CIE Chemistry A-Level

Topic 12 - An Introduction to the Chemistry of Transition Elements

(A level only)

Flashcards

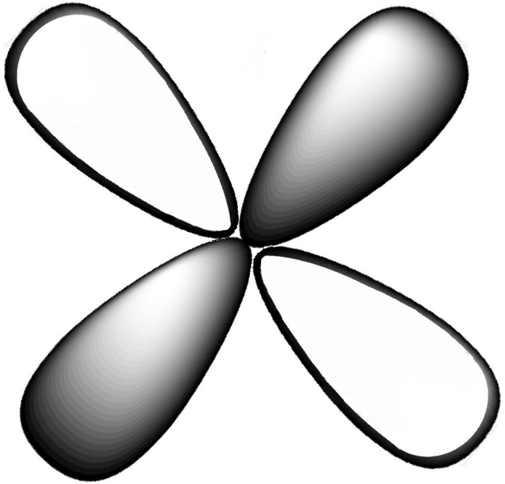
What is a transition element?

What is a transition element?

A d-block element that can form one or more stable ions with an incomplete d-subshell.

Sketch the shape of a d-orbital

Sketch the shape of a d-orbital



Write the electronic configuration for iron and iron(III) ions

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Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Write the electronic configurations of chromium and copper

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These are exceptions to the rules for filling up subshells:

- Chromium: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$**$4s^1$**
- Copper: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$**$4s^1$**

Describe and explain how the melting points of transition metals are different to those of typical s-block metals, such as calcium.

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- Transition metals have higher melting points than typical s-block metals.
- This is because transition metals have the extra 3d electrons which increase the strength of the metallic bonding meaning more energy is required to overcome these bonds when melting the metal.

Describe how the densities of transition metals are different to those of a typical s-block metal, such as calcium.

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Transition metals have greater densities than s-block metals such as calcium.

Explain why the densities of transition metals are greater than those of s-block metals, such as calcium.

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- Nuclear charge increases across the period while electron shielding remains the same. This causes the outer shell electrons to be drawn inwards, decreasing the atomic radius.
- As a result, the densities of transition metals are greater than s-block metals because the atoms are smaller so they can pack more closely together and atomic mass increases across the period.

Why do transition metals have variable oxidation states?

Why do transition metals have variable oxidation states?

Electrons in the 4s and 3d orbitals have very similar energies. This means a relatively similar amount of energy is required to gain / lose a different number of electrons.

How can you predict the likely oxidation states of a transition metal by using its electron configuration?

How can you predict the likely oxidation states of a transition metal by using its electron configuration?

- Most transition metal ions have a 2+ oxidation state due to presence of the 4s electrons.
- To work out the maximum oxidation state:
  maximum oxidation state = number of 4s electrons + the number of unpaired 3d electrons (copper is an exception to this rule).
- Other oxidation states between +2 and the maximum exist but are much more rare.

What is a ligand? Include the meanings of the terms monodentate, bidentate and polydentate

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A species that has a lone pair of electrons that forms a dative covalent bond with a central metal atom / ion.

Monodentate - forms 1 coordinate bond
Bidentate - forms 2 coordinate bonds
Polydentate - forms more than 2 coordinate bonds

What is a complex ion?

What is a complex ion?

A molecule containing a central metal ion surrounded by one or more ligands (joined via coordinate bonds).

What is ligand substitution?

What is ligand substitution?

A reaction in which one ligand in a complex ion is replaced by another.

How does hexaaquacopper(II) form?

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When a copper (II) compound dissolves to release Cu^{2+} ions, water molecules form dative covalent bonds with the metal ion. A complex ion is formed:

$$Cu^{2+} + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+}$$

Write an equation for the ligand substitution reaction between ammonia and $[Cu(H_2O)]^{2+}$ ions. Include any colours

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$$[Cu(H_2O)_6]^{2+} + 4NH_3 \leftrightharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

Pale blue solution **Dark blue solution**

A pale blue precipitate, $Cu(OH)_2$, initially forms

Describe and explain the shape of $[Cu(NH_3)_4(H_2O)_2]^{2+}$

Describe and explain the shape of $[Cu(NH_3)_4(H_2O)_2]^{2+}$

Distorted octahedral because the Cu-O bonds are longer than the Cu-N bonds.

