
UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

KTT 212 – Inorganic Chemistry II
[Kimia Takorganik II]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of SEVENTEEN pages of printed material before you begin the examination.

Instructions:

Answer **FIVE** (5) questions. **Section A** is **COMPULSORY**. Answer **TWO** (2) questions from **Section B**. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

Answers each question on a new page.

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

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

Appendix: Tanabe-Sugano Diagram

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SECTION A

1. (a) (i) What does chelating agent means?
 (ii) Co(III) ion reacts with three ethylenediamine ligands to form a coordination complex. Draw the structure of the complex and circle a chelate ring in the complex that you have drawn.
 (4 marks)
- (b) Give two different types of isomerism that can be observed in coordination complexes. Explain what they are (the types that you have chosen) and give an example of each one of them.
 (8 marks)
- (c) Based on the 18 electron rule, suggest whether $(\eta^5\text{-Cp})\text{Ni}(\mu\text{-PPh}_2)_2\text{Ni}(\eta^5\text{-Cp})$ might be expected to contain a metal-metal bond (show your method).
 (4 marks)
- (d) State why VSEPR model is not suitable for explaining the geometry of coordination complexes? How does Kerpert rationalizes the shapes of coordination complexes such as $[\text{ML}_n]$, $[\text{ML}_n]^{m+}$ or $[\text{ML}_n]^{m-}$?
 (4 marks)
2. For each of the following complexes:

<u>Complex</u>	<u>Magnetic Moment (B.M.)</u>
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	5.8
$[\text{Mn}(\text{CN})_6]^{4-}$	1.7
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	0
$[\text{CoF}_4]^{2-}$	3.9

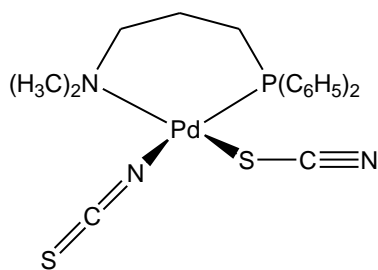
- (i) State whether the above complexes are high spin or low spin.
 (4 marks)
- (ii) Draw the structures of these complexes based on Valence Bond Theory. Give reasons for your answer.
 (8 marks)

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- (iii) Compare the structures predicted from Valence Bond Theory with those proposed from Crystal Field Theory. Your answers should include the calculations of Crystal Field Stabilisation Energy. (8 marks)
3. Explain the following statements/observations using appropriate diagrams/drawings.
- (a) $[\text{Cu}(\text{NH}_3)_4]^+$ is completely colorless while $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is intensely blue.
- (b) Tetrahedral complexes with d^2 , d^5 and d^7 configurations do not exhibit Jahn-Teller distortions.
- (c) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is pale pink and $[\text{CoCl}_4]^{2-}$ is deep blue.
- (d) Substitution reactions for square planar complexes usually proceed with associative mechanism instead of dissociative.
- (20 marks)

SECTION B

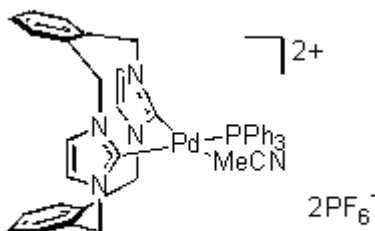
4. (a) (i) Give the structural formula for chlorotriphenylphosphinepalladium(II)- μ -dichlorochlorotriphenylphosphinepalladium(II).
- (ii) Name the following complex: $K[PtCl_3NH_3]$.
- (iii) How can IR spectroscopy be used to distinguish between the *cis* and *trans* isomers of the square planar complex $[PtCl_2(NH_3)_2]$?
- (7 marks)
- (b) Explain the following statements:
- (i) The Δ_{oct} for $[ReF_6]^{2-}$ is larger than $[MnF_6]^{2-}$.
- (ii) The $[CoCl_4]^{2-}$ ion is a regular tetrahedron but $[CuCl_4]^{2-}$ has a flattened tetrahedral structure.
- (7 marks)
- (c) (i) What is an ambidentate ligand?
- (2 marks)
- (ii) Consider the following palladium complex **1**. Suggest why the SCN ligands are bonded to the complex through different atoms.

**1**

(4 marks)

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5. (a) A palladium complex **2** of an *ortho*-cyclophane ligand has been synthesised. X-ray crystallography data show that the palladium metal is coordinated to two carbene centres, one MeCN and one PPh₃ ligands.

