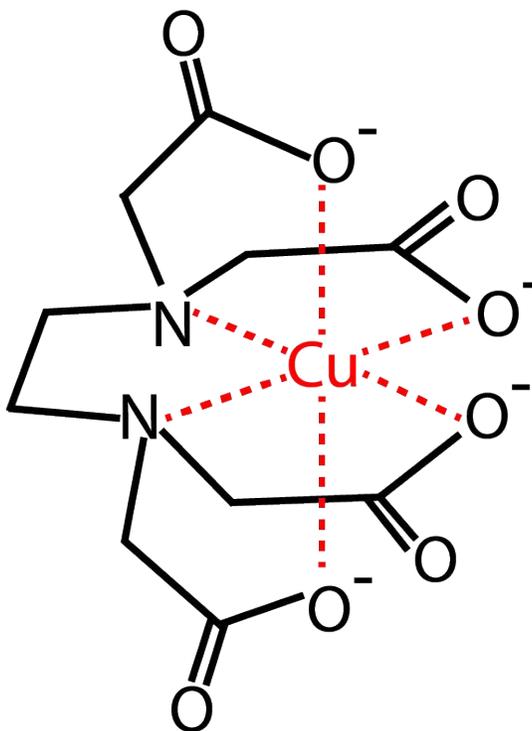


# Transition Metals Complexes and Reactions



# Material Covered

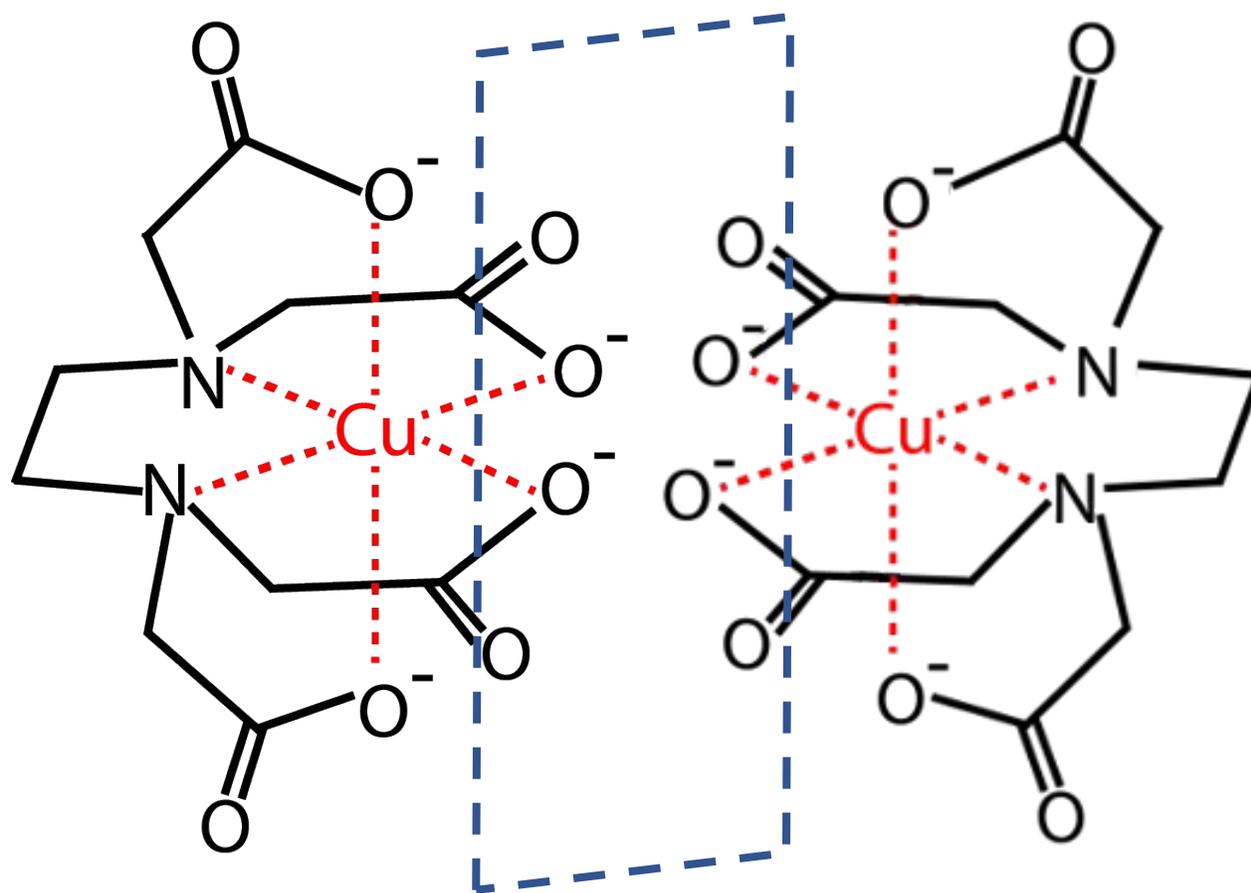
## **Structure of Transition Metals and their Complexes**

