UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2011/2012

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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

COMPULSORY questions

1. (a) Sketch all isomers of $[Co(NH_3)_2(H_2O)_2Cl_2]^+$. Identify any pairs of enantiomers.

(6 marks)

(b) For each of the following metal complexes, determine the oxidation states of the metals, the number of electrons on the metals (d^n) and whether the complexes obey the 18-electron rule.

(i) $[Rh(bipy)_2Cl]^+$

(ii) $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$

(iii) $[Ni(en)_3]^{2+}$

(iv) $[FeCl_4]^{2-}$

(v) $[(\eta^4\text{-}C_4H_4)(\eta^5\text{-}C_5H_5)Ni]^+$

(vi) $Na_4[Co(C_2O_4)_2Br_2]$

(9 marks)

(c) Consider the following reactions:

$$H^+ + CH_3HgOH \rightarrow H_2O + CH_3Hg^+ \qquad \log K_1 = 6.3$$

$$H^+ + CH_3HgS^- \rightarrow HS^- + CH_3Hg^+ \qquad \log K_2 = -8.4$$

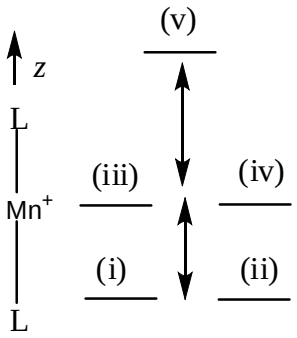
Comment on the relative values of the equilibrium constants for equations 1 and 2 based on the hard soft acid base (HSAB) principle.

(5 marks)

2. (a) How does crystal field theory and valence bond theory view bonding in coordination complexes? What are the weaknesses of valence bond theory that can be overcome by crystal field theory?

(6 marks)

(b) An energy-level diagram for a linear field oriented along the *z* axis is shown below:



energy levels

Identify the five d-orbitals, (i)-(v) in the diagram based on expected splitting and briefly rationalize your placement.

(6 marks)

(c) Would a diamagnetic $[Ni(CN)_4]^{2-}$ complex likely to have tetrahedral or square planar geometry? Show your working.

(4 marks)

(d) An aqueous solution of Zn^{2+} is colorless, that of $[Co(en)_3]^{3+}$ is yellow while that of $[CoF_6]^{3-}$ is blue. Explain why.

(4 marks)

3. (a) Consider the manganese(II) ion. The hexaaqua complex of this ion is pale pink while the hexacyano complex is intense violet.

i. Explain the difference in the intensity of the color of these two complexes. Include properly labeled orbital diagrams to illustrate your argument.

ii. Do these complexes differ in paramagnetism? If so explain why.

(10 marks)

(b) Most of the tetrahedral transition metal complexes are high-spin. Comment.

(5 marks)

(c) (i) Using the Tanabe-Sugano diagrams, what absorption band(s) are expected for a high-spin octahedral d^4 complex? Which one corresponds to Δ_o?

(ii) Which Tanabe-Sugano diagram would you use to predict the allowed electronic transitions for a d^3 tetrahedral complex? What transitions are expected and which one corresponds to Δ_t?

(5 marks)

Section B

Answer any **TWO** (2) question.

4. (a) According to the Kepert model, what geometry(ies) would you associate with the following coordination numbers?

(i) 2

(ii) 3

(iii) 4

(iv) 5

(v) 6

(7 marks)

(b) (i) Calculate ΔS for the following reaction at 25 °C. Given that $\Delta H = -27.6$ kJ mol^{-1} and $K = 1.4 \times 10^6$ at 25 °C.

$$[Cu(H_2O)_6]^{2+} + 3en \rightleftharpoons [Cu(en)_3]^{2+} + 6H_2O$$

(ii) Calculate the magnetic moment (in BM) for complex, $K_3[Fe(ox)_3].3H_2O$.

(7 marks)

(c) (i) Draw a general Molecular Orbital(MO) diagram for a simple metal-acceptor and ligand-donor interaction. Clearly label the donor, D and the acceptor, A.

(ii) Using the MO diagram determine the bond order for $[Ni(NH_3)_6]^{2+}$ and $[Cr(NH_3)_6]^{2+}$.