Write an equation for the ligand substitution reaction between chloride ions and $[Cu(H_2O)]^{2+}$ ions. Include any colours.

Write an equation for the ligand substitution reaction between chloride ions and $[Cu(H_2O)]^{2+}$ ions. Include any colours.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \leftrightharpoons [CuCl_4]^{2-} + 6H_2O$$

Pale blue solution

Yellow solution

Initially, the solution turns green

Name the shape of $[CuCl_4]^{2-}$

Name the shape of $[CuCl_4]^{2-}$

Tetrahedral

Cl^- is larger with stronger repulsion than water ligands so only 4 Cl^- ligands surround the copper ion.

Write an equation for the reaction between hexaaquacopper (II) and hydroxide ions. Include any colours.

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$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$

Blue solution **Blue solid**

Or more simply written as:

$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$

How does hexaaquacobalt (II) form?

How does hexaaquacobalt (II) form?

When a cobalt(II) compound dissolves and releases Co^{2+} ions, water molecules form dative covalent bonds with the metal ion. This forms a complex ion:

$$Co^{2+} + 6H_2O \rightarrow [Co(H_2O)_6]^{2+}$$

Write an equation for the ligand substitution reaction between ammonia and $[Co(H_2O)_6]^{2+}$. Include any colours.

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$$[Co(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Co(H_2O)_4(OH)_2]^{2+} + 2NH_4^+$$

Pink solution

Blue precipitate

In excess:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$$

Pink solution

Yellow brown solution

Write an equation for the ligand substitution reaction between chloride ions and $[Co(H_2O)_6]^{2+}$. Include any colours.

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

Pink solution

Rich blue solution

Write an equation for the reaction between hexaaquacobalt(II) and hydroxide ions. Include any colours.

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$[Co(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow [Co(H_2O)_4(OH)_2]_{(s)} + 2H_2O_{(l)}$

Pink solution **Blue precipitate**

Or more simply written as:

$Co^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Co(OH)_{2(s)}$

What is meant by *coordination number*?

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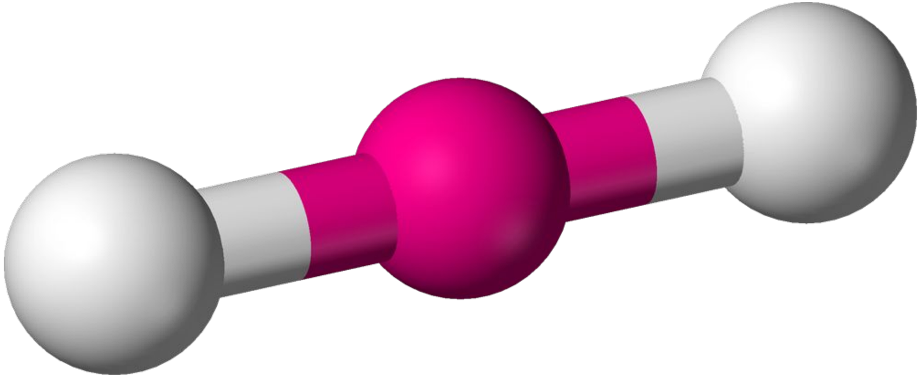
The number of coordinate bonds from ligands to the central metal ion / atom.

What is the shape and bond angle of a complex with a coordination number of 2?

What is the shape and bond angle of a complex with a coordination number of 2?