**2**

(note: MeCN= CH₃CN, PPh₃ = triphenylphosphine)

Based on **2**, answer the following questions:

- (i) What is the coordination number around the Pd centre?
 - (ii) What is the denticity of the cyclophane ligand?
 - (iii) The coordination geometry about the palladium metal is a distorted square planar, suggest why there is a deviation from regular geometry.
 - (iv) Does this complex follow the 18 electron rule? Show your calculations.
- (10 marks)
- (b) [Ni(NH₃)₄]²⁺ is a complex ion which forms on mixing aqueous solutions of ammonia and a nickel salt.
- (i) It has been found that this solution contains 1.5 x 10⁻⁴ % of the nickel ion in the form of Ni²⁺ when the concentration of free NH₃ (aq) is 0.5 M. Knowing that the only complex present in this solution is [Ni(NH₃)₄]²⁺, calculate the stability constant of the complex [Ni(NH₃)₄]²⁺.

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- (ii) The octahedral complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$ can be prepared by using a solution of ammonia which has been supersaturated with ammonia gas in which the $\log K_5 = 0.79$ and $\log K_6 = 0.36$. Calculate the overall β_6 for $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

(10 marks)

6. (a) (i) Why is ligand considered as a Lewis base?
- (ii) Give an example and draw the structure of a bidentate and a polydentate ligands.
- (iii) State (with reasons) whether the following octahedral complexes are *chiral* or *achiral*: *cis*- $[\text{CoCl}_2(\text{en})_2]^+$, $[\text{Cr}(\text{ox})_3]^{3-}$ and *trans*- $[\text{PtCl}_2(\text{en})_2]^{2+}$.

(10 marks)

- (b) (i) Using crystal field theory, briefly discuss the differences in geometric, magnetic and spectroscopic (color) properties of the four-coordinate complexes $[\text{NiCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$.

(4 marks)

- 7 -

- (ii) Use the spin selection rules and the Tanabe Sugano Diagram (Figure 1) to estimate the energy of the three spin allowed ligand field bands observed for $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. Given: $B = 695 \text{ cm}^{-1}$ and $\Delta_o = 17,000 \text{ cm}^{-1}$.

(6 marks)

Figure 1

- 7 (a) Give a brief explanation in relation to the characteristics of the following nickel chemistry based on Valence Bond Theory.
- (i) Two of the ionic complexes $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ at room temperature have the same effective magnetic moment of $\mu_{\text{eff}} = 3.1 \text{ B.M.}$

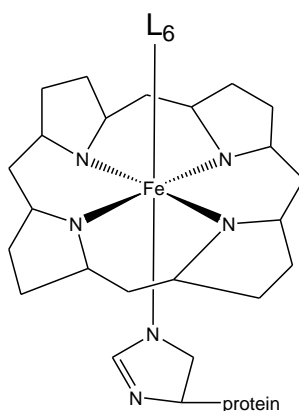
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- (ii) $K_2[NiF_6]$ complex shows a distorted tetragonal in its octahedral structure with two Ni-F bonds which appear to be longer than the other four.

(10 marks)

- (b) Haemoglobin contains an Fe^{2+} complex **3** that is octahedrally coordinated by a tetradentate porphyrin ligand, a monodentate ligand from the protein and a variable sixth ligand, L_6 . In oxygenated blood (red in color and *low spin*), $L_6 = O_2$ (oxygen molecule) and in deoxygenated blood (blue in color and *high spin*), $L_6 = H_2O$ (water molecule).

**3**

- (i) Draw the crystal field diagram for Fe^{2+} in oxygenated and deoxygenated blood. Explain the difference in the colors of the blood in the two cases.
- (ii) Cyanide (CN^-) behaves as a poison by irreversibly replacing oxygen in the haemoglobin. What do you expect the magnetic and colour properties of the complex, when CN^- replaces the oxygen?

(10 marks)

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BAHAGIAN A

1. (a) (i) Apakah yang dimaksudkan dengan istilah agen kelat?
 (ii) Ion Co(III) bertindakbalas dengan tiga ligan etilenadiamina untuk membentuk kompleks koordinatan. Lukiskan struktur kompleks yang terbentuk itu dan bulatkan gelang pengkelatan di dalam kompleks tersebut.
 (4 markah)
- (b) Berikan dua jenis keisomeran yang boleh terjadi dalam kompleks koordinatan. Jelaskan kedua-dua jenis isomer yang anda pilih itu berserta contoh untuk setiap satunya.
 (8 markah)
- (c) Berdasarkan peraturan 18 elektron, cadangkan adakah kompleks $(\eta^5\text{-Cp})\text{Ni}(\mu\text{-PPh}_2)_2\text{Ni}(\eta^5\text{-Cp})$ mengandungi ikatan logam-logam (tunjukkan cara anda).
 (4 markah)
- (d) Nyatakan kenapa model VSEPR tidak sesuai digunakan untuk menjelaskan geometri kompleks koordinatan. Bagaimanakah Kerpert memberi rasional tentang bentuk kompleks koordinatan seperti $[\text{ML}_n]$, $[\text{ML}_n]^{m+}$ atau $[\text{ML}_n]^{m-}$?
 (4 markah)
2. Bagi setiap kompleks berikut:

