

UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2011/2012 Academic Session

June 2012

KTT 212 – Inorganic Chemistry II
[Kimia Takorganik II]

Duration : 3 hours
[Masa : 3 jam]

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

Instructions:

Answer **FIVE** (5) questions. **Section A** is **COMPULSORY**. Answer **ONE** (1) question from **Section B**. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

Answer 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**COMPULSORY** questions

1. (a) The complex $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$ forms four geometric isomers, whereas the complex $[\text{Pt}(\text{en})(\text{SCN})_2]$ forms only one. Sketch and name all these isomers.

(5 marks)

- (b) Draw structural formulas for the following compounds:

(i) potassium *trans*-dichlorobis(oxalato)cobaltate(III)

(ii) (acetylacetonato)-*cis*-dichloro-*trans*-bis(triphenylarsine)rhenium(III)

Are any of these compounds optically active? Give reasons for your answer.

(5 marks)

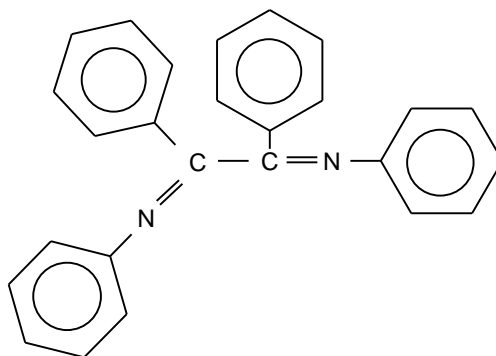
- (c) When complex salts of formula $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{X}$ were first synthesized, the NO_2^- anionic ligand was assumed to bond to the metal *via* the O atom. Draw the structures and give the names of the possible linkage isomers of this compound where X is the anion $[\text{AuCl}_4]^-$.

(6 marks)

- (d) Draw the optical isomers of $[\text{Co}(\text{en})_3]^{3+}$ showing the Δ (delta) and Λ (lambda) configurations.

(4 marks)

2. Compound bis(benzylideneaniline), **bba**, is a bidentate ligand. It is neutral and possesses the structural formula as follows:

**bba**

Compound **bba** reacts with Cr(II), Mn(II) and Ni(II) to give $\text{Cr}(\text{bba})_2\text{X}_2$, $\text{Mn}(\text{bba})_2\text{X}_2$ and $\text{Ni}(\text{bba})_2\text{X}_2$.

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- (a) Predict the magnetism for $\text{Cr}(\text{bba})_2\text{X}_2$, $\text{Mn}(\text{bba})_2\text{X}_2$ and $\text{Ni}(\text{bba})_2\text{X}_2$ if X is
- (i) Cl
 - (ii) CN
- (6 marks)

- (b) Propose the electronic spectrum for each of the following complexes based on Tanabe-Sugano Diagram:
- (i) $\text{Cr}(\text{bba})_2(\text{CN})_2$
 - (ii) $\text{Mn}(\text{bba})_2\text{Cl}_2$
 - (iii) $\text{Ni}(\text{bba})_2\text{Cl}_2$
- (9 marks)

For each spectrum, briefly explain the bands with high and low intensities.

- (c) Among all complexes in (b), which one is expected to undergo Jahn-Teller distortion. Give a reason.
- (5 marks)

3. (a) Determine whether or not the following compounds obey the 18-electron rule.
- (i) $\text{RhCl}(\text{H})_2(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2$
 - (ii) $[(\eta^2\text{-Cp})(\text{CoMe}(\text{PMe}_3)_2)]^+$ (Cp = cyclopentadienyl, C_5H_5)
 - (iii) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 - (iv) $[\text{Fe}(\text{CN})_6]^{4-}$
- (6 marks)

- (b) The magnetic moment, μ values for $\text{Cs}_2[\text{MnCl}_4]$ and $\text{K}_2[\text{Ni}(\text{CN})_4]$ are 5.9 and 0 B.M, respectively. Based on valence bond theory rationalize the hybridization of the metal orbitals and predict the structure of the complexes.
- (6 marks)

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- (c) When the blue, paramagnetic *trans*-[Ni(H₂O)₂(deen)₂]Br₂, *trans*-diaquabis(*N,N*-diethylethylenediamine)nickel(II) bromide is heated to drive off the two water ligands, it forms the orange, diamagnetic [Ni(deen)₂]Br₂, bis(*N,N*-diethylethylenediamine)nickel(II) bromide. Rationalize the colour and magnetic changes that occur during this reaction.

