Instructions:

Answer 4 questions.
Answer one question from each of Sections A and B and two questions from Section C.

Duration: 2 Hr.

No. of Answer books: 1

Requirements:

Handout
MCQ
Statistical Tables
Graph Paper
Log Graph Paper
Other Material

No. of Pages: 7

Department(s): Chemistry
Section A

Answer one question from this section.

1. Answer each of the following:

(a) Below is a magnetic susceptibility ($\chi_M T$) vs. Temperature curve obtained from a polycrystalline sample of a monomeric (distorted octahedral) Fe$^{2+}$ species of general formula [Fe(L)$_2$].

(i) Describe the above $\chi_M T$ vs. T plot. What does the shape of the curve tell you about the nature of this magnetic complex? Explain your reasoning. Give the name of this class of magnetic behaviour. [18 marks]

(ii) Label the critical temperature point ($T_c$) in the figure above. [2 marks]

(iii) The two ligands surrounding the single Fe$^{2+}$ centre in this complex each possess three N donor atoms, all of which bond to the metal centre. Explain the link between this structural characteristic and the resultant magnetic properties of this complex. [10 marks]

(iv) Upon cooling (say from point A to B in the above figure), such complexes often change colour. Explain why this can occur. [5 marks]

(v) Apart from Fe$^{2+}$ species, give two other metal ions that are able to exhibit this magnetic phenomenon. Give their high and low spin d-configurations. Use suitable illustrations to aid your answer. [10 marks]

(vi) Explain why these type of complexes are regularly given as examples of potential Molecular Switches and sensors. [5 marks]

(b) Consider the analogous dinuclear anionic and neutral complexes [V$_2$O$_2$(L)$_6$]$^{2-}$ and [MoO$_2$(L)$_6$] as shown in the general schematic below.

(i) Which d-orbitals are shown in the figure above? [2 marks]

...Question 1 continued on next page
(ii) Give the correct 3d-configuration for the V$^{4+}$ and Mo$^{5+}$ metal ions respectively. Which d-orbital would their unpaired electron(s) occupy? Draw a crystal field splitting diagram to aid your answer. [10 marks]

(iii) The complex [V$_2$O$_2$(L)$_6$] possesses an S = 0 ground spin state with a thermally accessible 1$^{st}$ excited state (S = $Y$). However the complex [Mo$_2$O$_2$(L)$_6$] is diamagnetic at room temperature (S = 0) and its 1$^{st}$ excited state (S = $Y$) is thermally inaccessible. Explain these findings, using illustrations where appropriate. Define $Y$ in your answer. [20 marks]

(iv) Using illustrations if necessary, briefly explain the terms:  
   (a) Superexchange [9 marks]  
   (b) The Orthogonality principle [9 marks]

2. Answer each of the following:

(a) Give an example for each of the following:
   (i) a metal used for MRI contrast agents. [2 marks]
   (ii) a radionuclide that is used in radiotherapy. [3 marks]
   (iii) an inorganic salt that has insulin mimetic effects. [3 marks]
   (iv) an antitumoural, photoactivatable Pt(IV) complex. [7 marks]

(b) Compare the chemistry of the antitumoural metalloene dihalides molybdocene dichloride and titanocene dichloride. In particular outline differences in solution behaviour, stability of the Cp and Cl ligands towards hydrolysis, and interaction with biomolecules. [40 marks]

(c) Discuss the expected effect on the biological behaviour of replacing the acetate ligands in trans,cis,cis-[Pt(CH$_3$COO)$_2$Cl$_2$(NH$_3$)$_2$] with trifluoracetate. [25 marks]

(d) Predict the trend of the wavenumbers of the $\nu$(Pt-H) vibration in the IR spectra of trans-[PtH(X)(PPh$_3$)$_2$] with X = CN$^-$, I$^-$, Br$^-$ Cl$^-$. Justify your answer. [20 marks]

... more on the next page
3. Answer each of the following:

(a) Discuss the chemistry of the lanthanoids under the following headings:
   (i) electronic configuration and oxidation states, lanthanoid contraction, coordination numbers and geometries, preferred donor atoms [25 marks]
   (ii) application of lanthanoid complexes as NMR shift reagents [25 marks]
   (ii) organometallic complexes of the lanthanoids and their importance as catalysts for organic transformations. Give two examples of organic transformations that are catalyzed by organolanthanoid complexes. [35 marks]

(b) (i) Determine the term symbol for the ground state of the Tb$^{3+}$ ion [7 marks]
   (ii) Calculate the magnetic moment of Tb$^{3+}$ using

   \[ g_I = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \]

4. Answer each of the following:

Discuss catalysis by metal activated hydroxide in zinc metalloenzymes under the following headings:
(a) Compare the structure and function of the enzyme carbonic anhydrase with those of carboxypeptidase A. [30 marks]
(b) Discuss the mechanisms of action of both enzymes. [40 marks]
(c) Contrast the use of crystallography with that of kinetic in studying these enzymes. [30 marks]
Section C

Answer two questions from this section.