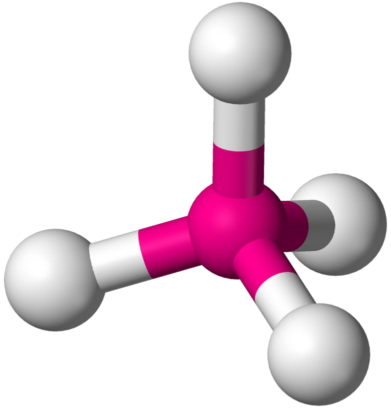
Linear, 180°



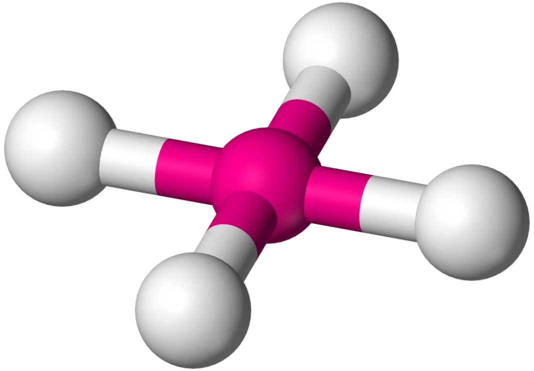
What two shapes and bond angles can complexes with a coordination number of 4 have?

What two shapes and bond angles can complexes with a coordination number of 4 have?

Tetrahedral, 109.5°



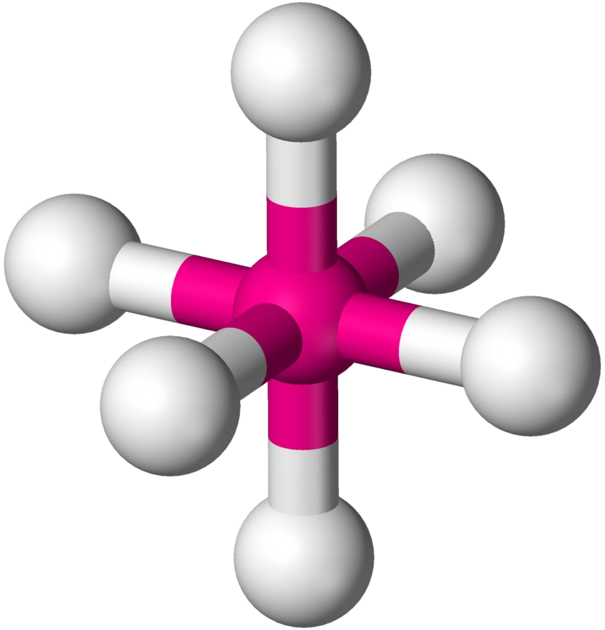
Square planar, 90°



What is the shape bond angle of a complex ion with a coordination number of 6?

What is the shape bond angle of a complex ion with a coordination number of 6?

Octahedral, 90°



What is an Fe^{3+}/ Fe^{2+} redox system? Which species are oxidised and reduced?

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$$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(aq)}$$

Orange-brown solution **Pale green solution** **Brown**

- Iron is reduced.
- Iodine is oxidised.
- Iron is the reducing agent (can be used to reduce other species).

What is a MnO_4^-/Mn^{2+} redox system? How can it be used?

What is a MnO_4^{-}/Mn^{2+} redox system? How can it be used?

$MnO_4^{-}{}_{(aq)} + 8H^{+}{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 4H_2O_{(l)}$

- The solution goes from **purple** to colourless.
- The reaction between manganate (VII) and iron (II) ions in acidic conditions is often used as a basis in redox titrations.

What MnO_4^- ions commonly used to analyse?

What MnO_4^- ions commonly used to analyse?

MnO_4^- titrations can be used to analyse a variety of reducing agents such as:

- Fe^{2+} ions
- Ethanedioic acid $(COOH)_2$

MnO_4^- is reduced to Mn^{2+}.

What is a $Cr_2O_7^{2-}/Cr^{3+}$ redox system? How can it be used?