(6 marks)

5. (a) The reaction of nickel(II) bromide with ethyldiphenylphosphine ($PEtPh_2$) in butanol gives a green compound. Elemental analysis reveals a composition of Ni 9.1%, Br 24.7%, P 9.6%, C 52.0% and H 4.6%. On dissolving the green compound in benzene, and cooling the solution below room temperature, a red compound is obtained with an identical composition. The isolated red crystals slowly convert to the green compound on standing at room temperature. Magnetic susceptibility values show that the green compound is paramagnetic and the red compound is diamagnetic. Identify the green and red compounds by **CLEARLY** showing the reactions involved and the **STRUCTURES** of these compounds.

Atomic weight: Ni 58.69 Br 79.90 P 30.97 C 12.07 H 1.00

(10 marks)

(b) (i) Relative solubility of silver halides in water decreases going from AgF (high) to AgCl (moderate), AgBr (low) and AgI (lowest). Explain this solubility trend and predict the relative solubilities of mercury(I) halides and lithium halides in water. Explain your predictions.

(ii) It has been known that 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.

(10 marks)

6. (a) Give an example for each of the following type of isomerism in metal complexes:

(i) Ionization

(ii) Hydration

(iii) Coordination

(iv) Linkage

(v) Geometric

(10 marks)

(b) Consider the following redox reaction between two coordination complexes:

$[Co(NH_3)_5Cl]^{2+} + [Ru(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_5Cl]^{+} + [Ru(NH_3)_6]^{3+}$

(i) Give the names of the products from the above redox reaction.

(ii) What type of redox mechanism is involved? State the effects on the reactants and the rate of electron transfer in this reaction.

(iii) Give the mechanistic details if the redox reaction occurred via an alternative redox mechanism.

(10 marks)

7. (a) Give brief description of the following: (i) peptide (ii) metalloprotein and (iii) haem unit. Give an account of the storage and transport of metalloproteins in mammals. How does the uptake of iron by aerobic microorganisms differ from that in mammals?

(10 marks)

(b) Give the IUPAC name for each of the following compounds:

(i) $[Ni(acac)\{P(C_6H_5)_3\}_4]NO_3$

(ii) $[(NH_3)_2(en)Cr(\mu\text{-}O_2)_2Co(NH_3)_4]Br_6$

(iii) $[Fe(en)_3][IrCl_6]$

(iv) $[(SCN)_3(H_2O)_2Cr(\mu\text{-}OH)Co(NH_3)_5]SO_4$

(v) $[Fe(CN)_2(CH_3NC)_4]$

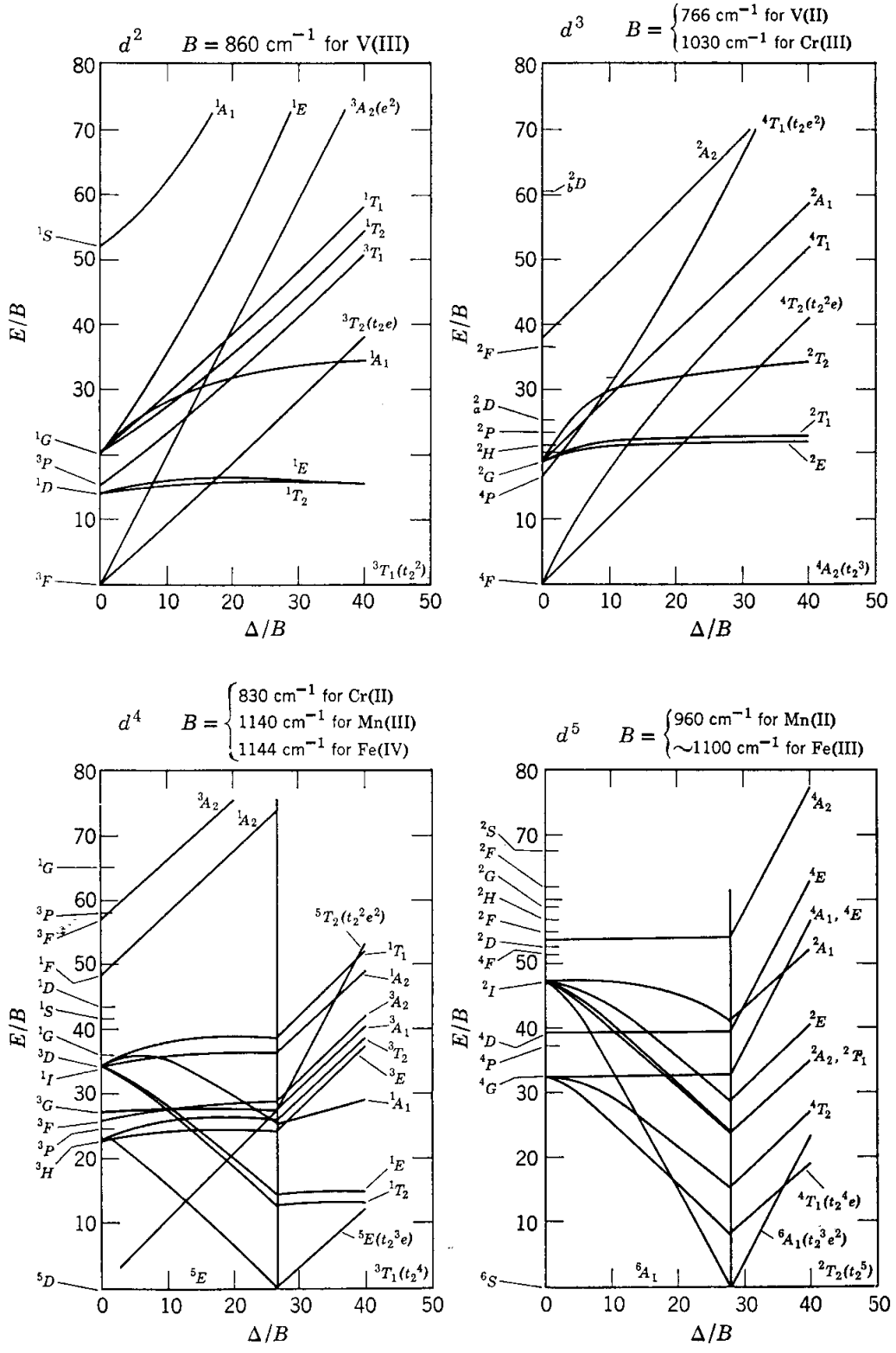
(5 marks)