1. Electronic Configuration
2. Ligands
3. Shape and Isomerism

## **Reactions of Transition Metals**

1. Ligand Substitution Reactions
2. Acid-base Reactions

# Structure of Transition Metals and their Complexes



# Edexcel

- |   |
|---|
| 1. be able to deduce the electronic configurations of atoms and ions of the <i>d</i> -block elements of period 4 (Sc–Zn), given the atomic number and charge (if any) |
| 2. know that transition metals are <i>d</i> -block elements that form one or more stable ions with incompletely-filled <i>d</i> -orbitals                             |
| 3. understand why transition metals show variable oxidation number  |
| 4. know what is meant by the term 'ligand'  |
| 5. understand that dative (coordinate) bonding is involved in the formation of complex ions   |
| 6. know that a complex ion is a central metal ion surrounded by ligands   |

- |  |
|--|
| 11. understand the meaning of the term 'coordination number'   |
| 12. understand why H <sub>2</sub> O, OH <sup>-</sup> and NH <sub>3</sub> act as monodentate ligands  |
| 13. understand why complexes with six-fold coordination have an octahedral shape, such as those formed by metal ions with H <sub>2</sub> O, OH <sup>-</sup> and NH <sub>3</sub> as ligands |

- |   |
|---|
| 14. know that transition metal ions may form tetrahedral complexes with relatively large ligands such as Cl <sup>-</sup>  |
| 15. know that square planar complexes are also formed by transition metal ions and that <i>cis</i> -platin is an example of such a complex                              |
| 16. understand why <i>cis</i> -platin used in cancer treatment is supplied as a single isomer and not in a mixture with the <i>trans</i> form                           |
| 17. be able to identify bidentate ligands, such as NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> and multidentate ligands, such as EDTA <sup>4-</sup> |

- |  |
|--|
| 28. understand, in terms of the large positive increase in $\Delta S_{\text{system}}$ , that the substitution of a monodentate ligand by a bidentate or multidentate ligand leads to a more stable complex ion |
|--|

# AQA

## Content

Transition metal characteristics of elements Ti–Cu arise from an incomplete d sub-level in atoms or ions.

The characteristic properties include:

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

A ligand is a molecule or ion that forms a co-ordinate bond with a transition metal by donating a pair of electrons.

A complex is a central metal atom or ion surrounded by ligands.

Co-ordination number is number of co-ordinate bonds to the central metal atom or ion.

## Content

$\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{Cl}^-$  can act as monodentate ligands.

Ligands can be bidentate (eg  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  and  $\text{C}_2\text{O}_4^{2-}$ ).

Ligands can be multidentate (eg  $\text{EDTA}^{4-}$ ).

Bidentate and multidentate ligands replace monodentate ligands from complexes. This is called the chelate effect.

**Students should be able to** explain the chelate effect, in terms of the balance between the entropy and enthalpy change in these reactions.

## Content

Transition metal ions commonly form octahedral complexes with small ligands (eg  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ).

Octahedral complexes can display *cis–trans* isomerism (a special case of *E–Z* isomerism) with monodentate ligands and optical isomerism with bidentate ligands.

Transition metal ions commonly form tetrahedral complexes with larger ligands (eg  $\text{Cl}^-$ ).

Square planar complexes are also formed and can display *cis–trans* isomerism.

Cisplatin is the *cis* isomer.

