UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2009/2010

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

SECTION A: Answer all questions. There are THREE questions in this section.

1. (a) Fill in the blanks in each of the following complexes below to indicate the oxidation state of the metal, the coordination number about the metal, the number of electrons on the metal (d^n) and whether the complex obeys the 18-electron rule:

	Complex	**Oxidation State**	**Coordination No.**	**d^n**	**18-electron count (Yes/No)**
i	$Rh(H)(CO)(dppe)_2$				
ii	$[MnO_4]^-$				
iii	$K[CuCl_2]$				
iv	$Na_4[Co(C_2O_4)_2Br_2]$				
v	$[Co(en)_2Br_2]$				

(10 marks)

(b) Name or write the chemical formula for each of the following coordination compounds using the IUPAC rules.

(i) $[Mn(H_2O)_5Cl]Br$

(ii) $Na_3[FeF_6]$

(iii) Sodium tetracyanonickelate(II)

(iv) *B*is(ethylenediamine)diiodomanganese(III) perchlorate

(2 marks)

(c) Draw and name ALL possible stereoisomers of the following complexes:

(i) $[Fe(en)(C_2O_4)Br_2]^-$

(ii) Ionization isomer of $[Fe(NH_3)_5I]Br_2$

(iii) Linkage isomer of $[Co(o\text{-phen})_2(NH_3)(SCN)]Cl$

(8 marks)

2. (a) The complex ion $[Fe(CN)_6]^{3-}$ is paramagnetic and has one unpaired electron. The complex ion $[Fe(SCN)_6]^{3-}$ is also paramagnetic but has five unpaired electrons.

(i) Briefly explain why the $[Fe(SCN)_6]^{3-}$ complex ion has so many more unpaired electrons compared to the $[Fe(CN)_6]^{3-}$ complex ion.

(ii) Draw the crystal field splitting diagram to illustrate your answer.

(8 marks)

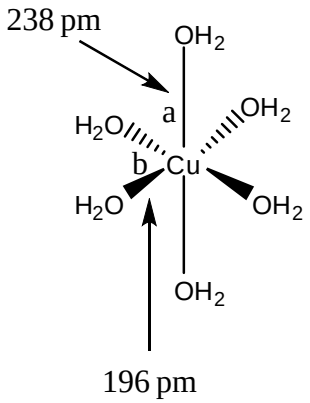
(b) What is the expected ordering values of Δ_{oct} for $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$? Rationalize your answer.

(5 marks)

(c) State Jahn Teller theorem.

(2 marks)

(d) A copper complex $[Cu(H_2O)_6][ClO_4]_2$ was found to have the following Cu─O bond lengths:



Explain the difference between bond lengths a and b according to Jahn Teller principles.

(5 marks)

3. The intensities of electronic transitions as observed from the UV-Vis spectra for $[Mn(H_2O)_6]^{2+}$, $[Ti(H_2O)_6]^{3+}$ and $[TiCl_6]^{3-}$ are summarized in the following table:

Compounds	**Extinction coefficients (ε, in $m^2\ mol^{-1}$)**
$[Mn(H_2O)_6]^{2+}$	0.1
$[Ti(H_2O)_6]^{3+}$	1
$[TiCl_6]^{3-}$	1000

(a) State the electronic configuration and the hybridized orbital of central metal atom in $[Mn(H_2O)_6]^{2+}$, $[Ti(H_2O)_6]^{3+}$ and $[TiCl_6]^{3-}$.

(6 marks)

(b) Compare the difference of crystal field stabilization energies, Δ (in 10Dq) among these compounds. Explain.

(6 marks)

(c) Using the Tanabe-Sugano Diagram, suggest the most probable type of transition, either (i) spin forbidden and Laporte forbidden, (ii) spin allowed and Laporte forbidden or (iii) spin allowed and Laporte allowed, for each compound.