(c) Which of the coordination complex in the following pairs is more stable? Give reason for your choice.

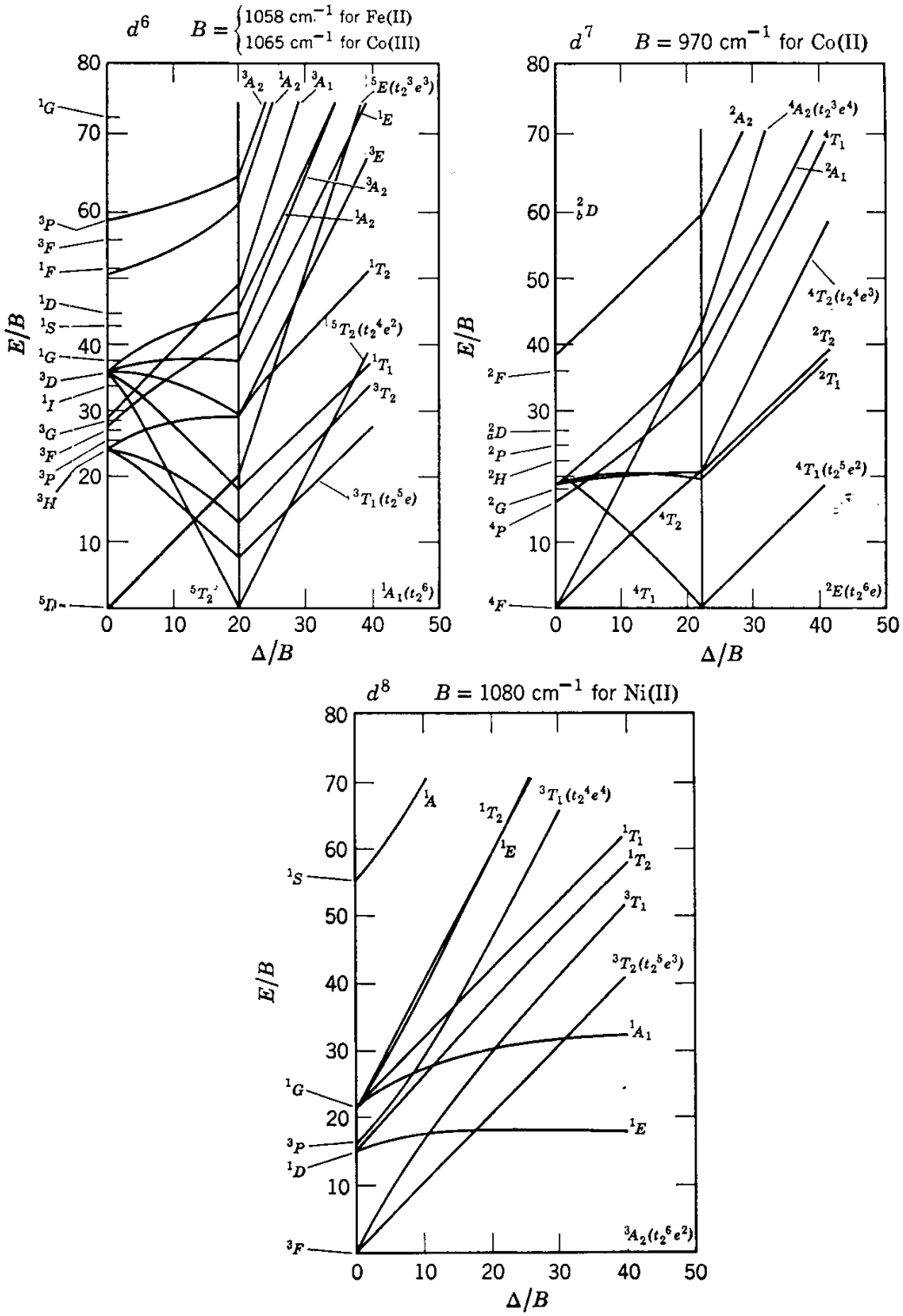
(i) $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5\ I\ ]^{2+}$;

