

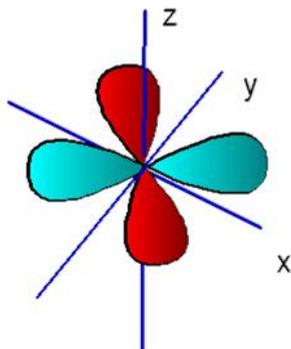
12. Transition Metals

General properties of transition metals

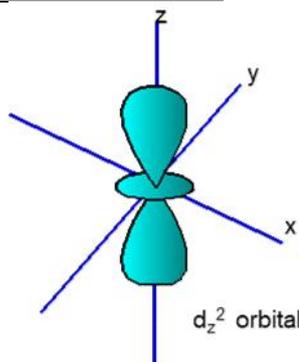
transition metal characteristics of elements Sc → Cu arise from one or more **incomplete d orbitals** in ions

these characteristics include

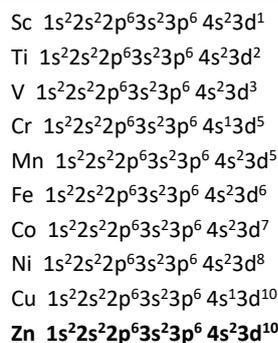
- **complex formation,**
- **formation of coloured ions,**
- **variable oxidation state**
- **catalytic activity.**



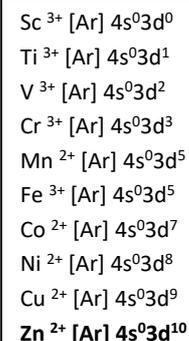
4 of the 5 d orbitals have this shape. Each one is arranged in a different geometry



The 5th d orbital has a different shape



When forming ions lose 4s before 3d



Why is Zn not a transition metal?

Zn can only form a +2 ion. In this ion the Zn^{2+} has a **complete** d orbital and so does not meet the criteria of having an incomplete d orbital in one of its compounds.

Why is Sc not a transition metal?

Sc can only form a +3 ion. In this ion the Sc^{3+} has an empty d orbital and so does not meet the criteria of having an incomplete d orbital in one of its ions.

Physical properties

Melting point and Density: The transition metals have high melting points. They are higher than group 2 element calcium. This is because they have stronger attractions between cations and electrons (as more delocalised electrons)
 Transition metals also have higher densities than calcium. This is because they have greater Ar's and smaller atomic radii.

Variable oxidation states

Transition elements show variable oxidation states

When transition metals form ions they lose the 4s electrons before the 3d

Transition metals form various oxidation states. They are able to donate and receive electrons and are able to oxidize and reduce. This is because they have many electrons of similar energy in their valence- shell orbital . The 4s + 3d orbitals have similar energies. The energy differences between the oxidation states are small.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+4	+5	+6	+7	+6	+5	+4	+3	+2
	+3	+4	+5	+6	+5	+4	+3	+2	
	+2	+3	+4	+5	+4	+3	+2	+1	
	+1	+2	+3	+4	+3	+2	+1		
		+1	+2	+3	+2	+1			
			+1	+2	+1				
				+1					

General trends

- Relative stability of +2 state with respect to +3 state increases across the period
- Compounds with high oxidation states tend to be oxidising agents e.g MnO_4^-
- Compounds with low oxidation states are often reducing agents e.g V^{2+} & Fe^{2+}

Complex formation

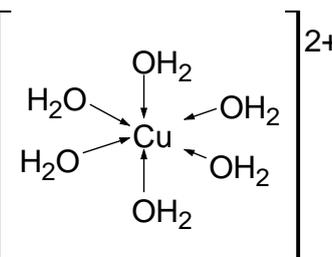
complex : is a central metal ion surrounded by ligands.

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 **monodentate** (e.g. H₂O, NH₃ and Cl⁻) which can form one coordinate bond per ligand or **bidentate** (e.g. NH₂CH₂CH₂NH₂ and ethanedioate ion C₂O₄²⁻) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g. EDTA⁴⁻ which can form six coordinate bonds per ligand).

Reaction of copper and cobalt complexes

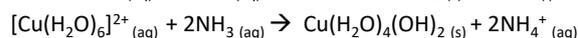
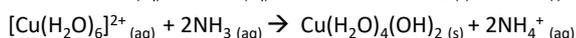
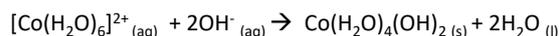
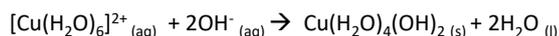
Metal aqua ions are formed in aqueous solution.

