Chem Factsheet

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Ligand Exchange Reactions

Prior knowledge

The meaning of the following terms: atomic number, period, electronic configuration, transition metal, d-block element, oxidation state, types of chemical bond, organic nomenclature, shapes of complex ions, K_c, ΔS and ΔG.

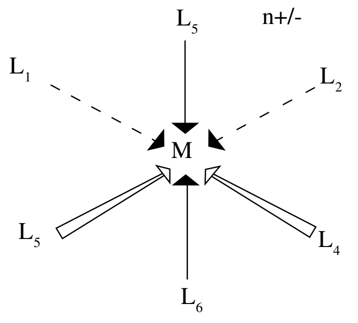
After working through this Factsheet you should understand the various types of ligand exchange reactions and their associated entropy effects as well as the terms connected with such reactions.

Terms associated with transition metal complexes

Each complex consists of a central transition metal ion (M^{n+}). (It can also be an atom but such complexes are far less common.)

Bonded via co-ordinate bonds to this central ion are a specific number of ligands. Here six ligands, L_1 to L_6, are shown.

Together they produce a complex which can be a cation, anion or a neutral molecule depending upon the charges on M and L and the numbers of ligands involved. Overall, the complex will have a specific shape. An octahedral shape is illustrated.



octahedral shape

The arrows → indicate that the ligand, L, is providing both electrons (a Lewis base) for the co-ordinate bond to M^{n+}. Thus for M^{n+} to be able to accept a lone pair. M^{n+} must have vacant orbitals of suitable energy (a Lewis acid) to allow this.

The ligands most often are molecules or negatively charged ions and they donate one or more lone pairs of electrons. The number of donated lone pairs per ligand is called its denticity. Thus ligands can be monodentate, bidentate, etc. The total number of co-ordinate bonds being formed is called the co-ordination number of the transition metal ion; in the above diagram this is 6.

What is a ligand exchange reaction?

A chemical reaction where there is a swapping of ligands.

Examples of ligand exchange reactions

(a) Reactions that occur without change in co-ordination number using monodentate ligands.

This can occur when both ligands are of similar size and the same charge. e.g. H_2O and NH_3.

(Diameters: O = 0.146 nm and N = 0.150 nm.) It is the size of the atom donating the electron pair that is important and not the size of the whole ligand.

e.g. 1. $[Co(H_2O)_6]^{2+}$ to $[Co(NH_3)_6]^{2+}$

If **dilute** ammonia (2M) is added to a pink cobalt(II) chloride solution (this contains pink $[Co(H_2O)_6]^{2+}$ ions - the chloride ions are merely spectator ions) there is an immediate blue-green precipitate, ($[Co(OH)_2(H_2O)_4]$), formed by removal of two protons from two of the six water ligands by the basic ammonia molecules. However, in excess dilute ammonia the precipitate dissolves forming a straw-yellow coloured solution by a series of six ligand substitution reactions.

The nett equation being:
$[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightarrow [Co(NH_3)_6]^{2+}(aq) + 6H_2O(l)$

e.g. 2. $[Cr(H_2O)_6]^{3+}$ to $[Cr(NH_3)_6]^{3+}$

If **concentrated** ammonia is added to a green chromium(III) chloride solution (this contains green $[Cr(OH)(H_2O)_5]^{2+}$ ions - the chloride ions are merely spectator ions) there is an immediate green precipitate, ($[Cr(OH)_3(H_2O)_3]$), formed by removal of three protons from three of the six water ligands by the basic ammonia molecules. However, if enough concentrated ammonia is added the precipitate dissolves forming a purple solution by ligand substitution.

The nett equation being:
$[Cr(H_2O)_6]^{3+}(aq) + 6NH_3(aq) \rightarrow [Cr(NH_3)_6]^{3+}(aq) + 6H_2O(l)$

Note: The normal complex, $[Cr(H_2O)_6]^{3+}(aq)$, is lilac but a solution of $CrCl_3(aq)$ looks green due to its hydrolysis to $[Cr(OH)(H_2O)_5]^{2+}$.

e.g. 3. $[Cu(H_2O)_6]^{2+}$ to $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Partial ligand substitution)

If dilute ammonia (2M) is added to a pale blue solution of copper(II) sulphate (this contains blue $[Cu(H_2O)_6]^{2+}$ ions - the sulphate ions are merely spectator ions) there is an immediate pale blue precipitate ($[Cu(OH)_2(H_2O)_4]$), formed by removal of two protons from two of the six water ligands by the basic ammonia molecules. However, as in the previous examples, if excess dilute ammonia is added the precipitate dissolves forming a deep blue solution by *partial* ligand substitution. The tetraamminediaquacopper(II) ion has the two water molecules as L_5 and L_6.