(deen = *N,N*-Diethylethylenediamine (CH₃CH₂)₂NCH₂CH₂NH₂, a bidentate ligand)

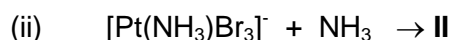
(8 marks)

4. (a) Give an explanation for each of the following:

- (i) Magnetic moment value, μ , for *trans*-Fe(phen)₂(NCS)₂ complex increases from 0.65 to 5.2 B.M. when the temperature is increased from 80 to 300 K.
- (ii) Complex [Cu(H₂O)₆]²⁺ in aqueous solution has two separate water exchange rates (k_1 and k_2).
- (iii) Pt(II) forms square planar complex but Ni(II) forms square planar and tetrahedral complexes.

(9 marks)

- (b) For each of the following reactions:



Predict the products **I** and **II**, and give a reason.

(6 marks)

- (c) Briefly explain the terms 'spectrochemical series'. Use the appropriate example to support your answer.

(5 marks)

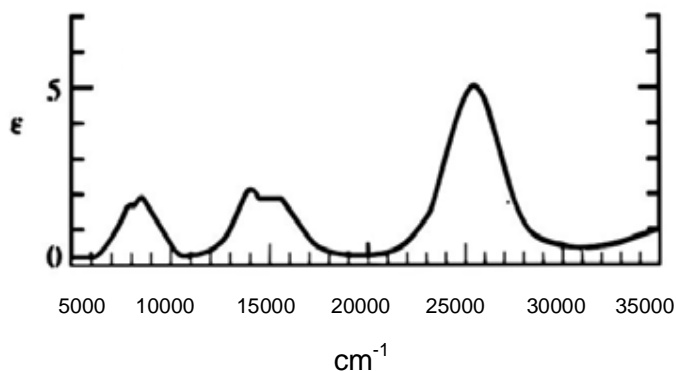
Section B

Answer any **ONE** (1) question.

5. (a) (i) How many unpaired electrons are there in strong field complex, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$?
- (ii) Give the structural formula for chlorotriphenylphosphinepalladium(II)- μ -dichlorochlorotriphenylphosphinepalladium(II).
- (iii) What is the meaning of a chelating agent?
- (iv) Give the name and draw the structure of a tridentate and a tetradentate ligand.
- (v) Give an example of a bridging ligand with two donor atoms.
- (10 marks)
- (b) (i) Determine the number of unpaired electrons and ligand field stabilization energy for each of the following complexes:
- $[\text{Cr}(\text{CN})_6]^{4-}$
 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 MnO_4^-
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- (ii) The tetrahedral geometry is more stable for Co(II) than Ni(II). Explain.
- (10 marks)
6. (a) Based on the HSAB Theory answer the following questions giving reasons where needed:
- (i) Why is a ligand considered as a Lewis base?
- (ii) State the HSAB (Hard and Soft Acid and Base) Theory
- (iii) Will Cu^{2+} react more strongly with OH^- or NH_3 ?
- (iv) Will Ag^+ react more strongly with NH_3 or PH_3 ?
- (v) Which complex is more stable, $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$?
- (10 marks)

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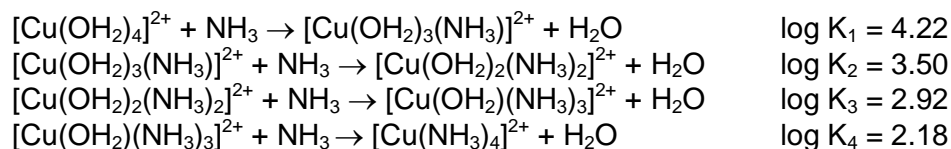
- (b) The electronic spectrum for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion is shown by the following figure:



Describe the spectrum pattern using crystal field theory and then correlate all the bands in the above figure with possible electronic transition.

