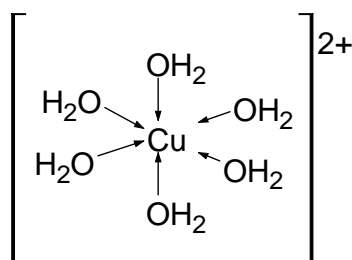


Complex formation

complex : is a central metal ion surrounded by ligands.

ligand.: An atom, ion or molecule which can donate a **lone electron pair**.



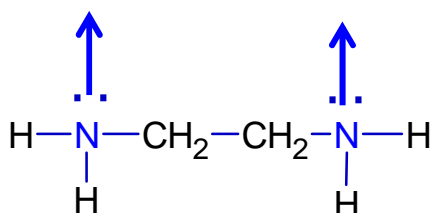
Co-ordinate bonding is involved in complex formation.

Co-ordinate bonding is when **the shared pair of electrons** in the covalent bond come from **only one of the bonding atoms**.

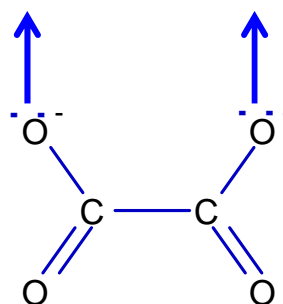
Co-ordination number: The number of co-ordinate bonds formed to a central metal ion.

Ligands can be **unidentate** (e.g. H_2O , NH_3 and Cl^-) which can form one coordinate bond per ligand or **bidentate** (e.g. $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and ethanedioate ion $\text{C}_2\text{O}_4^{2-}$) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g. EDTA^{4-} which can form six coordinate bonds per ligand).

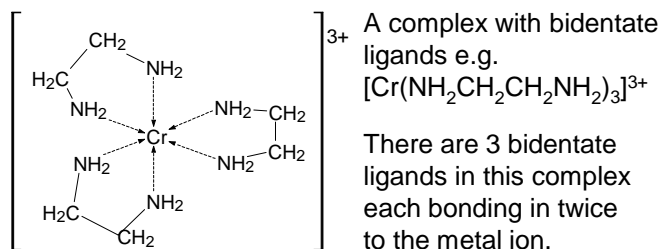
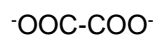
Bidentate ligands contain two donor atoms. They bond to the metal ion through two atoms.



1,2-diaminoethane $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$



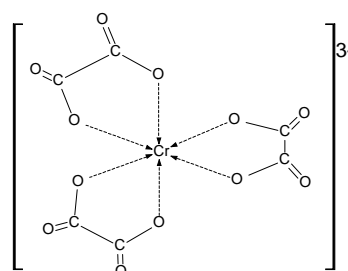
Ethanedioate(oxalate) ion $\text{C}_2\text{O}_4^{2-}$



A complex with bidentate ligands e.g. $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$

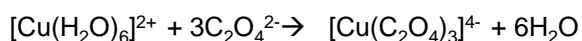
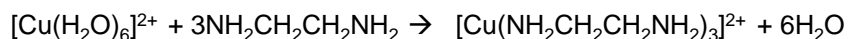
There are 3 bidentate ligands in this complex each bonding in twice to the metal ion.

It has a coordination number of 6

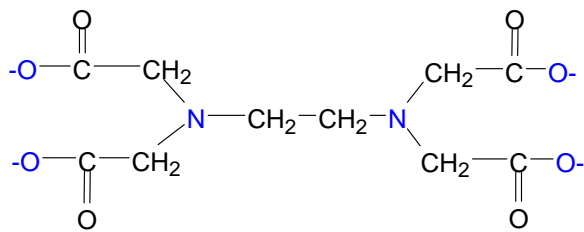


A complex with bidentate ethanedioate ligands e.g. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