The nett equation being:
$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

(b) Reactions that occur with a change in co-ordination number using monodentate ligands.

Cl^- is larger than the O atom in H_2O (diameters: O = 0.146 nm and Cl^- = 0.360 nm). As a result of this and repulsions between negative charges, less Cl^- ligands can fit around Co^{2+}or Cu^{2+}. Hence the co-ordination numbers decrease from 6 to 4 and the shape changes for octahedral to tetrahedral.

e.g. 1. $[Co(H_2O)_6]^{2+}$ (pink) to $[CoCl_4]^{2-}$ (blue) and
e.g. 2. $[Cu(H_2O)_6]^{2+}$ (blue) to $[CuCl_4]^{2-}$ (yellow).

These substitutions can be achieved by adding sufficient concentrated hydrochloric acid – this provides a high concentration of Cl^- ligands.

Nett equation:
$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CoCl_4]^{2-}(aq) + 6H_2O(l)$

Nett equation:
$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$

Note: In example 2, if the mixture appears green rather than yellow, then there is a lot of blue $[Cu(H_2O)_6]^{2+}(aq)$ still present as blue and yellow gives green. i.e. insufficient HCl has been added to complete the ligand exchange.

(c) Ligand exchange equations that involve bidentate and hexadentate ligands.

All of the following examples involve no change in co-ordination number as the atoms donating the electron pairs are of similar size. However, the ethandioate ($C_2O_4^{2-}$) and 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$) ligands are bidentate and the EDTA ligand (edta^{4-}) is hexadentate. Hence the combining ratios become 1:3 and 1:1 respectively instead of 1:6.

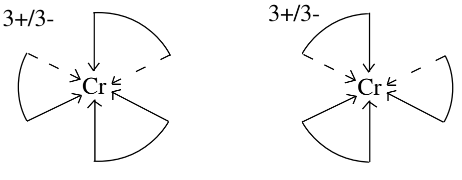
e.g. 1.
Hexaaquachromium(III) ion $[Cr(H_2O)_6]^{3+}$ to
tris(ethanedioate)chromate(III) ion $[Cr(C_2O_4)_3]^{3-}$.

Equation:
$[Cr(H_2O)_6]^{3+} + 3C_2O_4^{2-} \rightarrow [Cr(C_2O_4)_3]^{3-} + 6H_2O$ ---- (A)

e.g. 2.
Hexaaquachromium(III) ion $[Cr(H_2O)_6]^{3+}$ to
tris(diammineethane)chromium(III) ion $[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$

Equation:
$[Cr(H_2O)_6]^{3+} + 3H_2NCH_2CH_2NH_2 \rightarrow [Cr(H_2NCH_2CH_2NH_2)_3]^{3+} + 6H_2O$ ---- (B)

Both $[Cr(C_2O_4)_3]^{3-}$ and $[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$ exist as optical isomers where the non-superimposable mirror images may simply be represented as shown below. The curves represent N-C-C-N or O-C-C-O from the $H_2NCH_2CH_2NH_2$ and $C_2O_4^{2-}$ ligands respectively.



Non-super impossable mirror images

When ligands with denticity is higher than one complex with a metal ion, closed rings are formed. The formation of such rings is called "chelation" and the complex is called a "chelate". (Chelate comes from the Greek for "claw".)

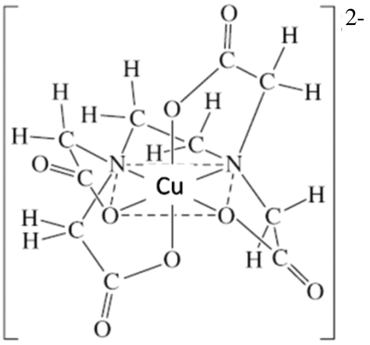
Chelate. A metal co-ordination complex in which at least one ligand co-ordinates at two or more points to the same metal ion.