(8 marks)

SECTION B: Choose and answer TWO questions. There are FOUR questions in this section

4. (a) Ligand, dimethylglyoxime ($dmgH_2$), below, form transition complexes $Ni(dmgH)_2$ and $Cu(dmgH)_2$ with Ni and Cu metals. Explain why the copper complex is more soluble than the nickel complex.

Dimethylglyoxime ($dmgH_2$) - $C_4H_7O_2N_2$

(7 marks)

(b) Explain the bonding scheme in $[Ni(NH_3)_6]^{2+}$ based on valence bond theory. Draw the appropriate orbital diagram.

(7 marks)

(c) The existence of high spin or low spin Fe(II) is essential for the supply of oxygen in human body. Explain.

(6 marks)

5. (a) Explain the following statements:

(i) The existence of a series of entering groups with different rate constants is an evidence for an associative mechanism (A and I_a).

(ii) The high spin d^4 complex $[Cr(H_2O)_6]^{2+}$ is labile, but the low spin d^4 complex ion $[Cr(CN)_6]^{4-}$ is inert.

(10 marks)

(b) (i) Assume that in the reaction of Cu^{2+} with ammonia, the only complex ion to form is the tetraammine species, $[Cu(NH_3)_4]^{2+}$. Given a solution where the initial $[Cu^{2+}]$ is 0.10 M, and the initial $[NH_3]$ is 1.0 M and that $\beta_4 = 2.1 \times 10^{13}$, calculate the equilibrium concentration of the Cu^{2+} ion.

(6 marks)

(ii) Consider the following reaction:

$$Zn^{2+} + en \rightleftharpoons [Zn(en)]^{2+}$$

Calculate the entropy change for the reaction at 25 °C, given that

$\Delta H = -27.6$ kJ mol^{-1}, $\ln \beta = 14.16$ and $R=8.314$ $JK^{-1}mol^{-1}$.

(4 marks)

6. (a) (i) State the highest oxidation state observed for the metal vanadium and explain your answer.

(ii) The Δ_{oct} values for Cr(III) complexes with various ligands are given in the table below. Explain the differences in the Δ_{oct} values in the context of σ or π donor and acceptor.

Ligand	Cl^-	H_2O	CN^-
Δ_{oct} (cm^{-1})	13,200	17,400	33,500

(10 marks)

(b) Draw the structure of the products for the reaction of $Ir(CO)Cl(PPh_3)_2$ with the following:

(i) O_2

(ii) H_2

(iii) MeI

(iv) CO

(10 marks)

7. (a) Consider a complex ion $K_3[Fe(ox)_3].3H_2O$.

(i) Would you expect this complex to be low spin or high spin? Explain your answer.

(ii) Calculate the magnetic moment (B.M.) for this complex.

(5 marks)

(b) A complex resulting from coordination with a chelating ligand is much more stable compared to that resulting from coordination with monodentate ligand (chelate effect). Explain how the chelate effect contributes to this enhanced stability by looking at both the enthalphy and entropy contributions.

(5 marks)

(c) (i) Draw the orbital-energy diagram for the *d* orbitals showing the electronic configurations for $[Zn(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ tetrahedral.

(ii) What are the color properties that you expect from the above complexes? Explain.

(iii) State the magnetic properties of these complexes.

(10 marks)

TANABE-SUGANO DIAGRAMS

BAHAGIAN A

1. (a) Isi ruang kosong memperihalkan keadaan pengoksidaan, nombor koordinatan, bilangan elektron pada logam pusat (d^n) dan samada kompleks berikut mematuhi peraturan 18 elektron:

	Kompleks	**Keadaan Pengoksidaan**	**Nombor Koordinatan**	**d^n**	**Bilangan 18-elektron (Ya/Tidak)**
i	$Rh(H)(CO)(dppe)_2$				
ii	$[MnO_4]^-$				
iii	$K[CuCl_2]$				
iv	$Na_4[Co(C_2O_4)_2Br_2]$				
v	$[Co(en)_2Br_2]$				

(10 markah)

(b) Berikan nama atau tulis formula kimia bagi setiap kompleks berikut mengikut peraturan IUPAC.