What is a $Cr_2O_7^{2-}/Cr^{3+}$ redox system? How can it be used?

$$\underset{\text{Orange}}{Cr_2O_7^{2-}{}_{(aq)}} + 3Zn_{(s)} + 14H^+_{(aq)} \rightarrow \underset{\text{Green}}{2Cr^{3+}_{(aq)}} + 7H_2O_{(l)} + 3Zn^{2+}_{(aq)}$$

With excess zinc:

$$Zn_{(s)} + \underset{\text{Green}}{2Cr^{3+}_{(aq)}} \rightarrow Zn^{2+}_{(aq)} + \underset{\text{Pale blue}}{2Cr^{2+}_{(aq)}}$$

Acidified $Cr_2O_7^{2-}$ can be used as an oxidising agent when converting alcohols to aldehydes or carboxylic acids.

How do you predict which half-cell is being oxidised and which is being reduced?

How do you predict which half-cell is being oxidised and which is being reduced?

- The more **negative** the E^θ value, the greater the tendency for the system to be **oxidised**.
- The more **positive** the E^θ value, the greater the tendency for the system to be **reduced**.
- Hence the half-cell with the more positive E^θ is oxidised and the half-cell with the more negative E^θ is reduced.

How do you predict the feasibility of a redox reaction?

How do you predict the feasibility of a redox reaction?

- The reaction is feasible if the oxidising agent has a lower standard cell potential than the reducing agent.
- The greater the difference in E^θ value, the more likely the reaction is to occur.

It has been predicted using standard electrode potentials that a redox reaction is feasible. Why might this reaction not occur spontaneously?

It has been predicted using standard electrode potentials that a redox reaction is feasible. Why might this reaction not occur spontaneously?

- Non-standard conditions
- Ambient energy of the system is lower than the activation energy.

What are degenerate orbitals?

What are degenerate orbitals?

Orbitals with the same energy level.

How are degenerate d-orbitals split into two energy levels in octahedral complexes?

How are degenerate d-orbitals split into two energy levels in octahedral complexes?

- The ligand electrons repel the d-orbital electrons of the transition metal. This raises the energy of the d orbitals.
- These orbitals are split into 2 groups, one with a slightly higher energy than the other.
- The group with the higher energy has 2 d-orbitals while the other group has 3 d-orbitals.

How are degenerate d-orbitals split into two energy levels in tetrahedral complexes?

How are degenerate d-orbitals split into two energy levels in tetrahedral complexes?

- Ligand electrons repel d-orbital electrons of the transition metal. This raises the energy level of the d-orbitals.
- These orbitals are split into 2 groups, one with a slightly higher energy than the other.
- The group with a higher energy contains 3 d-orbitals while the other group contains 2 d-orbitals.
- This is the opposite way round to octahedral complexes.

How does the quantity of energy absorbed due to the split d-orbitals correspond with the colour of the transition metal ion complex?

How does the quantity of energy absorbed due to the split d-orbitals correspond with the colour of the transition metal ion complex?

- When white light is passed through the complex, some energy is absorbed and used to raise an electron from the lower d-orbital energy level to the higher d-orbital energy level.
- The equivalent wavelength/ frequency for this quantity of energy is the wavelength / frequency of light that is absorbed.
- The transition metal will be seen as the complementary colour to the colour that was absorbed (e.g. blue will be seen when yellow is absorbed).

What factors affect the colour of transition metal ion complexes?

What factors affect the colour of transition metal ion complexes?

- The nature of the ligand.
- The oxidation state of the metal.
- The coordination of the transition metal ion.

How does the nature of the ligand affect the transition metal ion complex colour?

How does the nature of the ligand affect the transition metal ion complex colour?

- If the ligands have a **strong** electric field, there will be a **larger** gap between d-orbitals.
- If the ligands have a **weak** electric field, there will be a **smaller** gap between d-orbitals.
- The larger the gap, the more energy is absorbed which means the corresponding wavelength of light gets smaller and hence the colour will move away from the red end of the spectrum and towards orange and then yellow etc.

How does the oxidation state of the metal affect the colour of the transition metal ion complex?

How does the oxidation state of the metal affect the colour of the transition metal ion complex?

- As the oxidation state of the metal increases, the amount of d-orbital splitting increases.
- This therefore affects the amount of energy absorbed and hence the corresponding wavelength of light.

How does the coordination of the ion affect the colour of the transition metal ion complex?