Equations to show formation of bidentate and multidentate complexes

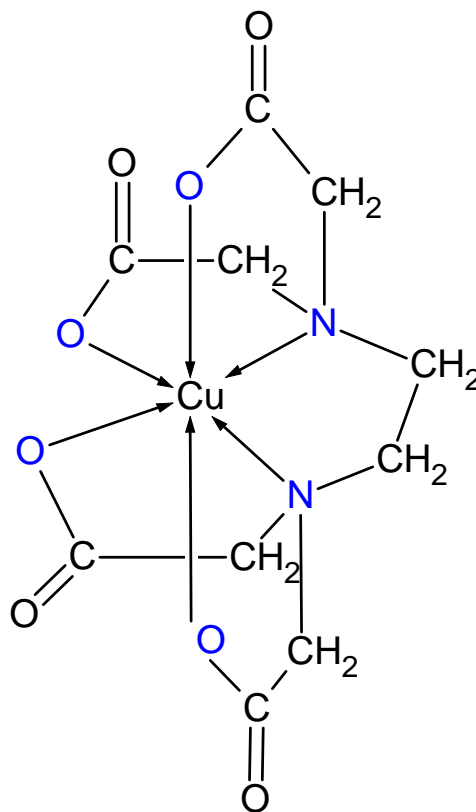
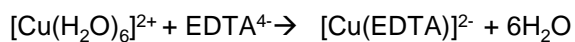


The EDTA⁴⁻ anion has the formula



with six donor sites (4O and 2N) and forms a 1:1 complex with metal(II) ions

As it can form six dative covalent bonds with the metal ion, EDTA will only ever have a ratio of one molecule of EDTA to one ion of the metal.
eg [Ni(EDTA)]²⁻



The stability of the EDTA complexes has many applications. It can be added to rivers to remove poisonous heavy metal ions as the EDTA complexes are not toxic. It is in many shampoos to remove calcium ions present in hard water, so helping lathering.

Quantitative calculations with complex ions

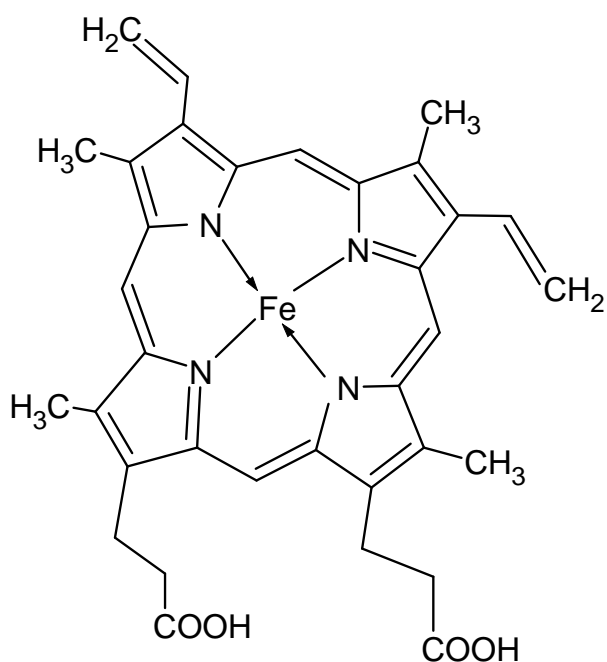
EDTA titrations

The formation of the stable EDTA complex with metal ions can with the choice of suitable indicator be done in a quantitative titration.



A river was polluted with copper(II) ions. 25.0 cm³ sample of the river water was titrated with a 0.0150 mol dm⁻³ solution of EDTA⁴⁻, 6.45 cm³ were required for complete reaction.
Calculate the concentration, in mol dm⁻³, of copper(II) ions in the river water.

Step 1 : find moles of KMnO₄
moles = conc x vol = 0.0150 x 6.45/1000
= 9.68x10⁻⁵ mol
Step 2 : using balanced equation find moles Cu²⁺
1:1 ratio
= 9.68x10⁻⁵ mol
Step 3 : find conc Cu²⁺ in 25cm³
= 9.68x10⁻⁵ / 0.025
= 0.00387 mol dm⁻³



Haem is an iron(II) complex with a multidentate ligand.

