UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2010/2011

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.

1. (a) Terpyridine (tpy) is a tridentate ligand.

Terpyiridine (tpy)

i. Name and draw the two possible isomers for the complex $[Fe(tpy)Cl_3]$.

ii. Propose which of the isomers you expect to be more stable and give an explanation.

iii. Why is the overall stability constant, β_6 for $[Fe(tpy)Cl_3]$ complex higher than that for a similar isomer of $[Fe(py)_3Cl_3]$? (py = pyridine)

iv. Given that the magnetic moment for the stable isomer of $[Fe(tpy)Cl_3]$ complex is 5.85 BM at 298 K. Explain its magnetic properties and influence of the ligands.

(15 marks)

(b) Give the chemical formula and draw the structures for each of the following complexes.

i. μ-hydroxobis(pentaaminechromium(III)) chloride

ii. Bis(methylamine)silver(I) diaquadioxalatomanganate(II)

(5 marks)

2. (a) On the same scale of orbital energy, draw the crystal field splitting diagrams for octahedral and tetrahedral fields (referred to a common barycentre).

(4 marks)

(b) List the factors that determine Δ, the crystal field splitting energy.

(4 marks)

(c) Four-coordinate nickel(II) complexes exhibit both square-planar and tetrahedral geometries. The tetrahedral ones such as $[NiCl_4]^{2-}$ are paramagnetic while the square-planar ones such as $[Ni(CN)_4]^{2-}$ are diamagnetic. Show how the *d* electrons of nickel(II) populate the d orbitals in the appropriate crystal field splitting diagram in each case.

(5 marks)

(d) Calculate ligand field stabilization energies in 6-coordinate high-spin and low-spin complexes of Fe^{3+}.

(3 marks)

(e) Discuss Jahn-Teller effect on absorption spectrum of d^1 and d^9 complexes. What type of bands can be expected? Provide explanation for the appearance of the bands.

(4 marks)

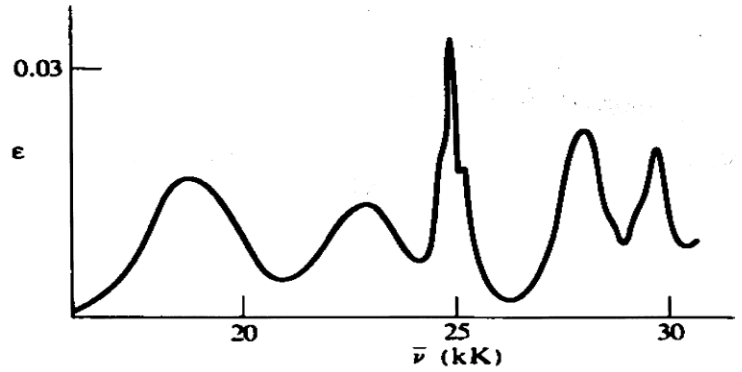
3. (a) Describe briefly the following terms using appropriate example:

i. *LaPorte*'s Rule

ii. Spin Selection Rule

(8 marks)

(b) It has been reported that a solution of 1.0 M $[Mn(H_2O)_6]^{2+}$ is very pale pink in colour or almost colourless. The electronic spectrum for this complex is shown as follows:



i. Based on the Tanabe-Sugano Diagram, determine which side of the vertical line will be used to explain the electronic transitions for $[Mn(H_2O)_6]^{2+}$.

ii. Based on the answer from (i), suggest the most probable type of transitions for this compound. Explain.

(12 marks)

SECTION B

4. (a) A large excess of concentrated hydrochloric acid is added to the cobalt(II) nitrate solution.

i. Write the equation for the above reaction.

ii. Draw the structure of the complex present in the solution.

iii. What is the hybridization of the cobalt ion? Give the electronic configuration of the metal ion.

iv. Predict the color of the complex which is formed. Is the molar absorptivity, ε, large or small? Explain.

(7 marks)

(b) i. Are these complex ions, $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ paramagnetic? Briefly explain your answer.

ii. Calculate spin-only magnetic moment in Bohr Magneton (BM) for the above complexes $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$.