(i) $[Mn(H_2O)_5Cl]Br$

(ii) $Na_3[FeF_6]$

(iii) Natrium tetrasianonikelat(II)

(iv) *B*is(etilenadiamina)diiodomangan(III) perklorat

(2 markah)

(c) Lukis dan berikan nama <u>SEMUA</u> stereoisomer bagi setiap kompleks berikut:

(i) $[Fe(en)(C_2O_4)Br_2]^-$

(ii) Isomer pengionan $[Fe(NH_3)_5I]Br_2$

(iii) Isomer linkej $[Co(o\text{-phen})_2(NH_3)(SCN)]Cl$

(8 markah)

2. (a) Ion kompleks $[Fe(CN)_6]^{3-}$ bersifat paramagnet dan mempunyai satu elektron tak berpasangan. Ion kompleks $[Fe(SCN)_6]^{3-}$ juga bersifat paramagnet tetapi mempunyai 5 elektron tak berpasangan.

(i) Terangkan secara ringkas kenapa ion kompleks $[Fe(SCN)_6]^{3-}$ mempunyai lebih banyak elektron tak berpasangan berbanding dengan ion kompleks $[Fe(CN)_6]^{3-}$.

(ii) Lukiskan gambarajah pemisahan medan hablur untuk menjelaskan jawapan anda.

(8 markah)

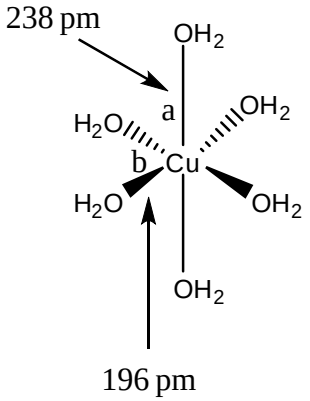
(b) Apakah nilai susunan Δ_{oct} yang dijangkakan untuk $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{3-}$ dan $[Fe(CN)_6]^{4-}$? Jelaskan jawapan anda.

(5 markah)

(c) Nyatakan teori Jahn Teller.

(2 markah)

(d) Satu kompleks kuprum $[Cu(H_2O)_6][ClO_4]_2$ didapati mempunyai panjang ikatan Cu─O seperti berikut:



Jelaskan perbezaan panjang ikatan a dan b berdasarkan prinsip Jahn Teller.

(5 markah)

3. Intensiti peralihan elektronik seperti yang diperhatikan daripada spektrum UV-Vis bagi $[Mn(H_2O)_6]^{2+}$, $[Ti(H_2O)_6]^{3+}$ and $[TiCl_6]^{3-}$ diringkaskan dalam jadual berikut:

Sebatian	**Pekali Pemadaman (ε, dalam $m^2\ mol^{-1}$)**
$[Mn(H_2O)_6]^{2+}$	0.1
$[Ti(H_2O)_6]^{3+}$	1
$[TiCl_6]^{3-}$	1000

(a) Nyatakan konfigurasi elektronik dan orbital penghibridan bagi atom logam pusat pada $[Mn(H_2O)_6]^{2+}$, $[Ti(H_2O)_6]^{3+}$ dan $[TiCl_6]^{3-}$.

(6 markah)

(b) Bandingkan perbezaan tenaga penstabilan medan hablur, Δ (dalam 10Dq) di kalangan sebatian tersebut. Jelaskan.

(6 markah)

(c) Dengan menggunakan Gambarajah Tanabe-Sugano, cadangkan jenis peralihan yang paling mungkin, sama ada (i) spin terhalang dan Laporte terhalang, (ii) spin terizinkan dan Laporte terhalang atau (iii) spin terizinkan dan Laporte terizinkan, bagi setiap sebatian.

(8 markah)

BAHAGIAN B

4. (a) Ligan, dimetilglioksim ($dmgH_2$), di bawah, membentuk kompleks **M**$(dmgH)_2$ dengan logam **M** = Ni dan logam **M** = Cu. Jelaskan kenapa kompleks $Cu(dmgH)_2$ lebih senang larut di dalam air berbanding dengan kompleks yang terbentuk dengan $Ni(dmgH)_2$.