How does the coordination of the ion affect the colour of the transition metal ion complex?

- For an octahedral molecule, splitting is greater than in a tetrahedral molecule.
- Greater splitting = more energy absorbed = wavelength of light is smaller.

Use diagrams of $[Cu(NH_3)_4(H_2O)]^{2+}$ to show how complex ions can show cis/trans isomerism

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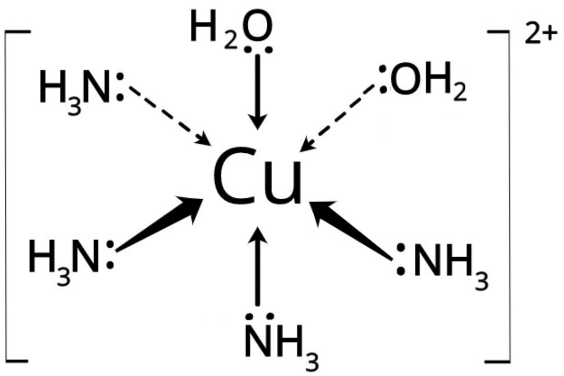
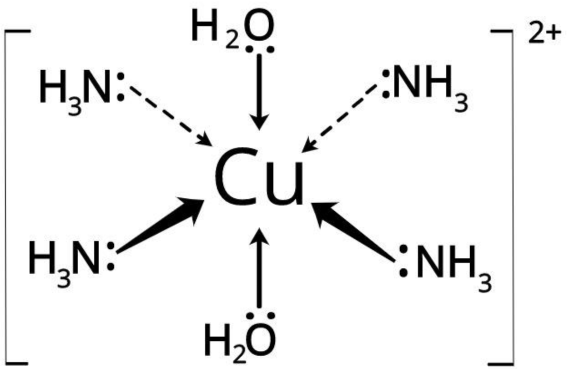
Cis isomer:



The two H_2O groups are adjacent.

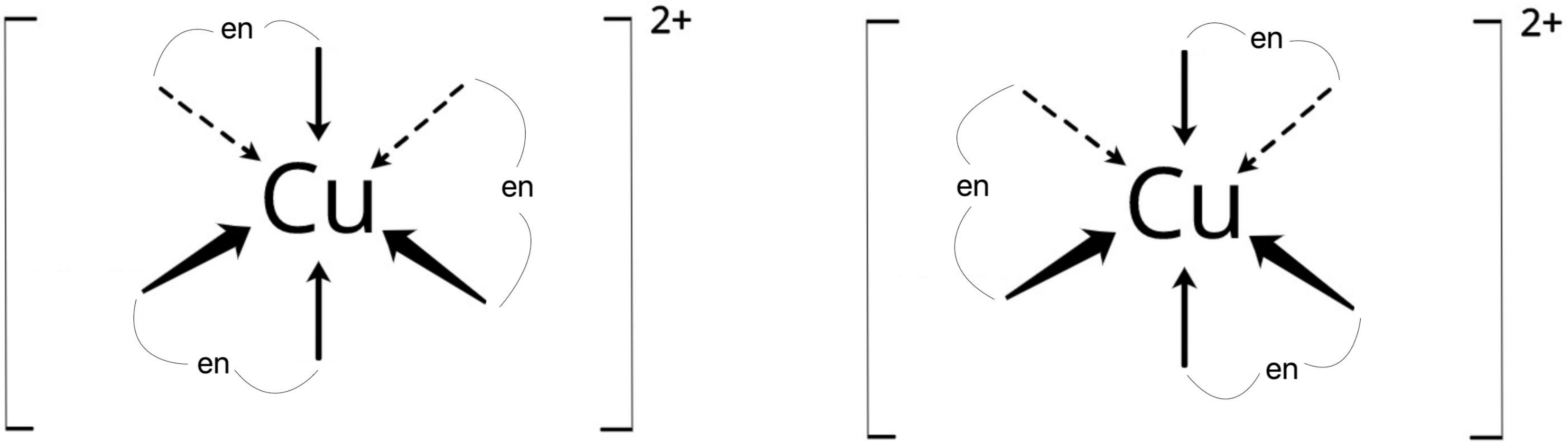
Trans isomer:



The two H_2O groups are opposite each other.