(7 marks)

(c) $[Fe(H_2O)_6]^{2+}$ and $[Ru(H_2O)_6]^{2+}$ react with chloride at the respective rate as follows:

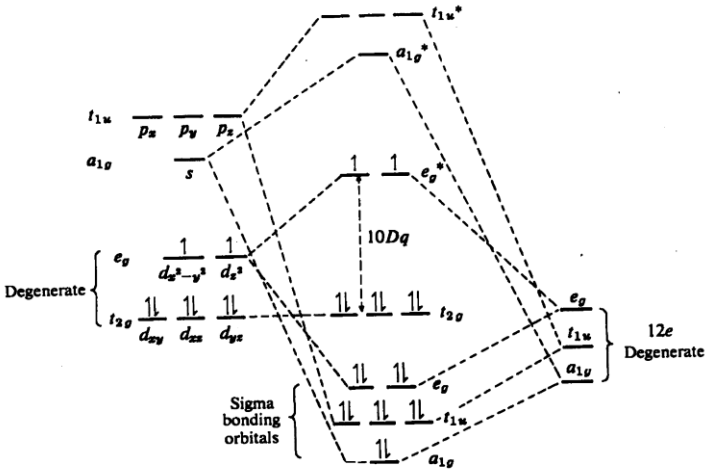
$$[Fe(H_2O)_6]^{2+} + Cl^- \longrightarrow [FeCl(H_2O)_5]^{2+} + H_2O \quad k = 10^6\ M^{-1}\ s^{-1}$$
$$[Ru(H_2O)_6]^{2+} + Cl^- \longrightarrow [RuCl(H_2O)_5]^{2+} + H_2O \quad k = 10^{-2}\ M^{-1}\ s^{-1}$$

i. Write the electronic configurations for Fe and Ru in $[Fe(H_2O)_6]^{2+}$ and $[Ru(H_2O)_6]^{2+}$ based on Molecular Orbital Theory.

ii. The rate constant for $[Fe(H_2O)_6]^{2+}$ is greater than that for $[Ru(H_2O)_6]^{2+}$. Explain.

(6 marks)

5. (a) The Molecular Orbital Diagram for $[Ni(H_2O)_6]^{2+}$ is shown as follows:



i. Which portion of the diagram is also considered by Crystal Field Theory?

ii. Based on the answer from (i), calculate the Ligand Filed Stabilization Energy (LFSE) for this complex.

iii. Valence Bond Theory is found to be not suitable in describing the electronic configuration for nickel in $[Ni(H_2O)_6]^{2+}$. Explain.

(10 marks)

(b) i. Relative solubilies of silver halides in water are given as follows:

$AgF(s) + H_2O \longrightarrow Ag^+(aq) + F^-(aq)$ k_{sp}: 205

$AgCl(s) + H_2O \longrightarrow Ag^+(aq) + Cl^-(aq)$ k_{sp}: 1.8×10^{-10}

$AgBr(s) + H_2O \longrightarrow Ag^+(aq) + Br^-(aq)$ k_{sp}: 5.2×10^{-13}

$AgI(s) + H_2O \longrightarrow Ag+(aq) + I^-(aq)$ k_{sp}: 8.3×10^{-17}

Provide explanation for the above k_{sp} data and predict the relative solubilies of mercury(I) halides and lithium halides in water. Explain your predictions.

ii. Ligand displacements in the following reactions have the corresponding Log K and ΔG_1^o values:

$[NiL_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6L(aq)$
Log K = 2.41, ΔG_1^o = -13.7 kJ mol^{-1}

$[NiL_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6L(aq)$
Log K = 9.27, ΔG_1^o = -52.9 kJ mol^{-1}

Explain the reasons for the difference in Log K and ΔG_1^o values for the above reactions from the entropy and enthalpy considerations. What is this effect called?

(10 marks)

6. (a) Equilibrium favors the most thermodynamically stable side. Factors that influence the stability of coordination complexes are the electron count on the metal and the strength of the ligand-metal interactions. For each of the following reactions, determine whether the equilibria lie to the left or the right and determine if the ligand exchange occurs by the associative or dissociative mechanism. Briefly explain your choice.

i. $Fe(CO)_4 + CO$ $Fe(CO)_5$

ii. $[CoCl_4]^{2-} + H_2O$ $[CoCl_3(H_2O)]^- + Cl^-$

iii. $RhCl_3(H_2O)_3 + P(CH_3)_3$ $[RhCl(H_2O)_3[P(CH_3)_3]] + 2Cl^-$

(10 marks)

(b) i. Which of the following complexes of Ti^{3+} exhibits the shortest wavelength absorption in the visible spectrum?