<u>Kompleks</u>	<u>Momen Magnet (B.M.)</u>
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	5.8
$[\text{Mn}(\text{CN})_6]^{4-}$	1.7
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$	0
$[\text{CoF}_4]^{2-}$	3.9

- (i) Nyatakan sama ada kompleks tersebut di atas ialah spin tinggi atau spin rendah.
 (4 markah)
- (ii) Lukiskan struktur bagi kompleks berdasarkan Teori Ikatan Valens. Berikan alasan untuk jawapan anda.
 (8 markah)

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- (iii) Bandingkan struktur yang diramalkan daripada Teori Ikatan Valens dengan yang dicadangkan daripada Teori Medan Hablur. Jawapan anda seharusnya termasuk pengiraan Tenaga Penstabilan Medan Hablur.

(8 markah)

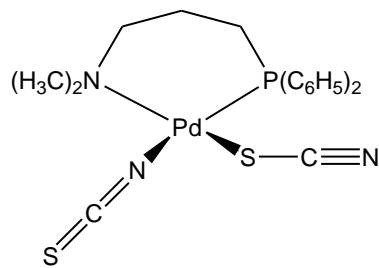
3. Jelaskan kenyataan/perhatian berikut dengan menggunakan gambarajah/lakaran yang berkaitan.

- (a) Kompleks $[\text{Cu}(\text{NH}_3)_4]^+$ tidak berwarna manakala kompleks $[\text{Cu}(\text{NH}_3)_4]^{2+}$ mempunyai warna biru pekat.
- (b) Kompleks tetrahedral dengan konfigurasi d^2 , d^5 dan d^7 tidak menunjukkan pengherotan Jahn-Teller.
- (c) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ berwarna merah jambu sementara kompleks $[\text{CoCl}_4]^{2-}$ berwarna biru pekat.
- (d) Tindakbalas penukargantian untuk kompleks satah segiempat sama, biasanya berlaku dengan mekanisme asosiatif and bukannya disosiatif.

(20 markah)

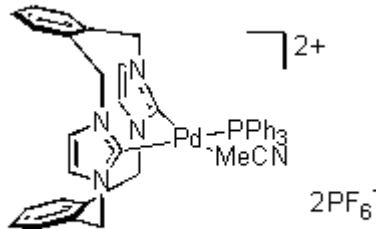
BAHAGIAN B

4. (a) (i) Berikan formula struktur untuk kompleks trifenilfosfinakloropaladium(II) - μ -diklorotrifenilfosfinakloropaladium(II).
- (ii) Namakan kompleks berikut: $K[PtCl_3NH_3]$
- (iii) Bagaimanakah spektroskopi IR boleh digunakan untuk membezakan isomer *cis* dan *trans* untuk kompleks satah segiempat sama $[PtCl_2(NH_3)_2]$? (7 markah)
- (b) Terangkan pernyataan berikut:
- (i) Δ_{oct} bagi $[ReF_6]^{2-}$ lebih besar daripada $[MnF_6]^{2-}$.
- (ii) Ion $[CoCl_4]^{2-}$ merupakan tetrahedron biasa manakala $[CuCl_4]^{2-}$ mempunyai struktur tetrahedral yang serata. (7 markah)
- (c) (i) Apakah yang dimaksudkan dengan ligan ambidentat? (2 markah)
- (ii) Pertimbangkan kompleks paladium **1** berikut. Jelaskan kenapa ligan SCN terikat pada kompleks Pd itu melalui atom yang berbeza.

**1**

(4 markah)

5. (a) Kompleks paladium **2** berdasarkan ligan orto-siklofan telah disintesis. Data kristalografi sinar-X menunjukkan logam paladium berkoordinat dengan dua pusat karbon, satu MeCN dan satu ligan PPh_3 .



(nota: $\text{MeCN} = \text{CH}_3\text{CN}$, $\text{PPh}_3 = \text{trifenilfosfina}$)

Berdasarkan **2**, jawab soalan-soalan berikut:

- (i) Apakah nombor koordinatan pada atom pusat Pd?
- (ii) Apakah dentisiti bagi ligan siklofan?
- (iii) Geometri koordinatan sekitar logam paladium adalah satah segiempat terherot, cadangkan mengapakah ada sedikit perbezaan dari geometri biasa.
- (iv) Adakah kompleks ini mematuhi peraturan 18 elektron? Tunjukkan pengiraan anda.