(10 marks)

7. (a) (i) A coordination compound is found by analysis to contain 21.79% Co, 18.09% NH_3 and 39.32% Cl with the remaining molecules being H_2O . Derive an empirical formula for the compound.
- (ii) The individual step-wise equilibrium constants K_1 , K_2 , K_3 and K_4 , for the ammoniolysis of tetraaquacopper(II) cation is as follows:

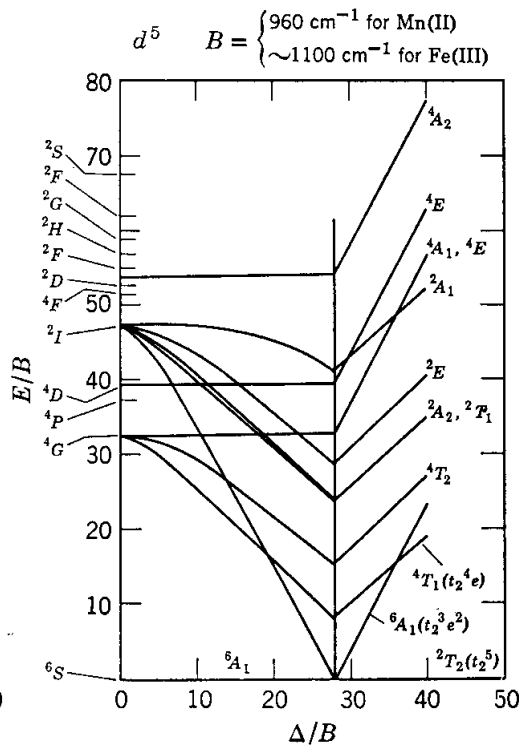
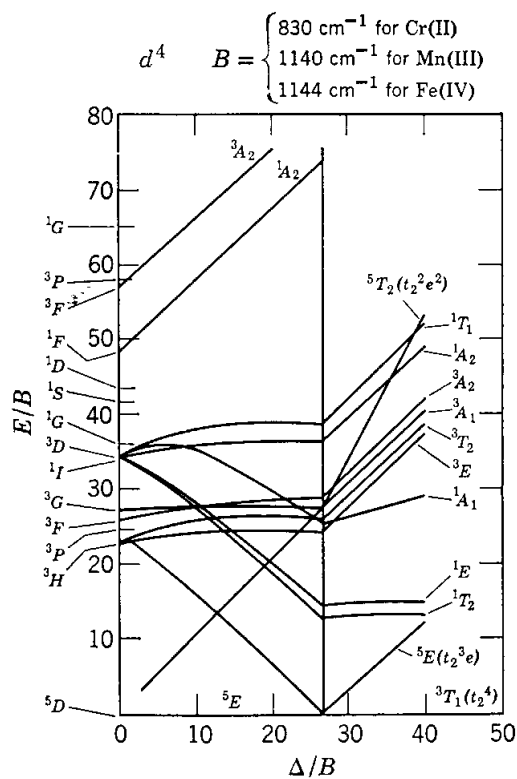
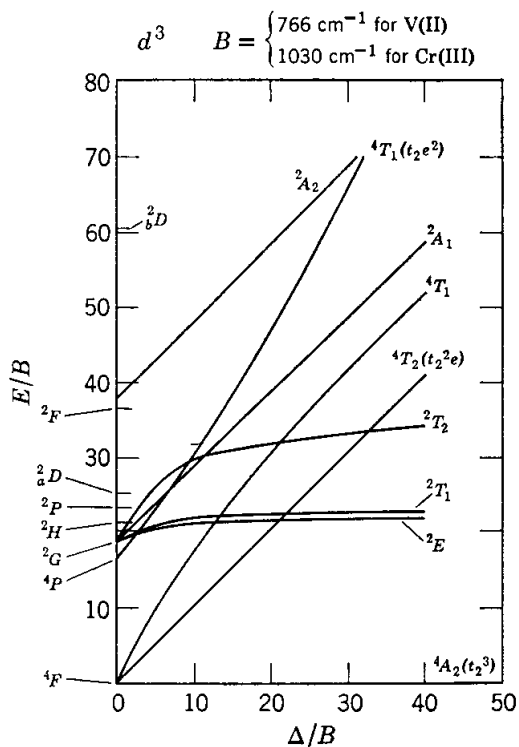
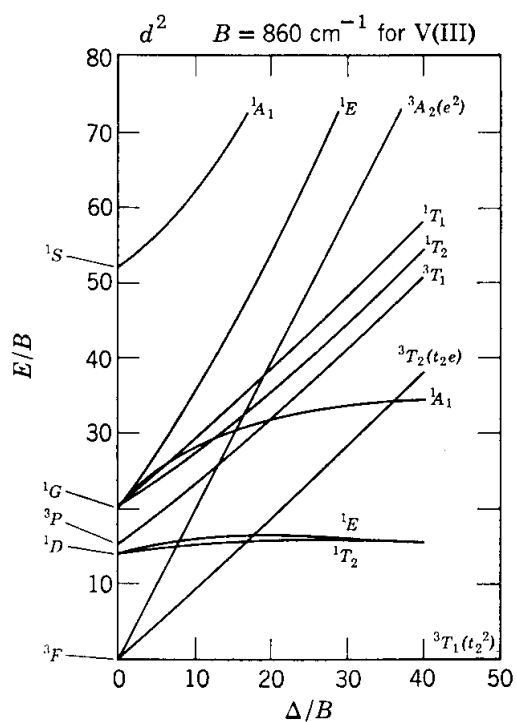