$[Ti(H_2O)_6]^{3+}$; $[Ti(en)_3]^{3+}$; $[TiCl_6]^{3-}$

Explain.

ii. List the weaknesses of Valence Bond Theory in explaining the properties of coordination complexes.

(10 marks)

7. (a) i. Explain how iron is stored and transported in mammals.

ii. Provide a description on cytochrome chain and its advantages of having such a complex system.

(10 marks)

(b) Name according to IUPAC, draw the structures, types of hybridization and draw the isomers (if any) for each of the following complexes.

i. $K[VF_4]\bullet H_2O$

ii. $[Pt(CO)_2(CN)_2]$

iii. $[Ir(Br)_2(CH_3)(CO)(PPh_3)]$; Ph = C_6H_5

iv. $[Co(PMe_3)_3(Me)_2Br]Cl_2$; Me = CH_3

(10 marks)

TANABE-SUGANO DIAGRAMS

BAHAGIAN A

1. (a) Terpiridina (tpy) adalah suatu ligan tridentat.

Terpiridina (tpy)

i. Berikan nama dan lukiskan dua isomer yang wujud bagi kompleks $[Fe(tpy)Cl_3]$.

ii. Cadangkan isomer yang lebih stabil dan berikan penjelasan.

iii. Kenapa pemalar penstabilan keseluruhan, β_6 bagi kompleks $[Fe(tpy)Cl_3]$ adalah lebih tinggi daripada kompleks $[Fe(py)_3Cl_3]$ yang terdiri daripada jenis isomer yang sama? (py = piridina)

iv. Momen kemagnetan isomer yang lebih stabil bagi kompleks $[Fe(tpy)Cl_3]$ ialah 5.85 BM pada suhu 298 K. Jelaskan sifat kemagnetan dan pengaruh ligan terhadapnya.

(15 markah)

(b) Berikan formula kimia dan lukiskan struktur bagi setiap kompleks berikut.

i. μ-hidroksobis(pentaaminakromium(III) klorida

ii. Bis(metilamina)argentum(I) diakuadioksalatomanganat(II)

(5 markah)

2. (a) Atas skala tenaga orbital yang sama, lukis rajah pemecahan medan hablur bagi medan oktahedral dan tetrahedral (merujuk kepada *barycentre* yang sama).

(4 markah)

(b) Senaraikan faktor yang menentukan Δ, tenaga pemecahan medan hablur.

(4 markah)

(c) Kompleks empat-koordinat nikel(II) mempunyai kedua-dua geometri satah segiempat dan tetrahedral. Kompleks bergeometri tetrahedral seperti $[NiCl_4]^{2-}$ adalah bersifat paramagnetik manakala kompleks bergeometri satah segiempat seperti $[Ni(CN)_4]^{2-}$ adalah bersifat diamagnetik. Tunjukkan bagaimana elektron *d* nikel(II) menduduki orbital d dalam rajah pemecahan medan hablur yang bersesuaian untuk setiap kes.

(5 markah)

(d) Kira tenaga penstabilan medan hablur dalam kompleks Fe^{3+} berkoordinatan 6 dalam keadaan spin tinggi dan rendah.

(3 markah)

(e) Bincangkan kesan Jahn-Teller pada spektrum penyerapan kompleks d^1 dan d^9. Apakah jenis jalur yang dijangkakan? Beri penjelasan tentang kehadiran jalur tersebut.

(4 markah)

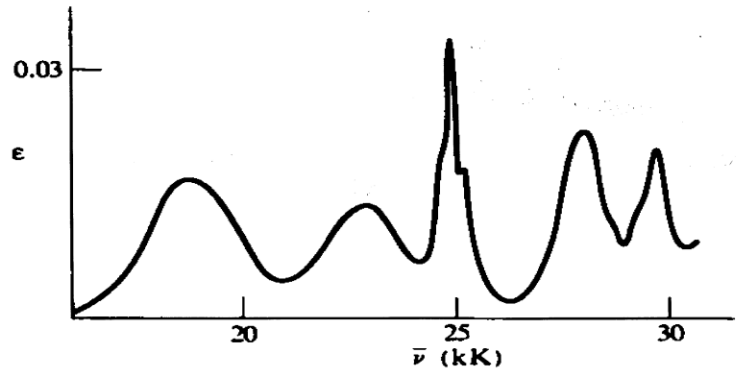
3. (a) Huraikan secara ringkas setiap istilah berikut dengan contoh yang sesuai:

i. Peraturan *LaPorte*

ii. Peraturan Pemilihan Spin

(8 markah)