[Cu(H₂O)₆]²⁺ is a blue solution
[Co(H₂O)₆]²⁺ is a pink solution

Reaction with limited amount of OH⁻ and limited NH₃

The bases OH⁻ and ammonia when added to aqueous complexes in limited amounts form the hydroxide precipitates. They form in **deprotonation acid base reactions**

Cu(OH)₂(H₂O)₄ (s) blue ppt,
Co(OH)₂(H₂O)₄ (s) blue ppt,



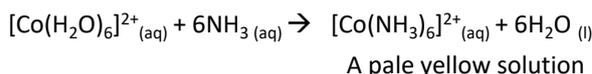
Here the NH₃ and OH⁻ ions are acting as **Bronsted-Lowry bases** accepting a proton

Ligand Exchange Reactions

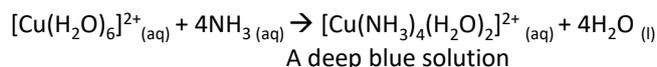
If **excess** ammonia is added to cobalt and copper aqueous ions a ligand exchange reaction occurs

The ligands NH₃ and H₂O are **similar in size** and are **uncharged**.

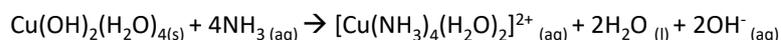
Exchange of the ligands NH₃ and H₂O occurs without change of co-ordination number (eg Co²⁺ and Cu²⁺).



This substitution may, however, be incomplete as in the case with Cu.



The equation can also be written from the hydroxide precipitate



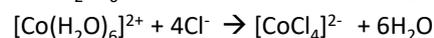
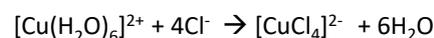
Reactions with Chloride Ions

Addition of a high concentration of chloride ions (from conc HCl or saturated NaCl) to an aqueous ion leads to a **ligand exchange** reaction.

The Cl⁻ ligand is larger than the uncharged H₂O and NH₃ ligands so therefore ligand exchange can involve a change of co-ordination number.

Addition of conc HCl to aqueous ions of Cu and Co lead to a change in coordination number from 6 to 4.

[CuCl₄]²⁻ yellow/green solution These are tetrahedral in shape
[CoCl₄]²⁻ blue solution

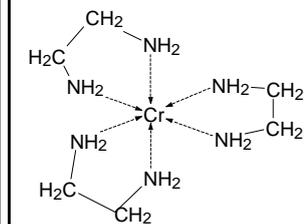


Be careful: If solid copper chloride (or any other metal) is **dissolved in water** it forms the **aqueous [Cu(H₂O)₆]²⁺** complex and **not** the chloride [CuCl₄]²⁻ complex.

Bidentate Ligands

Ligands can be **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

Ethane-1-2-diamine



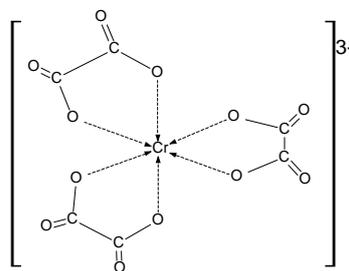
$3+$ Ethane-1-2-diamine is a common bidentate ligand.

A complex with Ethane-1-2-diamine 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

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

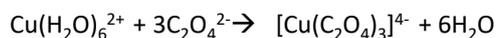
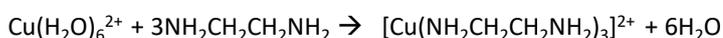


$3-$

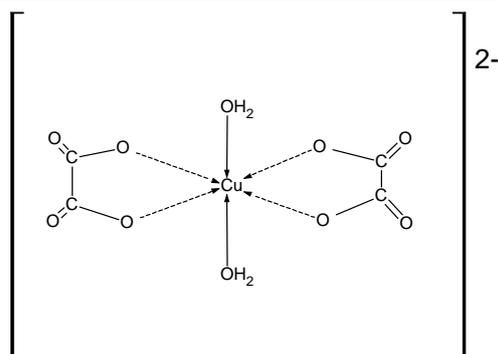
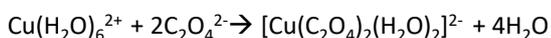
A complex with bidentate ethanedioate ligands e.g. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

Octahedral shape with 90° bond angles

Equations to show formation of bidentate complexes



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.