(ii) $[Co(CN)_5I]^{3-}$ and $[Co(CN)_5\ F]^{3-}$

(5 marks)


d^2 $B = 860$ cm^{-1} for V(III)
$^1A_1$
^1E
$^3A_2(e^2)$
$^1T_1$
$^1T_2$
$^3T_1$
$^3T_2(t_2e)$
$^1A_1$
^1S
^1G
^3P
^1D
^1E
$^1T_2$
^3F
$^3T_1(t_2^2)$
E/B
Δ/B
d^3 $B =$ 766 cm^{-1} for V(II), 1030 cm^{-1} for Cr(III)
$^4T_1(t_2e^2)$
$^2A_2$
^2D
$^2A_1$
$^4T_1$
$^4T_2(t_2^2e)$
^2F
$^2T_2$
^2D
$^2T_1$
^2P
^2H
^2E
^2G
^4P
^4F
$^4A_2(t_2^3)$
d^4 $B =$ 830 cm^{-1} for Cr(II), 1140 cm^{-1} for Mn(III), 1144 cm^{-1} for Fe(IV)
$^3A_2$
$^1A_2$
$^5T_2(t_2^2e^2)$
$^1T_1$
$^1A_2$
$^3A_2$
$^3A_1$
$^3T_2$
^3E
$^1A_1$
^1E
$^1T_2$
$^5E(t_2^3e)$
^1G
^3P
^3F
^1F
^1D
^1S
^1G
^3D
^1I
^3G
^3F
^3P
^3H
^5D
^5E
$^3T_1(t_2^4)$
d^5 $B =$ 960 cm^{-1} for Mn(II), ~1100 cm^{-1} for Fe(III)
$^4A_2$
^4E
$^4A_1, ^4E$
$^2A_1$
^2E
$^2A_2, ^2T_1$
$^4T_2$
$^4T_1(t_2^4e)$
$^6A_1(t_2^3e^2)$
^2S
^2F
^2G
^2H
^2F
^2D
^4F
^2I
^4D
^4P
^4G
^6S
$^6A_1$
$^2T_2(t_2^5)$

…9/-


d^6 $B = \begin{cases} 1058\ \text{cm}^{-1} \text{ for Fe(II)} \\ 1065\ \text{cm}^{-1} \text{ for Co(III)} \end{cases}$
d^7 $B = 970\ \text{cm}^{-1}$ for Co(II)
d^8 $B = 1080\ \text{cm}^{-1}$ for Ni(II)
E/B
Δ/B

Bahagian A

Soalan **WAJIB**

1. (a) Lukiskan kesemua isomer bagi $[Co(NH_3)_2(H_2O)_2Cl_2]^+$. Kenalpastikan pasangan enantiomer.