5. Answer each of the following:

(a) Predict the $^{31}$P NMR spectrum of cis-[PtCl$_2$(PPh$_3$)$_2$]. Explain how it differs from the $^{31}$P NMR spectrum of the trans-isomer. Suggest (with reasons) another spectroscopic method to distinguish the cis- and trans-isomer. [18 marks]

(b) Suggest a synthesis for trans,trans,trans-[Pt(N$_3$)$_2$(NH$_3$)$_2$(OH)$_2$] using transplatin as starting compound. [17 marks]

(c) What types of photoreactions can take place, when a neutral solution of the Pt(IV) complex cis,cis,trans-[Pt(N$_3$)$_2$(NH$_3$)$_2$(OH)$_2$] is irradiated with laser light? Draw the structures of all products that can form. [15 marks]

6. Answer each of the following:

In a recent study on the carrier-mediated delivery of Pt to tumour cells cisplatin was reacted with vitamin B$_{12}$ and the vitamin B$_{12}$-Pt conjugate B$_{12}$-C≡N-PtCl(NH$_3$)$_2$ was isolated. After reduction of the B$_{12}$ entity the cyano complex cis-[PtCl(CN)(NH$_3$)$_2$] was obtained.

(i) To confirm the cis geometry, the released cyano complex, cis-[PtCl(CN)(NH$_3$)$_2$], was treated with thiourea (Kurnakov test). Predict the outcome. Justify your answer. [20 marks]

(ii) To study the affinity of cis-[PtCl(CN)(NH$_3$)$_2$] for DNA, the complex was mixed with the model nucleobase 9-ethylguanine in D$_2$O and the reaction was monitored by $^{195}$Pt NMR. cis-[PtCl(CN)(NH$_3$)$_2$] gives a $^{195}$Pt NMR signal at -5578 ppm. After 10 min., the $^{195}$Pt NMR showed a new signal at -5863 ppm indicating the formation of product A. With longer reaction time, the concentration of A decreased and a new product B appeared (-5852 ppm). Draw the structures of A and B and predict the $^1$H NMR spectrum of A in D$_2$O. Explain your workings. [30 marks]

... more on the next page
7. Answer each of the following:

(a) Below is the magnetic susceptibility ($\chi_M T$ vs. $T$) curve obtained from a dinuclear Cu$^{2+}$ complex. Answer the following questions related to this curve, using illustrations where applicable.

(i) What does this curve tell you about the type of magnetic exchange occurring within this complex? Explain your reasoning. [6 marks]

(ii) Draw an energy level diagram illustrating the ground spin state and 1$^{st}$ excited state for this Cu$^{2+}$ dimer. Remember to include the microstate ($M_s$) levels associated with this system. [10 marks]

(iii) Electron Paramagnetic Resonance found the energy gap discussed in (ii) to be 60 cm$^{-1}$. Give the energy gap in terms of $D$ and give the $D$ value? Show your workings. [6 marks]

(iv) Give two other types of magnetic exchange which may occur in magnetic materials. Use illustrations to aid your answer. [8 marks]

(b) Tabulated below is the data obtained from the above dinuclear Cu$^{2+}$ complex (taken from the 100 - 300 K range only).

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<th>Temperature (K)</th>
<th>$\chi_M T$ (cm$^3$ mol$^{-1}$ K)$^*$</th>
<th>$\chi_M$ (cm$^3$ mol$^{-1}$)</th>
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<tbody>
<tr>
<td>301</td>
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</tr>
</tbody>
</table>

* Susceptibility data has been corrected for diamagnetic contributions

...Question contd. on next page
Calculate and plot the required data to deduce the Weiss constant $\theta$. Comment on what information you can take from this value. 

[20 marks]

8. Answer **each** of the following:

Read the following paragraph and consider the figure that accompanies it, taken from the literature$^\dagger$. Answer the questions that follow.

“In the catalytic cycle, H$_2$O/HO$^-$ first becomes displaced from the Zn$^{2+}$ by substrate (K$_m$, productive binding maximal only at pH< 5) and then the imidazole side chain of His-231, in its unprotonated form and assisted by Asp-226, functions as a general base to induce hydration of the metal-activated substrate in the $k_{cat}$ step (maximal only at pH > 8). Subsequent conversion to product, through a Zn$^{2+}$-ligated tetrahedral adduct derived from the scissile linkage, is probably facilitated through imidazolinium general acid catalysis, Scheme 3.”

(a) Explain the symbols $k_{cat}$ and K$_m$ and the terms ‘general-base catalysis’ and ‘general-acid catalysis’ as used above. 

[10 marks]

(b) Show that you understand the mechanisms presented. 

[20 marks]

(c) Relate this data to the wider context of metalloenzyme catalysed hydrolysis reactions. 

[20 marks]