Note: Chlorophyll and haemoglobin are naturally occurring chelate compounds.

e.g. 3.
Hexaaquacopper(II) ion $[Cu(H_2O)_6]^{2+}$ to edtacuprate(II) ion $[Cu(edta)]^{2-}$

Equation: $[Cu(H_2O)_6]^{2+} + edta^{4-} \rightarrow [Cu(edta)]^{2-} + 6H_2O$ ---- (C)

The $Cu(edta)]^{2-}$ chelated complex



The relationship between the denticity of a ligand and the energetic stability of the complex of a given transition metal ion.

$[Cr(edta)]^-$ is more stable than $[Cr(C_2O_4)_3]^{3-}$ which is more stable than $[Cr(H_2O)_6]^{3+}$.

This is (mainly) because of the size of the increase in entropy of the system when the higher dentate ligands are exchanged for lower dentate ligands. (Don't assume that all complexes of edta are more stable than all complexes with bidentate ligands – they are not.)

In equations (A) and (B) above, six monodentate ligands (L) are replaced by three bidentate ligands (B).

In general : $ML_6 + 3B \rightarrow MB_3 + 6L$

Thus, there is a net increase of three particles when the reaction occurs and so the entropy of the system increases (ΔS +ve). Since $\Delta G = \Delta H - T\Delta S$ and ΔH is approximately zero because six metal-ligand bonds are replaced by six similar metal-ligand bonds, this helps to make the free energy change (ΔG) for the reaction negative and hence the complex of bidentate ligands more energetically stable than the complex with monodentate ligands.

Similarly for equation (C) there is an increase of five particles.

In general : $ML_6 + H \rightarrow MH + 6L$ where H is a hexadentate ligand.

Hence the entropy increase of the system is even higher and ΔG even more negative and hence the hexadentate complex even more energetically stable relative to a monodentate ligand complex.

In general, $MH > MB_3 > ML_6$ in stability meaning bidentate for monodentate ligand exchange is more likely than mono-mono. Similarly hexadentate for monodentate ligand exchange is more likely than mono-mono and hexadentate for bidentate ligand exchange is more likely than bidentate for monodentate.

Stability constants, K_{stab}

Stability constants are equilibrium constants in terms of molar concentrations (i.e. K_c) for ligand exchange reactions.

e.g. Consider the ligand exchange reaction:

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ - - - - (D)

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2{}^{2+}]}{[Cu(H_2O)_6{}^{2+}][NH_3]^4} = 1.20 \times 10^{13}\ dm^{12}\ mol^{-4}$$

<u>Note</u>. The square brackets that enclose the complex ions have been omitted for clarity.

The high value for the stability constant indicates that the position of equilibrium lies well to the right, $[Cu(NH_3)_4(H_2O)_2{}^{2+}] >> [Cu(H_2O)_6{}^{2+}]$ showing that $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is more energetically stable than $[Cu(H_2O)_6]^{2+}$

Comparing stability constants for exchange reactions with ligands of various denticity

(a) Exchanging two monodentate water ligands for two monodentate ammonia ligands.

$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O \quad K_1 = 7.2 \times 10^8\ dm^6\ mol^{-2}$

(b) Exchanging two monodentate ligands for one bidentate 1,2-diamminoethane ligand.

$[Cu(H_2O)_6]^{2+} + NH_2CH_2CH_2NH_2 \rightleftharpoons [Cu(H_2O)_4(NH_2CH_2CH_2NH_2)]^{2+} + 2H_2O \quad K_2 = 3.9 \times 10^{10}\ dm^3 mol^{-1}$

(c) Exchanging six monodentate water ligands for three bidentate 1,2-diamminoethane ligands.

$[Cu(H_2O)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \rightleftharpoons [Cu(NH_2CH_2CH_2NH_2)_3]^{2+} + 6H_2O \quad K_3 = 5.0 \times 10^{18}\ dm^9 mol^{-3}$

Thus the greater the degree of chelation the higher the stability constant and the greater the stability of the complex due to the increased entropy of the system as explained above.

(d) Exchanging six monodentate water ligands for one hexadentate edta ligand.

$[Cu(H_2O)_6]^{2+} + edta^{4-} \rightleftharpoons [Cu(edta)]^{2-} + 6H_2O \quad K_4 = 6.3 \times 10^{18}\ dm^3 mol^{-1}$

K_3 and K_4 are fairly similar as both complexes have three chelate rings.