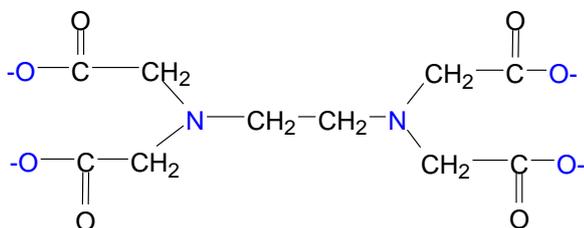


$2-$

Multidentate Ligands

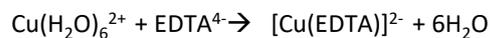
Ligands can be **multidentate** (e.g. EDTA^{4-} which can form six coordinate bonds per ligand).

The EDTA^{4-} anion has the formula



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

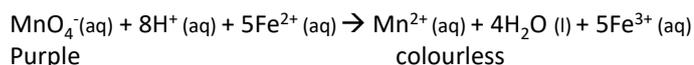
Equations to show formation of multidentate complexes



Learn the two bidentate ligands mentioned above but it is not necessary to remember the structure of EDTA.

Manganate Redox Titration

The redox titration between Fe^{2+} with MnO_4^- (purple) is a very common exercise. This titration is self indicating because of the significant colour change from reactant to product.



The purple colour of manganate can make it difficult to see the bottom of meniscus in the burette.

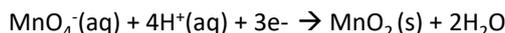
If the manganate is in the burette then the end point of the titration will be the first permanent pink colour.
Colourless \rightarrow purple

Choosing correct acid for manganate titrations.

The acid is needed to supply the 8H^+ ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.

Only **use dilute sulphuric acid** for manganate titrations.

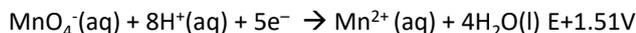
Insufficient volumes of sulphuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+} .



The brown MnO_2 will mask the colour change and lead to a greater (inaccurate) volume of Manganate being used in the titration.

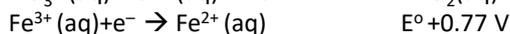
Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed (8H^+).

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the $E^\circ \text{MnO}_4^-/\text{Mn}^{2+} > E^\circ \text{Cl}_2/\text{Cl}^-$



This would lead to a greater volume of manganate being used and poisonous Cl_2 being produced.

It cannot be nitric acid as it is an oxidising agent. It oxidises Fe^{2+} to Fe^{3+} as $E^\circ \text{NO}_3^-/\text{HNO}_2 > E^\circ \text{Fe}^{3+}/\text{Fe}^{2+}$



This would lead to a smaller volume of manganate being used.

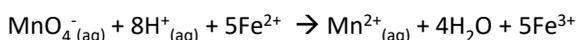
Be able to perform calculations for these titrations and for others when the reductant and its oxidation product are given.

Manganate titration example

A 2.41g nail made from an alloy containing iron is dissolved in 100cm^3 acid. The solution formed contains $\text{Fe}(\text{II})$ ions.

10cm^3 portions of this solution are titrated with potassium manganate (VII) solution of 0.02M. 9.80cm^3 of KMnO_4 were needed to react with the solution containing the iron.

What is the percentage of Iron by mass in the nail?



Step 1 : find moles of KMnO_4

moles = conc x vol

$$0.02 \times 9.8/1000$$

$$= 1.96 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles Fe^{2+} in 10cm^3

$$= \text{moles of } \text{KMnO}_4 \times 5$$

$$= 9.8 \times 10^{-4} \text{ mol}$$

Step 3 : find moles Fe^{2+} in 100cm^3

$$= 9.8 \times 10^{-4} \text{ mol} \times 10$$

$$= 9.8 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of Fe in $9.8 \times 10^{-3} \text{ mol}$

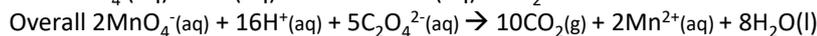
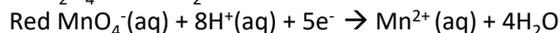
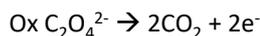
$$\text{mass} = \text{moles} \times \text{RAM} = 9.8 \times 10^{-3} \times 55.8 = 0.547\text{g}$$

Step 5 : find % mass

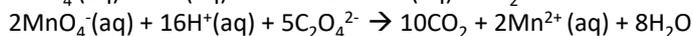
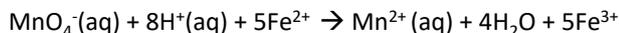
$$\% \text{mass} = 0.547/2.41 \times 100$$

$$= 22.6\%$$

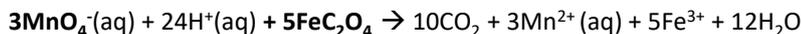
With ethanedioate



With Iron (II) ethanedioate both the Fe^{2+} and the $\text{C}_2\text{O}_4^{2-}$ react with the MnO_4^- .
 1MnO_4^- reacts with 5Fe^{2+} and 2MnO_4^- reacts with $5\text{C}_2\text{O}_4^{2-}$



So overall



So overall the ratio is **3** MnO_4^- to **5** FeC_2O_4

The reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ is slow to begin with (as the reaction is between two negative ions). To do as a titration the conical flask can be heated to 60°C to speed up the initial reaction.

