ANSWERS TO EXERCISES

Exercise 1

1. a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
   c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
   d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

2. a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
   c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
   d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

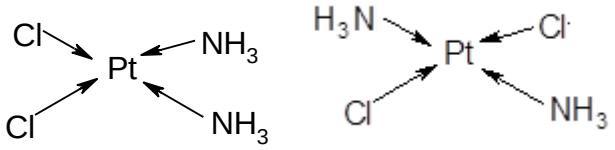
3. a) They do not form any stable ions with partially filled d-orbitals
   b) They have empty d-orbitals of low energy which can accept electron pairs
   c) The presence of ligands causes the d-orbitals to split. In the presence of visible light, electrons are excited from low energy d-orbitals to high energy d-orbitals, absorbing the light in the process. The resultant light is coloured.
   d) Cu^+ has a full 3d sublevel, so there are no available d-orbitals into which electrons can be excited.

4. Prepare samples of the transition metal ion over a range of known concentrations.
   Add a small quantity of a suitable ligand to each in order to identify the colour.
   Choose the filter which gives the largest absorbance, and measure the absorbance of each sample using this filter.
   Plot a graph of absorbance against concentration.
   Take the sample of unknown concentration, add the ligand to intensify the colour, and measure its absorbance using the same filter.
   Use the graph to deduce the concentration of the solution.

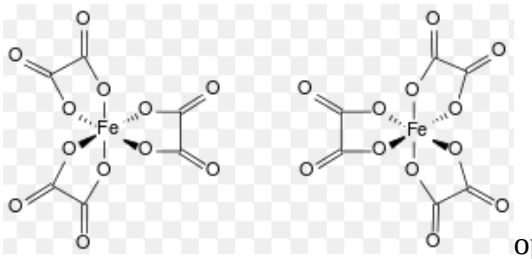
Exercise 2

1. a) ion containing a central metal ion attached to one or more ligands by means of co-ordinate bonds
   b) species containing a lone pair of electrons which can form a co-ordinate bond with a metal ion
   c) the total number of co-ordinate bonds formed between the metal ion and the ligands

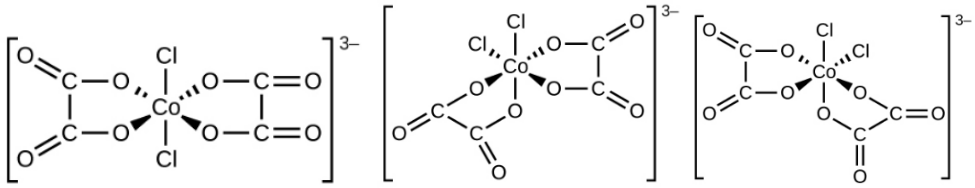
2. a) $Fe^{2+} + 6H_2O \rightarrow Fe(H_2O)_6^{2+}$ unidentate
   b) $Fe^{2+} + 6CN^- \rightarrow Fe(CN)_6^{4-}$ unidentate
   c) $Fe^{3+} + 6CN^- \rightarrow Fe(CN)_6^{3-}$ unidentate
   d) $Cr^{3+} + 6NH_3 \rightarrow Cr(NH_3)_6^{3+}$ unidentate
   e) $Ag^+ + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-}$ unidentate
   f) $Co^{2+} + 4Cl^- \rightarrow CoCl_4^{2-}$ unidentate
   g) $Fe^{2+} + 3H_2NCH_2CH_2NH_2 \rightarrow Fe(H_2NCH_2CH_2NH_2)_3^{2+}$ bidentate
   h) $Cr^{3+} + 3C_2O_4^{2-} \rightarrow Cr(C_2O_4)_3^{3-}$ bidentate
   i) $Cu^{2+} + edta^{4-} \rightarrow Cu(edta)^{2-}$ hexadentate

3. a) 

cis-trans

   b) 
optical

   c)


cis-trans optical

Exercise 3

1. a) acid-base
   $Fe(H_2O)_6^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(H_2O)_4(OH)_2(s) + 2H_2O(l)$
   b) acid-base
   $Al(H_2O)_6^{3+}(aq) + 3OH^-(aq) \rightarrow Al(H_2O)_3(OH)_3(s) + 3H_2O(l)$
   $Al(H_2O)_3(OH)_3(s) + 3OH^-(aq) \rightarrow Al(OH)_6^{3-}(aq) + 3H_2O(l)$
   c) acid-base
   $Cu(H_2O)_6^{2+}(aq) + 2NH_3(aq) \rightarrow Cu(H_2O)_4(OH)_2(s) + 2NH_4^+(aq)$
   Ligand exchange
   $[Cu(H_2O)_4(OH)_2](s) + 4NH_3(aq) == [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l) + 2OH^-(aq)$
   d) ligand exchange
   $[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) == [CoCl_4]^{2-}(aq) + 6H_2O(l)$
   ligand exchange
   $[CoCl_4]^{2-}(aq) + 6H_2O(l) == [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$

e) acid-base
$2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2[Al(H_2O)_3(OH)_3](s) + 3CO_2(g) + 3H_2O(l)$

f) precipitation
$[Co(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CoCO_3(s) + 6H_2O(l)$

2. Fe^{3+} has a greater charge density than Fe^{2+}
So the electrons in the O-H bonds in the complex ion $Fe(H_2O)_6^{3+}$ are pulled more strongly towards the central metal ion than in $Fe(H_2O)_6^{2+}$
which means the O-H bonds are more likely to dissociate to form H^+ in $Fe(H_2O)_6^{3+}$
So $Fe(H_2O)_6^{3+}$ is more acidic and has a lower pH

3. The reaction involves breaking six O-H bonds and making six O-H bonds
so ΔH is close to 0
the reaction involves an increase in the number of species in aqueous solution from 2 to 7
so there is a large increase in entropy
so ΔG is negative and the reaction is thermodynamically favoured

Exercise 4

1. Solution turns yellow when acidified
Due to formation of VO_2^+
Yellow solution turns blue then green then violet
as the vanadium is reduced from oxidation state +5 to +4 to +3 to +2

2. a) i) $2SO_2 + O_2 == 2SO_3$
a step in the manufacture of sulphuric acid
ii) $N_2 + 3H_2 == 2NH_3$
the manufacture of ammonia
iii) $2CO + 2NO \rightarrow N_2 + 2CO_2$
removal of pollutants in car engines

b) heterogeneous catalysts provide active sites at their surface where the reaction can take place. Catalyst poisons block these sites.

c) The catalyst is expensive and must be used in small quantities
It needs to have a large surface area to maximize its effectiveness
So it is spread thinly over an inert support.

3. using Fe^{2+}:
$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
using Fe^{3+}:
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$
these steps are all fast because they involve a collision between oppositely charged ions, which attract each other

The uncatalysed reaction involves a collision between two anions, which repel, making the reaction slow

4. a) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

b) Initially the reaction is slow because it requires a collision between two repelling anions
But after the reaction has started the Mn^{2+} produced can catalyse the reaction, so it proceeds faster towards the end-point. It is an example of autocatalysis

Topic 5 Exercise 5

1. n = 12 2. 1.37 $moldm^{-3}$ 3. x = 2 4. +5