleks kobalt ini dengan menggunakan tenaga penstabilan medan ligan bagi kedua-dua kompleks tersebut dan maklumat berikut:
- Kedua kompleks Co(III) adalah spin-rendah; kedua-dua kompleks Co(II) adalah spin-tinggi.
  - $\Delta_o [\text{Co}(\text{NH}_3)_6]^{3+} = 24,000 \text{ cm}^{-1}$
  - $\Delta_o [\text{Co}(\text{NH}_3)_6]^{2+} = 13,000 \text{ cm}^{-1}$
  - $\Delta_o [\text{Co}(\text{H}_2\text{O})_6]^{3+} = 18,000 \text{ cm}^{-1}$
  - $\Delta_o [\text{Co}(\text{H}_2\text{O})_6]^{2+} = 9,700 \text{ cm}^{-1}$
- (14 markah)
- (b) Jelaskan kenapa  $\text{TiO}_2$  memberikan warna putih, sementara  $\text{Fe}_2\text{O}_3$  pula menunjukkan warna 'karat'.
- (3 markah)
- (c) Perihalkan fenomena kekonduksian, penebat dan semikonduktor menggunakan teori Jalur.
- (3 markah)
7. (a) Berikan definisi istilah istilah berikut:
- (i) Kompleks koordinatan
  - (ii) Nombor koordinatan
  - (iii) Prinsip keelektroneutralan Pauli
- (7 markah)
- (b) Terangkan mengapa kedua-dua Pd(II) dan Pt(II) membentuk kompleks satah persegi manakala Ni(II) membentuk kedua-dua kompleks satah persegi dan tetrahedral.
- (7 markah)

- (c) Jelaskan secara ringkas:
- (i) Kepentingan dan peranan kompleks organologam sebagai mangkin dengan menggunakan satu contoh, atau
  - (ii) Peranan kompleks logam peralihan sebagai ubatan dengan memberikan satu contoh.

(6 markah)

oooOOooo