(b) Telah dilaporkan bahawa larutan 1.0 M $[Mn(H_2O)_6]^{2+}$ adalah berwarna merah jambu yang pucat atau hampir tidak berwarna. Spektrum elektronik bagi kompleks ini ditunjukkan di bawah:



i. Berdasarkan Gambarajah Tanabe-Sugano, tentukan bahagian manakah dari garisan yang tegak akan digunakan untuk menjelaskan peralihan elektronik bagi $[Mn(H_2O)_6]^{2+}$.

ii. Berdasarkan jawapan dari (i), cadangkan jenis peralihan yang paling mungkin bagi sebatian ini. Jelaskan.

(12 markah)

BAHAGIAN B

4. (a) Asid hidroklorik telah ditambah secara berlebihan kepada suatu larutan kobalt nitrat(II).

i. Tulis persamaan bagi tindak balas tersebut.

ii. Lukis struktur kompleks yang wujud di dalam larutan tersebut.

iii. Apakah jenis penghibridan pada ion kobalt? Berikan konfigurasi elektronik ion logam kobalt.

iv. Ramal warna kompleks yang terbentuk. Apakah nilai penyerapan molar, ε, besar atau kecil? Jelaskan.

(7 markah)

(b) i. Adakah ion kompleks $[Co(H_2O)_6]^{2+}$ dan $[CoCl_4]^{2-}$ bersifat paramagnetik? Jelaskan secara ringkas jawapan anda.

ii. Kirakan momen magnet spin-sahaja dalam Bohr Magneton (BM) bagi kompleks di atas $[Co(H_2O)_6]^{2+}$ dan $[CoCl_4]^{2-}$.

(7 markah)

(c) $[Fe(H_2O)_6]^{2+}$ dan $[Ru(H_2O)_6]^{2+}$ bertindakbalas dengan klorida masing-masing pada kadar seperti berikut:

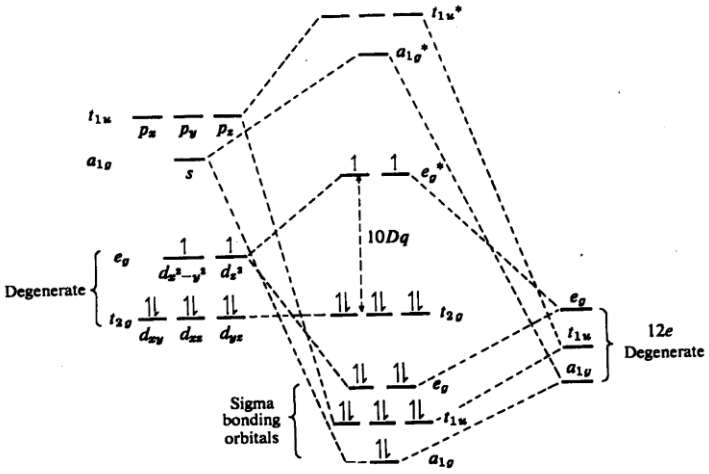
$$[Fe(H_2O)_6]^{2+} + Cl^- \longrightarrow [FeCl(H_2O)_5]^{2+} + H_2O \quad k = 10^6\ M^{-1}\ s^{-1}$$
$$[Ru(H_2O)_6]^{2+} + Cl^- \longrightarrow [RuCl(H_2O)_5]^{2+} + H_2O \quad k = 10^{-2}\ M^{-1}\ s^{-1}$$

i. Tuliskan konfigurasi elektronik bagi Fe dan Ru dalam $[Fe(H_2O)_6]^{2+}$ dan $[Ru(H_2O)_6]^{2+}$ berdasarkan Teori Orbital Molekul.

ii. Pemalar kadar bagi $[Fe(H_2O)_6]^{2+}$ lebih besar daripada $[Ru(H_2O)_6]^{2+}$. Jelaskan.