Practice questions

1. When dilute ammonia is added to cobalt(II) chloride solution the following reactions occur.

   $[Co(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [Co(H_2O)_4(OH)_2](s) + 2NH_4{}^+(aq)$ -(1)
   Blue-green precipitate

   $[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{2+}(aq) + 6H_2O(l)$ - (2)
   Coloured solution

   (i) What types of reactions are occurring in stages (1) and (2)?

   (ii) Use Le Chatelier's principle to explain why the blue-green precipitate dissolves when excess ammonia is added.

   (iii) State the colour of the solution formed.

2. Complexes can have positive charges, negative charges or no charge.
   (a) Write equations for the conversion of
      (i) a cationic complex of chromium into a neutral complex and
      (ii) an anionic complex of chromium into a neutral complex.

   (b) State the shape of each complex ion.
   (c) State the number of co-ordinate bonds to each chromium ion in each of the complex ions.

3. Haemoglobin is an octahedral transition metal complex of a Fe^{2+} ion surrounded by a tetradentate haem ligand in a square planar arrangement with globin (a protein) and a water molecule arranged axially. The water molecule is replaced by an oxygen molecule when haemoglobin transports oxygen in the blood. During carbon monoxide poisoning the oxygen molecule is replaced by a carbon monoxide molecule.
   (a) What do water, oxygen and carbon monoxide molecules have that enables them to be part of the complex?
   (b) Name the type of bond that these molecules form in the complex?
   (c) Explain the chemistry involved in taking a person suffering from the effects of carbon monoxide inhalation into the open air?

4. For the equilibrium shown below the value of the stability constant ate 298 K is $1 \times 10^7\ dm^6 mol^{-2}$ and each of the complex ions is linear.
   $[Ag(H_2O)_2]^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + 2H_2O$

   (a) Write an expression for the stability constant?
   (b) Which complex ion is more stable?
   (c) How could the value of the stability constant be altered?
   (d) Draw a diagram of the shape of either complex ion?

5. Consider an equimolar mixture of $[Co(H_2O)_6]^{2+}(aq)$ which is pink and $[CoCl_4]^{2-}(aq)$ which is blue. The mixture appears purple since it is a mixture of these two colours.
   (a) Write an equation showing the dynamic equilibrium that exits between these two complex ions.
   (b) Suggest a reagent that would turn the purple solution i) pink and ii) blue?
   (c) The purple solution turns blue on heating. Deduce if the forward reaction is endothermic.
   (d) Write the formula of a possible *neutral* complex that can exist in the purple solution.

Answers

1. (i) (1) = acid-base and (2) ligand exchange.

   (ii) With excess ammonia equilibrium (2) moves to the right so the concentration of $[Co(H_2O)_6]^{2+}(aq)$ is reduced. This causes (1) to move to the left so as to increase the concentration of $[Co(H_2O)_6]^{2+}(aq)$ as required by Le Chatelier's principle; thus the precipitate dissolves.

   (iii) $[Co(NH_3)_6]^{2+}(aq)$ is straw-yellow coloured.

2. (a) (i) e.g. $[Cr(H_2O)_6]^{3+} + 3Cl^- \rightarrow [Cr(H_2O)_3Cl_3] + 3H_2O$
   (ii) e.g. $[Cr(H_2O)_2Cl_4]^- + H_2O \rightarrow [Cr(H_2O)_3Cl_3] + Cl^-$

   (b) Both are octahedral.

   (c) 6 for both.

3. (a) Lone pairs of electrons.

   (b) Co-ordinate bonds.

   (c) The $[O_2]$:[CO] ratio is much higher in the open air causing O_2 molecules to exchange for CO molecules in the complex.

4. (a)

$$K_{stab} = \frac{[Ag(NH_3)_2{}^+]}{[Ag(H_2O)_2{}^+][NH_3]^2}$$

   (b) $[Ag(NH_3)_2]^+$

   (c) Alter the temperature.

   (d) 2 ligands → linear shape. Hence, $[H_2O\rightarrow Ag\leftarrow OH_2]^+$ or $[H_3N\rightarrow Ag\leftarrow NH_3]^+$

5. (a) $[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$ (Or Reverse)

   (b) (i) Water

   (ii) Conc. HCl(aq).

   (c) Forward. On heating the equilibrium moves to oppose the change so the forward reaction must take in energy, i.e. it's endothermic. (Or reverse if the equation is reversed.)

   (d) $[Co(H_2O)_2Cl_2]$

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