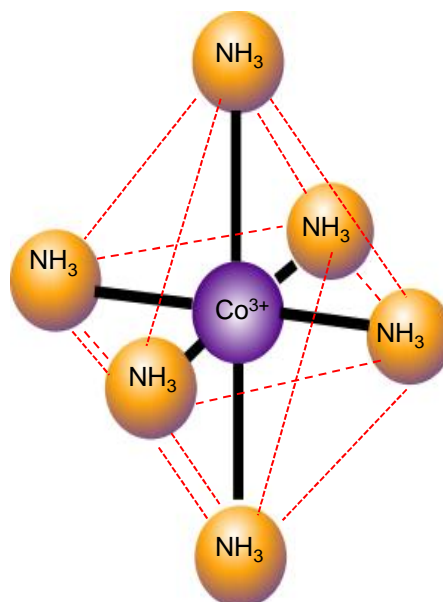
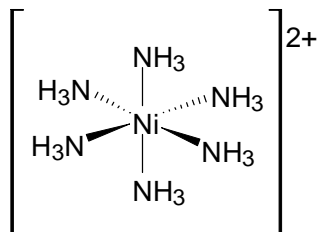
Fe(II) in haemoglobin enables oxygen to be transported in the blood. Haem is an iron(II) complex with a multidentate ligand.

CO is toxic to humans as CO can form a strong coordinate bond with haemoglobin. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin.

Shapes of complex ions

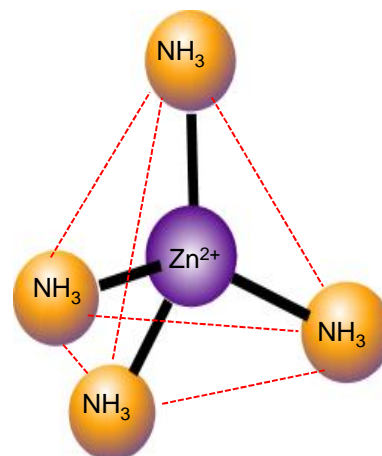
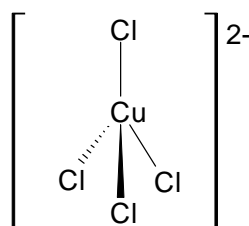
Octahedral

Transition metal ions commonly form **octahedral** complexes with small ligands (e.g. H₂O and NH₃).



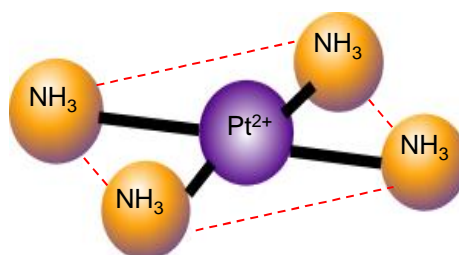
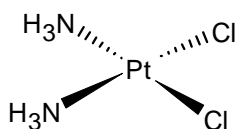
Tetrahedral

Transition metal ions commonly form **tetrahedral** complexes with larger ligands (e.g. Cl⁻).



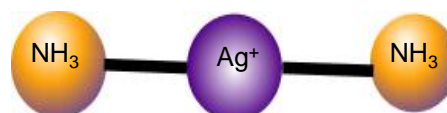
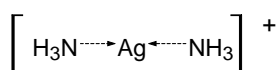
Square planar

square planar complexes are also formed, e.g. cisplatin



Linear

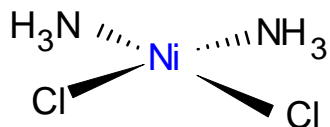
Ag⁺ commonly forms **linear** complexes e.g. [Ag(NH₃)₂]⁺, [Ag(S₂O₃)₂]³⁻ and [Ag(CN)₂]⁻ (all colourless).