(6 markah)

5. (a) Gambarajah Orbital Molekul bagi $[Ni(H_2O)_6]^{2+}$ ditunjukkan berikut:



i. Di bahagian gambarajah yang manakah juga dipertimbangkan oleh Teori Medan Hablur?

ii. Berdasarkan jawapan dari (i), hitungkan Tenaga Penstabilan Medan Hablur (CFSE) bagi kompleks ini.

iii. Teori Ikatan Valens didapati tidak sesuai untuk menghuraikan konfigurasi elektron bagi ion nikel dalam $[Ni(H_2O)_6]^{2+}$. Jelaskan.

(10 markah)

(b) i. Keterlarutan relatif argentum halida dalam air diberi seperti berikut:

$AgF(p) + H_2O \longrightarrow Ag^+(ak) + F^-(ak)$ k_{sp}: 205

$AgCl(p) + H_2O \longrightarrow Ag^+(ak) + Cl^-(ak)$ k_{sp}: 1.8×10^{-10}

$AgBr(p) + H_2O \longrightarrow Ag^+(ak) + Br^-(ak)$ k_{sp}: 5.2×10^{-13}

$AgI(p) + H_2O \longrightarrow Ag+(ak) + I^-(ak)$ k_{sp}: 8.3×10^{-17}

Berikan penjelasan untuk data k_{sp} di atas dan ramalkan keterlarutan relatif bagi merkuri(I) halida dan litium halida dalam air. Jelaskan ramalan anda.

ii. Penukargantian ligan dalam tindak balas di bawah mempunyai nilai Log K dan ΔG_1^o seperti berikut:

$[NiL_6]^{2+}(ak) + 6NH_3(ak) \rightleftharpoons [Ni(NH_3)_6]^{2+}(ak) + 6L(ak)$
Log K = 2.41, $\Delta G_1^o = -13.7$ kJ mol^{-1}

$[NiL_6]^{2+}(ak) + 3en(ak) \rightleftharpoons [Ni(en)_3]^{2+}(ak) + 6L(ak)$
Log K = 9.27, $\Delta G_1^o = -52.9$ kJ mol^{-1}

Jelaskan sebab perbezaan dalam nilai Log K dan ΔG_1^o bagi tindak balas di atas dari pertimbangan entropi dan entalpi. Apakah nama kesan ini?

(10 markah)

6. (a) Keseimbangan tindak balas cenderung kepada kompleks yang lebih stabil daripada segi termodinamik. Faktor yang mempengaruhi kestabilan kompleks koordinatan adalah bilangan elektron pada logam dan kekuatan interaksi ligan-logam. Bagi setiap tindak balas berikut, nyatakan sama ada keseimbangan memihak ke kanan atau ke kiri dan nyatakan sama ada pertukaran ligan berlaku melalui mekanisme asosiatif atau disosiatif. Berikan penjelasan.

i. $Fe(CO)_4 + CO$ $Fe(CO)_5$

ii. $[CoCl_4]^{2-} + H_2O$ $[CoCl_3(H_2O)]^- + Cl^-$

iii. $RhCl_3(H_2O)_3 + P(CH_3)_3$ $[RhCl(H_2O)_3[P(CH_3)_3]] + 2Cl^-$

(10 markah)

(b) i. Manakah antara kompleks Ti^{3+} berikut menunjukkan jalur gelombang penyerapan paling rendah dalam spektrum ternampakkan?

$[Ti(H_2O)_6]^{3+}$; $[Ti(en)_3]^{3+}$; $[TiCl_6]^{3-}$

Jelaskan.

ii. Senaraikan kelemahan Teori Ikatan Valens dalam menjelaskan sifat kompleks koordinatan.

(10 markah)

7. (b) i. Terangkan bagaimana ferum disimpan dan diangkut dalam mamalia.

ii. Berikan huraian mengenai rantai sitokrom dan kebaikannya memiliki sistem yang kompleks.

(10 markah)

(b) Namakan mengikut IUPAC, lukiskan struktur, jenis penghibridan dan lukiskan isomer yang wujud(jikalau ada) bagi setiap kompleks berikut.

i. $K[VF_4]\bullet H_2O$

ii. $[Pt(CO)_2(CN)_2]$

iii. $[Ir(Br)_2(CH_3)(CO)(PPh_3)]$; Ph = C_6H_5

iv. $[Co(PMe_3)_3(Me)_2Br]Cl_2$; Me = CH_3

(10 markah)

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