Dimethylglyoxime ($dmgH_2$) - $C_4H_7O_2N_2$

(7 markah)

(b) Jelaskan skema pengikatan dalam $[Ni(NH_3)_6]^{2+}$ berdasarkan teori ikatan valens. Lukiskan gambarajah orbital yang sesuai.

(7 markah)

(c) Kewujudan spin tinggi atau spin rendah pada Fe(II) diperlukan untuk pembekalan oksigen ke tubuh badan manusia. Huraikan.

(6 markah)

5. (a) Jelaskan penyataan berikut:

(i) Kewujudan suatu siri kumpulan masuk dengan pemalar kadar yang berlainan merupakan bukti bagi mekanisme assosiatif (A dan I_a).

(ii) Kompleks spin tinggi $[Cr(H_2O)_6]^{2+}$ adalah labil, tetapi kompleks spin rendah $[Cr(CN)_6]^{4-}$ adalah lengai.

(10 markah)

(b) (i) Andaikan dalam tindakbalas Cu^{2+} dengan ammonia, ion kompleks yang terbentuk hanyalah spesis tetraamina, $[Cu(NH_3)_4]^{2+}$. Diberi satu larutan yang mempunyai kepekatan awal $[Cu^{2+}]$ sebanyak 0.10 M, kepekatan awal $[NH_3]$ sebanyak 1.0 M dan $\beta_4 = 2.1 \times 10^{13}$, kirakan kepekatan ion Cu^{2+} pada keseimbangan.

(6 markah)

(ii) Pertimbangkan tindak balas di bawah:

$$Zn^{2+} + en \rightleftharpoons [Zn(en)]^{2+}$$

Kirakan perubahan entropi bagi tindak balas itu pada suhu 25 °C, dengan

$\Delta H = -27.6$ kJ mol^{-1}, $\ln \beta = 14.16$ dan $R=8.314$ $JK^{-1}mol^{-1}$.

(4 markah)

6. (a) (i) Nyatakan keadaan pengoksidaan paling tinggi bagi logam vanadium dan berikan penjelasan terhadap kewujudan keadaan yang tinggi tersebut.

(ii) Nilai Δ_{okt} bagi kompleks Cr(III) dengan pelbagai ligan diberikan seperti berikut. Jelaskan perbezaan terhadap nilai Δ_{okt} mengikut konteks penerima dan penderma σ atau π.

Ligan	Cl^-	H_2O	CN^-
Δ_{okt} (cm^{-1})	13,200	17,400	33,500

(10 markah)

(b) Lukiskan struktur hasil bagi tindak balas di antara $Ir(CO)Cl(PPh_3)_2$ dengan berikut:

(i) O_2

(ii) H_2

(iii) MeI

(iv) CO

(10 markah)

7. (a) Pertimbangkan ion kompleks $K_3[Fe(ox)_3].3H_2O$.

(i) Adakah anda menjangka kompleks ini akan bersifat spin rendah atau tinggi? Jelaskan jawapan anda.

(ii) Kirakan momen magnet (B.M.) bagi kompleks ini.

(5 markah)

(b) Kompleks yang terhasil dari pengkoordinatan dengan ligan kelat adalah lebih stabil berbanding yang terhasil dari pengkoordinatan dengan ligan monodentat (kesan kelat). Jelaskan bagaimana kesan kelat menyumbang kepada kestabilan yang lebih tinggi dengan mengambilkira sumbangan entalpi dan entropi.

(5 markah)

(c) (i) Lukiskan gambarajah tenaga-orbital bagi orbital d dan konfigurasi elektron bagi kompleks $[Zn(H_2O)_6]^{2+}$ dan $[CoCl_4]^{2-}$ tetrahedral.

(ii) Apakah warna yang dapat dijangkakan daripada kompleks tersebut? Berikan penjelasan.

(iii) Nyatakan sifat kemagnetan keuda kompleks tersebut

(10 markah)

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