A 1.412 g sample of impure $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in an excess of dilute sulphuric acid and made up to 250 cm^3 of solution. 25.0 cm^3 of this solution decolourised 23.45 cm^3 of a $0.0189\text{ mol dm}^{-3}$ solution of potassium manganate(VII).

What is the percentage by mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the original sample?

Step 1 : find moles of KMnO_4

moles = conc x vol

$$0.0189 \times 23.45/1000$$

$$= 4.43 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 25 cm^3

$$= \text{moles of } \text{KMnO}_4 \times 5/3 \text{ (see above for ratio)}$$

$$= 7.39 \times 10^{-4} \text{ mol}$$

Step 3 : find moles $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 250 cm^3

$$= 7.39 \times 10^{-4} \text{ mol} \times 10$$

$$= 7.39 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in $7.39 \times 10^{-3} \text{ mol}$

$$\text{mass} = \text{moles} \times \text{Mr} = 7.39 \times 10^{-3} \times 179.8 = 1.33\text{g}$$

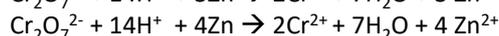
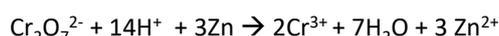
Step 5 ; find % mass

$$\% \text{mass} = 1.33/1.412 \times 100$$

$$= 94.1\%$$

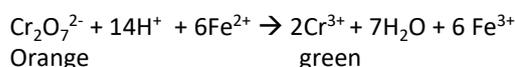
Reducing Chromium

Cr^{3+} (green) and then Cr^{2+} (blue) are formed by reduction of $\text{Cr}_2\text{O}_7^{2-}$ (orange) by the strong reducing agent **zinc** in (HCl) acid solution. Fe^{2+} is a less strong reducing agent and will **only** reduce the dichromate to Cr^{3+}

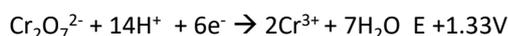


Keeping the zinc/dichromate under a hydrogen atmosphere is needed to reduce it to Cr^{2+} , because O_2 in air will oxidise Cr^{2+} up to Cr^{3+}

The Fe^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ in acid solution reaction can be used as a quantitative redox titration. This does not need an indicator



Redox Potentials

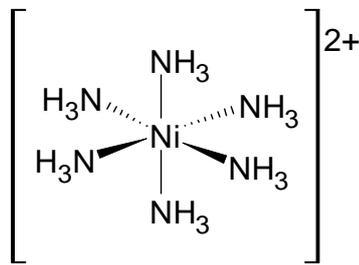
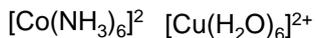


The electrode potential of Iron(II) is in between the two chromium half equations, so Fe^{2+} will reduce chromium down to Cr^{3+}

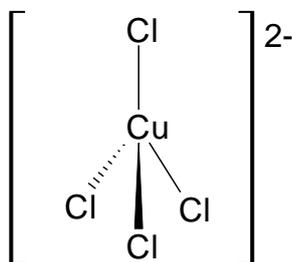
As zinc has a more negative electrode potential than all the chromium half equations, zinc will reduce chromium down to Cr^{2+}

Shapes of complex ions

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

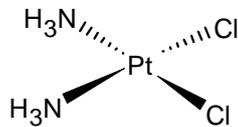


transition metal ions commonly form **tetrahedral** complexes with larger ligands (e.g. Cl⁻). [CoCl₄]²⁻

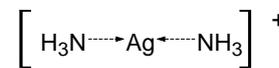


square planar

complexes are also formed, e.g. cisplatin



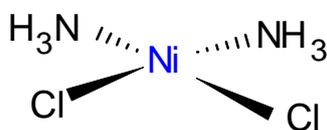
Ag⁺ commonly forms **linear** complexes e.g. [Ag(NH₃)₂]⁺ used as Tollen's Reagent