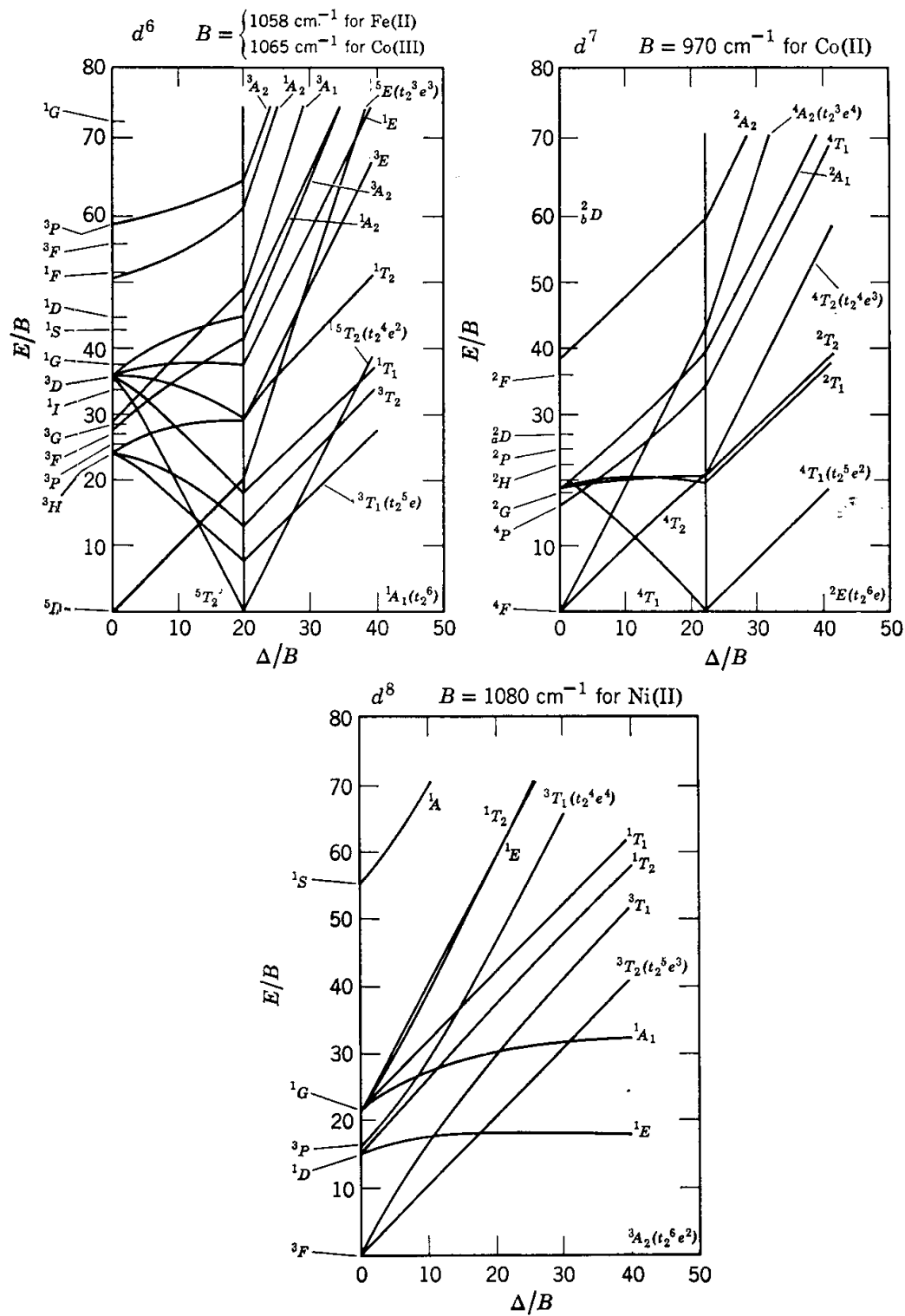
Calculate the overall equilibrium constants β_1 , β_2 , β_3 and β_4 .