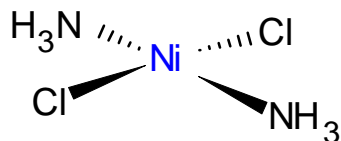
Isomerism in complex ions

Complexes can show two types of stereoisomerism: cis-trans isomerism and optical isomerism

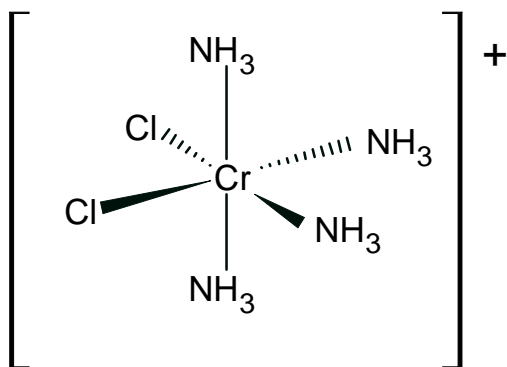
Cis-trans isomerism



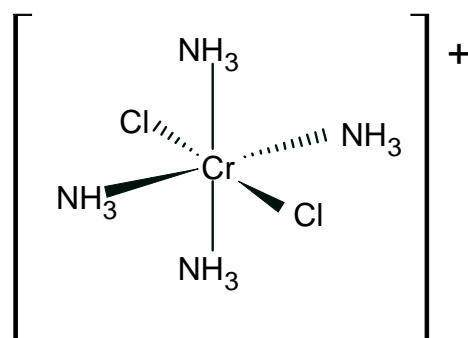
Cis- $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$



trans- $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$



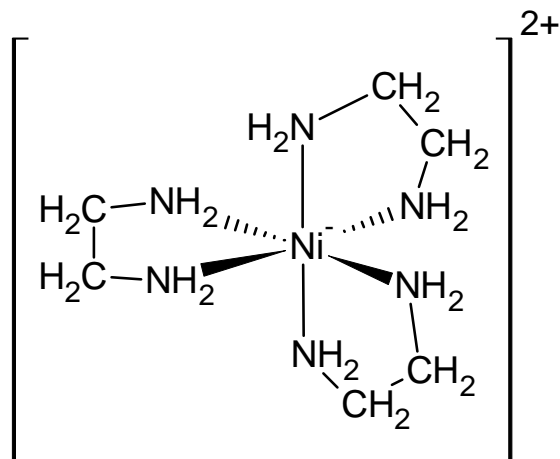
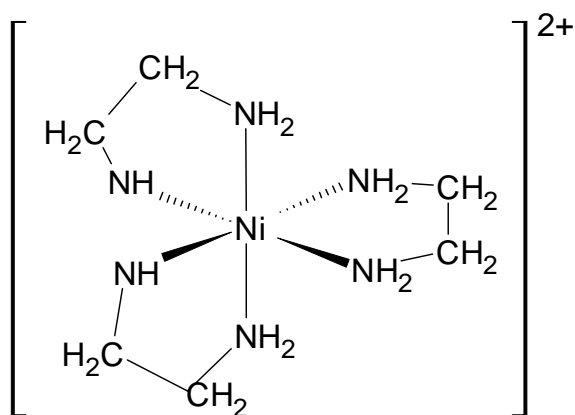
Cis- $[\text{CoCl}_2(\text{NH}_3)_4]^+$



trans- $[\text{CoCl}_2(\text{NH}_3)_4]^+$

Optical isomerism

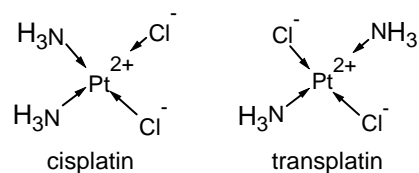
Complexes with 3 bidentate ligands can form two optical isomers (non-superimposable mirror images).



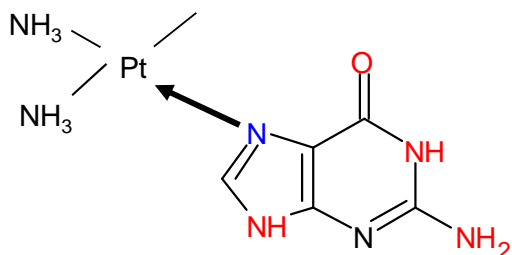
Cisplatin

The Pt(II) complex cisplatin is used as an anticancer drug.