(6 markah)

(b) Bagi setiap kompleks logam di bawah, tentukan keadaan pengoksidaan bagi logam, bilangan elektron pada logam (d^n) dan sama ada kompleks berikut mematuhi peraturan 18-elektron.

(i) $[Rh(bipy)_2Cl]^+$

(ii) $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$

(iii) $[Ni(en)_3]^{2+}$

(iv) $[FeCl_4]^{2-}$

(v) $[(\eta^4\text{-}C_4H_4)(\eta^5\text{-}C_5H_5)Ni]^+$

(vi) $Na_4[Co(C_2O_4)_2Br_2]$

(9 markah)

(c) Pertimbangkan tindak balas berikut:

$$H^+ + CH_3HgOH \rightarrow H_2O + CH_3Hg^+ \qquad \log K_1 = 6.3$$

$$H^+ + CH_3HgS^- \rightarrow HS^- + CH_3Hg^+ \qquad \log K_2 = -8.4$$

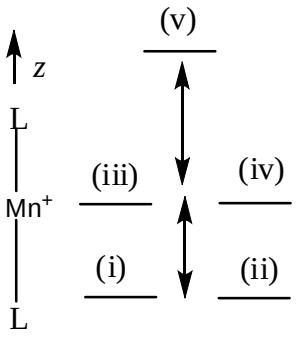
Komen tentang perbezaan nilai pemalar keseimbangan bagi persamaan 1 dan 2 berdasarkan prinsip acid bes keras lembut (HASB).

(5 markah)

2. (a) Bagaimanakah teori medan hablur dan teori ikatan valens melihat pengikatan dalam kompleks koordinatan? Apakah kelemahan teori ikatan valens yang dapat diatasi oleh teori medan hablur?

(6 markah)

(b) Gambarajah aras tenaga bagi medan linear berorientasi sepanjang paksi *z* ditunjukkan di bawah:



aras tenaga

Nyatakan kelima-lima orbital d, (i)-(v) dalam gambarajah ini berdasarkan pemisahan yang anda jangka serta jelaskan jawapan anda.

(6 markah)

(c) Adakah kompleks diamagnetik $[Ni(CN)_4]^{2-}$ lebih berkemungkinan mempunyai geometri tetrahedral atau satah empat segi sama? Tunjukkan jalan kerja anda.

(4 markah)

(d) Larutan akueus Zn^{2+} tidak berwarna, larutan akueus $[Co(en)_3]^{3+}$ berwarna kuning manakala larutan akueus $[CoF_6]^{3-}$ berwarna biru. Jelaskan.

(4 markah)

3. (a) Pertimbangkan ion mangan(II). Ion kompleks heksaakua tersebut berwarna merah-jambu pudar, sementara ion kompleks heksasiano berwarna ungu dengan keamatan yang tinggi.

(i) Jelaskan perbezaan keamatan warna bagi kedua-dua kompleks tersebut. Gunakan gambarajah orbital berlabel untuk menjelaskan pandangan anda.

(ii) Adakah kompleks ini mempunyai sifat kemagnetan yang berbeza? Jika benar, jelaskan kenapa.

(10 markah)

(b) Kebanyakan kompleks logam peralihan tetrahedral adalah jenis spin-tinggi Komen.

(5 markah)

(c) (i) Dengan menggunakan gambarajah Tanabe-Sugano, apakah jalur penyerapan yang dijangkakan bagi kompleks spin-tinggi d^4 oktahedral? Manakah antaranya yang memberikan nilai Δ_o?

(ii) Gambarajah Tanabe-Sugano yang manakah akan anda gunakan untuk meramal peralihan elektron bagi kompleks tetrahedral d^3? Apakah peralihan yang dijangkakan dan peralihan yang manakah memberikan Δ_t?

(5 markah)

Bahagian B

Jawab **DUA** (2) soalan

4. (a) Menurut model Kepert, geometri apakah yang akan anda kaitkan dengan nombor koordinatan berikut?

(i) 2

(ii) 3

(iii) 4

(iv) 5

(v) 6

(7 markah)

(b) (i) Hitung ΔS bagi tindak balas berikut pada 25 °C. Diberi $\Delta H = -27.6$ kJ mol^{-1} dan $K = 1.4 \times 10^6$ pada 25°C.

$$[Cu(H_2O)_6]^{2+} + 3en \rightleftharpoons [Cu(en)_3]^{2+} + 6H_2O$$

(ii) Kirakan momen magnet (dalam BM) bagi kompleks $K_3[Fe(ox)_3].3H_2O$.