(10 marks)

- (b) Iron metal (Fe) is an important element in the oxygen carrier process particularly in haemoglobin. Describe the characteristics of Fe in deoxyhaemoglobin and oxyhaemoglobin based on coordination chemistry.

(10 marks)



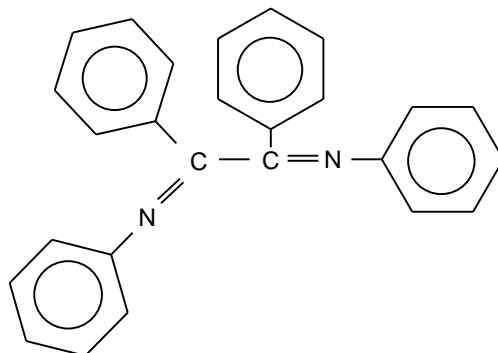


Bahagian ASoalan **WAJIB**.

1. (a) Kompleks $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$ membentuk empat isomer geometrik, manakala kompleks $[\text{Pt}(\text{en})(\text{SCN})_2]$ membentuk hanya satu isomer geometrik. Lakarkan dan beri nama kesemua isomer tersebut. (5 markah)
- (b) Lukiskan formula struktur bagi sebatian berikut:
- (i) kalium *trans*-diklorobis(oksalato)kobaltat(III)
- (ii) (asetilasetonato)-*cis*-dikloro-*trans*-bis(trifenilarsin)rhenium(III)
- Adakah sebarang dari sebatian ini aktif optik? Beri penjelasan bagi jawapan anda. (5 markah)
- (c) Bila garam kompleks dengan formula $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{X}$ pertama kali disintesis, ligan anion NO_2^- dianggapkan berikatan pada logam melalui atom O. Lukiskan struktur dan beri nama bagi isomer linkej yang mungkin bagi sebatian ini di mana X merupakan anion $[\text{AuCl}_4]^-$. (6 markah)
- (d) Lukiskan isomer optik bagi $[\text{Co}(\text{en})_3]^{3+}$ dengan menunjukkan konfigurasi Δ (delta) dan Λ (lambda). (4 markah)

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2. Sebatian bis(benzilidenaanilina), **bba**, merupakan sejenis ligan bidentat. Ia bersifat neutral dan mempunyai formula struktur berikut:

**bba**

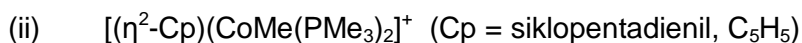
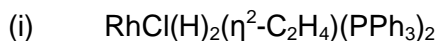
Sebatian **bba** bertindakbalas dengan Cr(II), Mn(II) dan Ni(II) menghasilkan $\text{Cr}(\text{bba})_2\text{X}_2$, $\text{Mn}(\text{bba})_2\text{X}_2$ dan $\text{Ni}(\text{bba})_2\text{X}_2$.