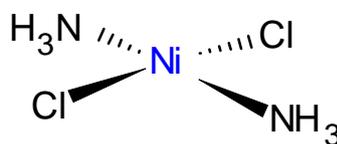
Isomerism in complex ions

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

Cis-trans isomerism in square planar complexes



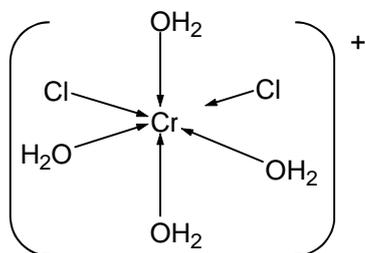
Cis-Ni(NH₃)₂Cl₂



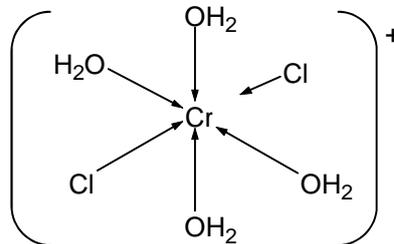
trans-Ni(NH₃)₂Cl₂

cis-trans isomerism is a special case of *E-Z* isomerism

Cis-trans isomerism in octahedral complexes



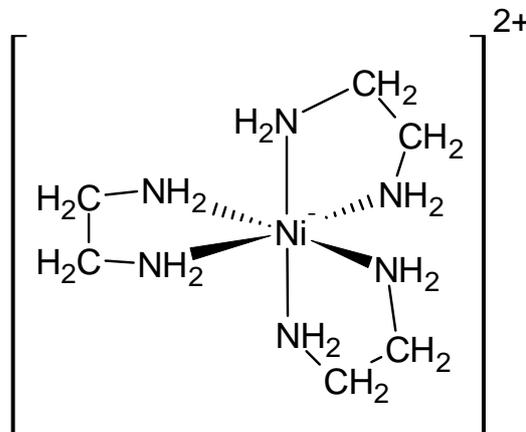
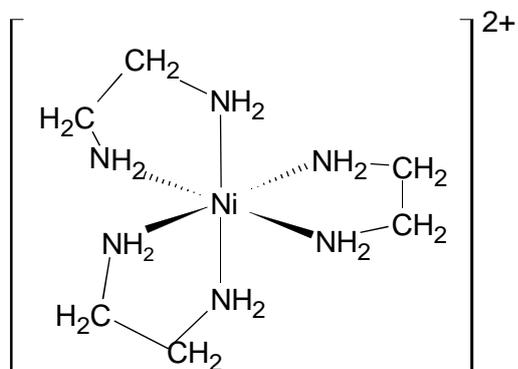
Cis-[Cr(H₂O)₄Cl₂]⁺



trans-[Cr(H₂O)₄Cl₂]⁺

Optical isomerism in octahedral complexes

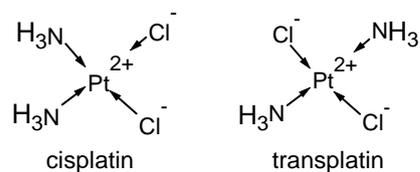
Complexes with 3 bidentate ligands can form two optical isomers (non-superimposable mirror images).



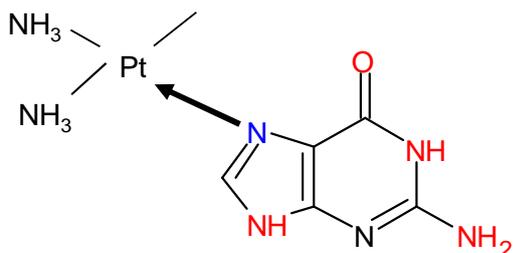
Cisplatin

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

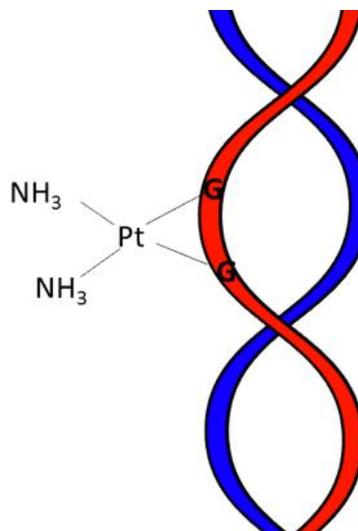
The cisplatin version only works as two chloride ions are displaced and the molecule joins on to the DNA. In doing this it stops the replication of cancerous cells.



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

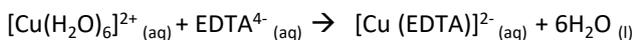


Cisplatin can also prevent the replication of healthy cells by bonding on to healthy DNA which may lead to unwanted side effects like hair loss. Society needs to assess the balance between the benefits and the adverse effects of drugs, such as the anticancer drug cisplatin.

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.



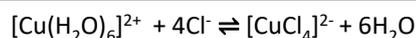
This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. **ΔS is positive**.

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



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

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.

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