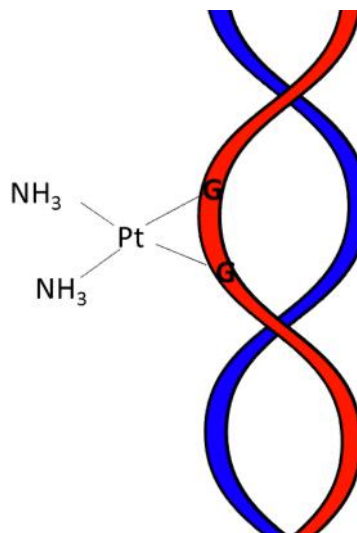
The cisplatin version only works as two chloride ions are displaced and the molecule joins on to the DNA. In doing this it stops the replication of cancerous cells.



Cisplatin prevents DNA replication in cancer cells by a ligand replacement reaction with DNA in which a dative covalent bond is formed between platinum and a nitrogen atom on guanine



The N and O atoms marked in red can't bond to cis-platin as they are involved in the bonding within the DNA

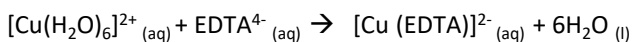


Cisplatin can also prevent the replication of healthy cells by bonding on to healthy DNA which may lead to unwanted side effects like hair loss. Society needs to assess the balance between the benefits and the adverse effects of drugs, such as the anticancer drug cisplatin.

Stability of complexes

The substitution of monodentate ligand with a bidentate or a multidentate ligand leads to a more stable complex. This is called the chelate effect

This chelate effect can be explained in terms of a positive entropy change in these reactions as more molecules of products than reactants



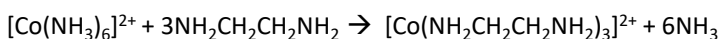
The copper complex ion has changed from having unidentate ligands to a multidentate ligand.

In this reaction there is **an increase** in the **entropy** because there are **more moles of products** than reactants (from 2 to 7), creating more disorder.

The enthalpy change is small as there are similar numbers of bonds in both complexes.

Free energy ΔG will be **negative** as **ΔS is positive** and **ΔH is small**.

The stability of the EDTA complexes has many applications. It can be added to rivers to remove poisonous heavy metal ions as the EDTA complexes are not toxic. It is in many shampoos to remove calcium ions present in hard water, so helping lathering.



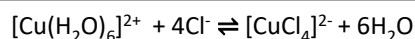
This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. **ΔS is positive**.

Its enthalpy change **ΔH** is close to zero as **the number** of dative covalent and **type** (N to metal coordinate bond) **are the same** so the energy required to break and make bonds will be the same.

Therefore **Free energy ΔG** will be **negative** and the complex formed is stable.

Stability constants K_{stab}

A ligand exchange reaction is considered as equilibria then an equilibrium expression can be written



$$K_{\text{stab}} = \frac{[\text{CuCl}_4^{2-}(\text{aq})]}{[\text{Cu}(\text{H}_2\text{O})_6^{2+}(\text{aq})][\text{Cl}^-]_{\text{aq}}^4}$$

H_2O is not included in the expression because its concentration is assumed to be constant.

The value of K is called the stability constant for complex ions. The larger the stability constant the more stable the complex ion.



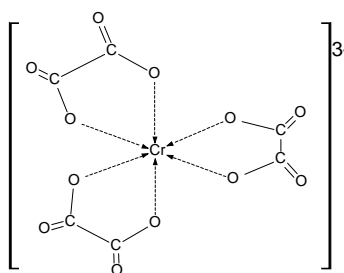
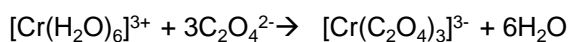
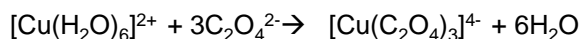
The value of K_{stab} is called the stability constant for complex ions. The larger the stability constant the more stable the complex ion.