- (a) Ramalkan kemagnetan bagi $\text{Cr}(\text{bba})_2\text{X}_2$, $\text{Mn}(\text{bba})_2\text{X}_2$ dan $\text{Ni}(\text{bba})_2\text{X}_2$ jika X ialah
- Cl
 - CN
- (6 markah)
- (b) Dengan berdasarkan Gambarajah Tanabe-Sugano, cadangkan spektrum elektron yang mungkin dipamerkan oleh setiap kompleks berikut:
- $\text{Cr}(\text{bba})_2(\text{CN})_2$
 - $\text{Mn}(\text{bba})_2\text{Cl}_2$
 - $\text{Ni}(\text{bba})_2\text{Cl}_2$
- (9 markah)

Bagi setiap spektrum tersebut, terangkan secara ringkas jalur yang mempunyai intensiti tinggi dan rendah.

- (c) Antara semua kompleks dalam (b), yang manakah dijangka mengalami herotan Jahn-Teller. Berikan satu penjelasan.
- (5 markah)

3. (a) Tentukan sama ada sebatian berikut mematuhi peraturan 18 elektron.



(6 markah)

(b) Nilai moment magnet, μ bagi $\text{Cs}_2[\text{MnCl}_4]$ dan $\text{K}_2[\text{Ni}(\text{CN})_4]$ masing-masing adalah 5.9 dan 0 B.M.. Berdasarkan teori ikatan valens, beri alasan terhadap penghibridan orbital logam dan ramalkan struktur bagi kompleks tersebut.

(6 markah)

(c) Bila kompleks biru, berparamagnet *trans*- $[\text{Ni}(\text{H}_2\text{O})_2(\text{deen})_2]\text{Br}_2$, *trans*-diakuabis(*N,N*-dietiletilenadamina)nikel(II) bromida dipanaskan untuk mengeluarkan dua ligan air, kompleks berwarna oren, berdiamagnet $[\text{Ni}(\text{deen})_2]\text{Br}_2$, bis(*N,N*-dietiletilenadamina)nikel(II) bromida terbentuk. Beri alasan terhadap perubahan warna dan magnetik yang berlaku semasa tindak balas ini dijalankan.

(deen = *N,N*-dietiletilenadamina adalah $(\text{CH}_3\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NH}_2$, suatu ligan bidentat).

(8 markah)

4. (a) Berikan penjelasan ringkas tentang setiap perkara berikut:

(i) Nilai momen magnet, μ , bagi kompleks *trans*- $\text{Fe}(\text{phen})_2(\text{NCS})_2$ didapati bertambah dari 0.65 B.M. ke 5.2 B.M. apabila suhu meningkat dari 80 K ke 300 K.

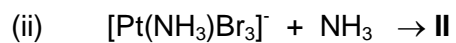
(ii) Kompleks $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ dalam larutan akueus mempunyai dua kadar penukaran air (k_1 dan k_2) yang berasingan.

(iii) Pt(II) membentuk kompleks satah persegi tetapi Ni(II) membentuk kedua-dua kompleks satah persegi dan tetrahedral.

(9 markah)

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(b) Bagi setiap tindak balas berikut:



Ramalkan produk I dan II yang dihasilkan dengan memberikan sebab.

(6 markah)

(c) Huraikan secara ringkas istilah 'siri spektrokimia'. Gunakan contoh yang sesuai untuk menyokong jawapan anda.