(10 markah)

- (b) $[\text{Ni}(\text{NH}_3)_4]^{2+}$ ialah suatu ion kompleks yang terbentuk apabila larutan akueus ammonia bercampur dengan garam nikel.
- (i) Larutan tersebut didapati mengandungi 1.5×10^{-4} % ion nikel dalam bentuk Ni^{2+} apabila kepekatan bagi ammonia bebas ialah 0.5 M. Diketahui bahawa hanya kompleks $[\text{Ni}(\text{NH}_3)_4]^{2+}$ sahaja didapati hadir dalam larutan itu, hitungkan pemalar kestabilan bagi kompleks $[\text{Ni}(\text{NH}_3)_4]^{2+}$.

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- (ii) Kompleks oktahedral $[\text{Ni}(\text{NH}_3)_6]^{2+}$ boleh disediakan dengan menggunakan larutan ammonia yang ditepukan dengan gas ammonia dengan nilai $\log K_5 = 0.79$ dan $\log K_6 = 0.36$. Hitungkan β_6 keseluruhannya bagi $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

(10 markah)

6. (a) (i) Kenapakah ligan disifatkan sebagai bes Lewis?
- (ii) Berikan contoh beserta lukisan struktur untuk satu ligan bidentat dan satu ligan polidentat.
- (iii) Nyatakan (dengan sebab) samada kompleks-kompleks oktahedral berikut adalah bersifat *kiral* atau *akiral*: *cis*- $[\text{CoCl}_2(\text{en})_2]^+$, $[\text{Cr}(\text{ox})_3]^{3-}$ dan *trans*- $[\text{PtCl}_2(\text{en})_2]^{2+}$.

(10 markah)

- (b) (i) Dengan menggunakan teori medan hablur, berikan penjelasan tentang perbezaan sifat geometri, kemagnetan dan spektroskopi (warna) bagi kompleks $[\text{NiCl}_4]^{2-}$ dan $[\text{PtCl}_4]^{2-}$.

(4 markah)

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- (ii) Gunakan peraturan pemilihan spin dan Gambarajah Tanabe Sugano (Rajah 1) bagi menganggarkan tenaga jalur medan ligan untuk tiga spin yang dibenarkan bagi kompleks $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. Nilai $B = 695 \text{ cm}^{-1}$ dan $\Delta_o = 17,000 \text{ cm}^{-1}$.

(6 markah)

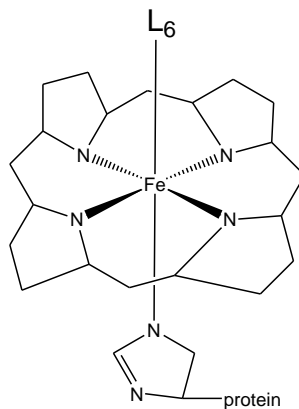
Rajah 1

7. (a) Berikan penjelasan ringkas berkaitan dengan ciri-ciri kimia nikel berikut berdasarkan Teori Ikatan Valens.

- (i) Dua ion kompleks $[\text{Ni}(\text{NH}_3)_6]^{2+}$ dan $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ pada suhu bilik memiliki momen magnet efektif yang sama iaitu $\mu_{\text{eff}} = 3.1 \text{ B.M.}$
- (ii) Kompleks $\text{K}_2[\text{NiF}_6]$ menunjukkan tetragonal terherot dalam bentuk oktahedral dengan dua ikatan Ni-F didapati lebih panjang daripada empat ikatan yang lain.

(10 markah)

(b) Hemoglobin adalah kompleks **3** oktahedral Fe^{2+} terkoordinat dengan satu ligan porphyrin tetradentat, ligan monodentat protin dan satu ligan 'tukarganti' keenam, L_6 . Bagi darah teroksigen (berwarna merah dan spin rendah), $\text{L}_6 = \text{O}_2$ (molekul oksigen) dan bagi darah ternyahoksigen (berwarna biru dan spin tinggi), $\text{L}_6 = \text{H}_2\text{O}$ (molekul air).



3

- (i) Lakarkan gambarajah medan hablur bagi ion Fe^{2+} untuk darah teroksigen dan ternyahoksigen. Jelaskan perbezaan warna untuk kedua keadaan tersebut.
- (ii) Sianida (CN^-) adalah bahan racun dengan sifat pengganti oksigen secara tetap pada hemoglobin. Apakah sifat magnetik dan warna yang dijangkakan apabila CN^- menggantikan oksigen?

(10 markah)