(7 markah)

(c) (i) Lukiskan suatu gambarajah Orbital Molekul(MO) bagi interaksi antara logam-penerima dan ligan-penderma. Label dengan jelas penderma, D dan penerima, A.

(ii) Dengan menggunakan gambarajah MO, nyatakan tertib ikatan bagi $[Ni(NH_3)_6]^{2+}$ dan $[Cr(NH_3)_6]^{2+}$.

(6 markah)

5. (a) Tindak balas nikel(II) bromida bersama etildifenilfosfina ($PEtPh_2$) dalam butanol menghasilkan suatu sebatian berwarna hijau. Analisis unsure menunjukkan peratus komposisi; Ni 9.1%, Br 24.7%, P 9.6%, C 52.0% dan H 4.6%. Apabila sebatian hijau dilarutkan dalam benzena dan disejukkan di bawah suhu bilik, suatu sebatian merah dengan komposisi unsur yang sama diperolehi. Namun hablur merah yang diasingkan kembali menjadi warna hijau apabila dibiarkan pada suhu bilik. Nilai kemagnetan sebatian hijau menunjukkan sifat paramagnetik dan sebatian merah diamagnetik. Kenalpasti sebatian hijau dan merah dengan menunjukkan **SECARA JELAS** tindak balas yang berlaku dan **STRUKTUR** bagi semua sebatian tersebut.

Jisim atom: Ni 58.69 Br 79.90 P 30.97 C 12.07 H 1.00

(10 markah)

(b) (i) Keterlarutan relatif argentum halida menurun dari AgF (tinggi) ke AgCl (sederhana), AgBr (rendah) dan AgI (paling rendah). Jelaskan tren keterlarutan ini dan ramalkan keterlarutan relatif untuk merkuri(I) halida dan litium halida dalam air. Jelaskan ramalan anda.

(ii) 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 penambahan kestabilan ini dari sudut entalpi dan entropi.

(10 markah)

6. (a) Berikan satu contoh bagi setiap jenis keisomeran berikut dalam kompleks logam:

(i) Pengionan

(ii) Hidratan

(iii) Koordinatan

(iv) Linkej

(v) Geometrik

(10 markah)

(b) Pertimbangkan tindak balas redoks berikut antara dua kompleks koordinatan:

$[Co(NH_3)_5Cl]^{2+} + [Ru(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_5Cl]^{+} + [Ru(NH_3)_6]^{3+}$

(i) Berikan nama bagi kompleks yang terhasil dalam tindak balas redoks tersebut.

(ii) Apakah jenis mekanisme redoks yang berlaku? Nyatakan kesan terhadap bahan tindak balas dan kadar pemindahan elektron dalam tindak balas tersebut.

(iii) Berikan perincian mekanisme yang berlaku jika tindak balas redoks tersebut mengikut laluan mekanisme alternatif yang lain.

(10 markah)

7. (a) Berikan huraian ringkas mengenai perkara berikut: (i) peptida (ii) metalloprotein dan (iii) unit haem. Berikan huraian tentang penyimpanan dan pengangkutan metalloprotein dalam mamalia. Bagaimana pengambilan besi oleh mikroorganisma aerobik berbeza daripada apa yang terdapat pada mamalia?

(10 markah)

(b) Berikan nama IUPAC bagi setiap sebatian berikut:

(i) $[Ni(acac)\{P(C_6H_5)_3\}_4]NO_3$

(ii) $[(NH_3)_2(en)Cr(\mu\text{-}O_2)_2Co(NH_3)_4]Br_6$

(iii) $[Fe(en)_3][IrCl_6]$

(iv) $[(SCN)_3(H_2O)_2Cr(\mu\text{-}OH)Co(NH_3)_5]SO_4$

(v) $[Fe(CN)_2(CH_3NC)_4]$

(5 markah)

(c) Yang manakah antara pasangan kompleks koordinatan berikut lebih stabil? Berikan sebab bagi pilihan anda.

(i) $[Co(NH_3)_5F]^{2+}$ dan $[Co(NH_3)_5\ I\ ]^{2+}$;

(ii) $[Co(CN)_5I]^{3-}$ dan $[Co(CN)_5\ F]^{3-}$

(5 markah)

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