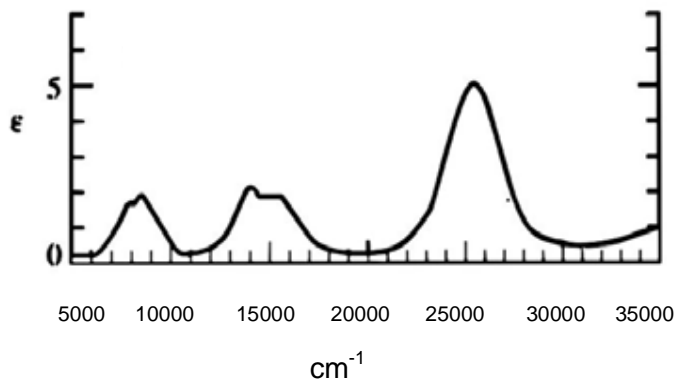
(5 markah)

Bahagian B

Jawab **SATU** (1) soalan.

5. (a) (i) Berapakah bilangan elektron takberpasangan yang terdapat di dalam kompleks $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ medan kuat?
- (ii) Beri formula struktur untuk klorotrifenilfosfinpaladium(II)- μ -dikloroklorotrifenilfosfinpaladium(II).
- (iii) Apakah makna agen pengkelatan?
- (iv) Beri nama dan lukiskan struktur bagi suatu ligan tridentat dan suatu ligan tetradentat.
- (v) Beri suatu contoh ligan titian dengan dua atom penderma.
- (10 markah)
- (b) (i) Tentukan bilangan elektron tak-berpasangan dan tenaga penstabilan medan ligan bagi setiap kompleks berikut:
- $[\text{Cr}(\text{CN})_6]^{4-}$
 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 MnO_4^-
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- (ii) Geometri tetrahedral bagi Co(II) didapati lebih stabil daripada Ni(II). Jelaskan.
- (10 markah)
6. (a) Berdasarkan pada Teori HSAB jawab soalan berikut dengan memberi sebab jika diperlukan:
- (i) Mengapa sesuatu ligan dipertimbangkan sebagai suatu bes Lewis?
- (ii) Nyatakan Teori HSAB (Asid dan Bes yang Keras dan Lembut)
- (iii) Adakah Cu^{2+} akan bertindakbalas lebih kuat dengan OH^- atau NH_3 ?
- (iv) Adakah Ag^+ akan bertindakbalas lebih kuat dengan NH_3 atau PH_3 ?
- (v) Kompleks yang manakah lebih stabil, $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$ atau $[\text{Co}(\text{NH}_3)_6]^{3+}$?
- (10 markah)

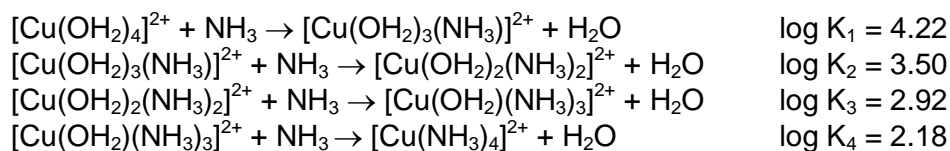
- (b) Spektrum elektron bagi ion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ditunjukkan oleh rajah berikut:



Huraikan corak spektrum yang diperolehi dengan teori medan hablur dan seterusnya hubungkan semua jalur yang terdapat dalam rajah di atas dengan peralihan elektron yang mungkin.

(10 markah)

7. (a) (i) Suatu sebatian koordinatan didapati mengandungi 21.79% Co, 18.09% NH_3 dan 39.32% Cl dengan molekul tertinggal sebagai H_2O . Terbitkan suatu formula empirik bagi sebatian tersebut.
- (ii) Pemalar keseimbangan berlangkah individu K_1 , K_2 , K_3 dan K_4 , untuk ammoniolisis kation tetraakuakuprum(II) adalah seperti berikut:



Kira pemalar keseimbangan keseluruhan β_1 , β_2 , β_3 dan β_4 .

(10 markah)

- (b) Logam (Fe) merupakan unsur yang penting dalam proses pembawa oksigen terutamanya dalam hemoglobin. Huraikan ciri bagi Fe dalam deoksihemoglobin dan oksihemoglobin dengan berdasarkan kimia koordinatan.

(10 markah)