Use diagrams of $[Cu(en)_6]$ to show how complex ions can show optical isomerism

Use diagrams of [Cu(en)$_6$] to show how complex ions can show optical isomerism



‘en’ represents the bidentate ligand $NH_2CH_2CH_2NH_2$. The positions of the ligands change in each isomer.

Draw diagrams of cisplatin and transplatin. What is the shape of these stereoisomers?

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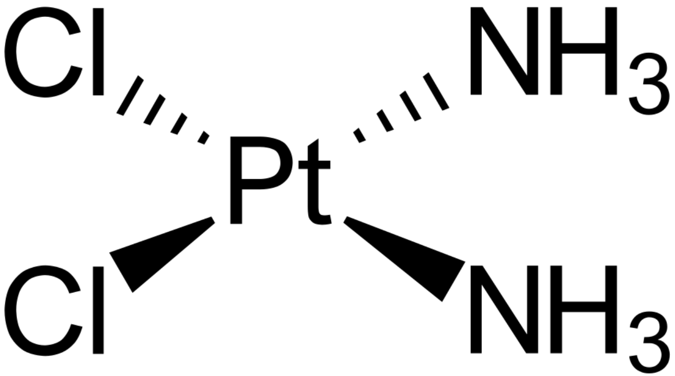
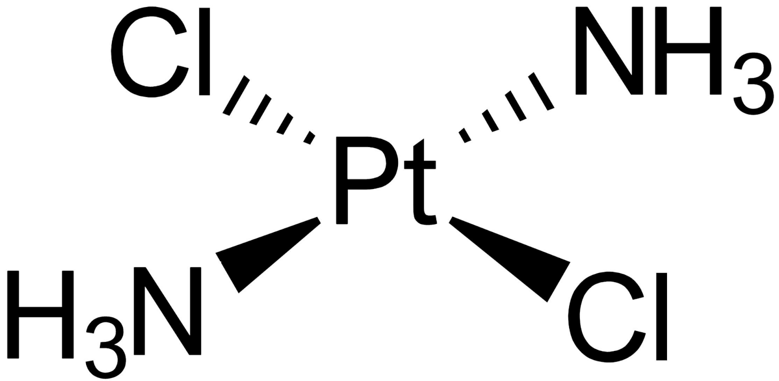
Square planar



Cisplatin



Transplatin

Cisplatin is used as an anti-cancer drug. What does it do?

Cisplatin is used as an anti-cancer drug. What does it do?

Cisplatin binds to DNA, preventing cells replicating. This leads to cell death (apoptosis), preventing uncontrolled cell division.

What is K_{stab}?

What is K_{stab}?

The equilibrium constant for the formation of a complex ion from its constituent molecules / ions, in a solvent.

Write an expression for K_{stab} for the ligand exchange reaction below:

$$[Cr(H_2O)_6]^{3+} + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 6H_2O$$

Write an expression for K_{stab} for the ligand exchange reaction below:

$$[Cr(H_2O)_6]^{3+} + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 6H_2O$$

- Square brackets now represent concentration (ignore any current square brackets).
- Power of each species = balancing number in chemical equation.
- Water isn't included in the equation because the reaction is happening in solution so it is in excess and doesn't affect expression.

$$K_{stab} = \frac{[Cr(NH_3)_6{}^{3+}]}{[Cr(H_2O)_6{}^{3+}][NH_3]^6}$$

What does it mean if the K_{stab} value is large?

What does it mean if the K_{stab} value is large?

The larger the stability constant, the greater the stability of the complex ion.

Describe ligand exchange in terms of competing equilibria

Describe ligand exchange in terms of competing equilibria

When there are two competing equilibria in a ligand exchange reaction, the reaction that forms the most stable complex will be prioritised. This will be the equilibrium with the greatest K_{stab} value.