A complex ion with a small stability constant will not displace the ligand from a more stable complex ion with a larger stability constant. eg adding ammonia to a complex ion of copper and edta will not result in a colour change

Ligand	Log K_{stab}
Cl^-	5.62
NH_3	13.1
Edta^{4-}	18.8

More on some common ligands

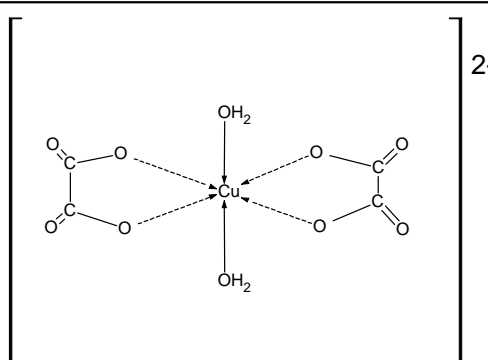
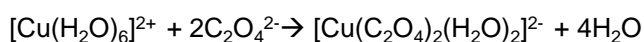
Ethanedioate $\text{C}_2\text{O}_4^{2-}$



A 6 coordination number complex with bidentate ethanedioate ligands e.g. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

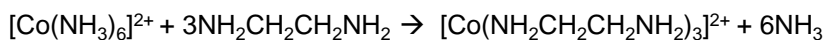
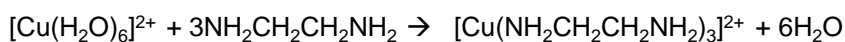
Octahedral shape with 90° bond angles

Partial substitution of ethanedioate ions may occur when a dilute aqueous solution containing ethanedioate ions is added to a solution containing aqueous copper(II) ions. In this reaction four water molecules are replaced and a new complex is formed.



Ethane-1-2-diamine

Ethane-1-2-diamine is a common bidentate ligand.

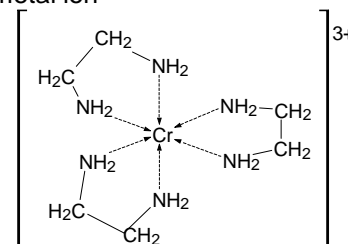


This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. **S is positive.**

Its enthalpy change **H** is close to zero as **the number of dative covalent and type (N to metal coordinate bond) are the same** so the energy required to break and make bonds will be the same.

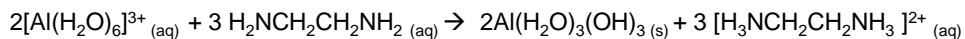
Therefore **Free energy G** will be **negative** and the complex formed is stable.

There are 3 bidentate ligands in this complex each bonding in twice to the metal ion



It has a coordination number of 6
Octahedral shape
Bond angle around Cr 90°

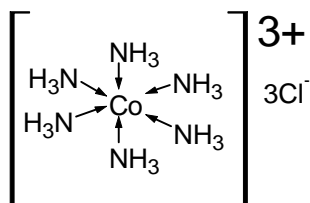
Ethane-1-2-diamine, as a base, can also carry out the deprotonation reactions (similar to those of ammonia) forming hydroxide precipitates.



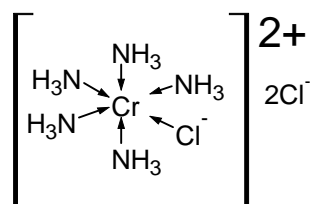
Using Silver nitrate to work out formulae of chloride containing complexes

Sometimes a compound containing a complex may have Cl^- ions acting as ligands inside the complex and Cl^- ions outside the complex attracted ionically to it. If silver nitrate is added to such a compound it will only form the silver chloride precipitate with the free chloride ions outside of the complex.

e.g. $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl^- ions. So all 3 Cls are outside the complex.



e.g. $\text{Cr}(\text{NH}_3)_5\text{Cl}_3$ reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl^- ions. So 1 Cl is a ligand and 2 are outside the complex.



e.g. $\text{Cr}(\text{NH}_3)_4\text{Cl}_3$ reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl^- ion. So 2 Cl^- 's are ligands and 1 is outside the complex.