$\text{Ag}^+$  forms the linear complex  $[\text{Ag}(\text{NH}_3)_2]^+$  as used in Tollens' reagent.

## Opportunities for skills development

### MS 4.1 and 4.2

Students understand and draw the shape of complex ions.

### MS 4.3

Students understand the origin of *cis–trans* and optical isomerism.

Students draw *cis–trans* and optical isomers.

Students describe the types of stereoisomerism shown by molecules/complexes.

# OCR

## Properties

- (a) the electron configuration of atoms and ions of the d-block elements of Period 4 (Sc–Zn), given the atomic number and charge **(see also 2.2.1 d)**
- (b) the elements Ti–Cu as transition elements i.e. d-block elements that have an ion with an incomplete d-sub-shell

## Ligands and complex ions

- (d) explanation and use of the term *ligand* in terms of coordinate (dative covalent) bonding to a metal ion or metal, including bidentate ligands
- (e) use of the terms *complex ion* and *coordination number* and examples of complexes with:
  - (i) six-fold coordination with an octahedral shape
  - (ii) four-fold coordination with either a planar or tetrahedral shape **(see also 2.2.2 g–h)**

- (f) types of stereoisomerism shown by complexes, including those associated with bidentate and multidentate ligands:
  - (i) *cis–trans* isomerism e.g.  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  **(see also 4.1.3 c–d)**
  - (ii) optical isomerism e.g.  $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$  **(see also 6.2.2 c)**
- (g) use of *cis-platin* as an anti-cancer drug and its action by binding to DNA preventing cell division

1 <b>H</b> Hydrogen 1.008																	2 <b>He</b> Helium 4.0026						
3 <b>Li</b> Lithium 6.94	4 <b>Be</b> Beryllium 9.0122																	5 <b>B</b> Boron 10.81	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998	10 <b>Ne</b> Neon 20.180
11 <b>Na</b> Sodium 22.990	12 <b>Mg</b> Magnesium 24.305																	13 <b>Al</b> Aluminum 26.982	14 <b>Si</b> Silicon 28.085	15 <b>P</b> Phosphorus 30.974	16 <b>S</b> Sulfur 32.06	17 <b>Cl</b> Chlorine 35.45	18 <b>Ar</b> Argon 39.948
19 <b>K</b> Potassium 39.098	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.956	22 <b>Ti</b> Titanium 47.867	23 <b>V</b> Vanadium 50.942	24 <b>Cr</b> Chromium 51.996	25 <b>Mn</b> Manganese 54.938	26 <b>Fe</b> Iron 55.845	27 <b>Co</b> Cobalt 58.933	28 <b>Ni</b> Nickel 58.693	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.630	33 <b>As</b> Arsenic 74.922	34 <b>Se</b> Selenium 78.971	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.798						
37 <b>Rb</b> Rubidium 85.468	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.906	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.906	42 <b>Mo</b> Molybdenum 95.95	43 <b>Tc</b> Technetium (98)	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.91	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.87	48 <b>Cd</b> Cadmium 112.41	49 <b>In</b> Indium 114.82	50 <b>Sn</b> Tin 118.71	51 <b>Sb</b> Antimony 121.76	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.90	54 <b>Xe</b> Xenon 131.29						
55 <b>Cs</b> Caesium 132.91	56 <b>Ba</b> Barium 137.33	57-71	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.95	74 <b>W</b> Tungsten 183.84	75 <b>Re</b> Rhenium 186.21	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.22	78 <b>Pt</b> Platinum 195.08	79 <b>Au</b> Gold 196.97	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.38	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)	86 <b>Rn</b> Radon (222)						
87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89-103	104 <b>Rf</b> Rutherfordium (267)	105 <b>Db</b> Dubnium (268)	106 <b>Sg</b> Seaborgium (269)	107 <b>Bh</b> Bohrium (270)	108 <b>Hs</b> Hassium (270)	109 <b>Mt</b> Meitnerium (278)	110 <b>Ds</b> Darmstadtium (281)	111 <b>Rg</b> Roentgenium (282)	112 <b>Cn</b> Copernicium (285)	113 <b>Nh</b> Nihonium (286)	114 <b>Fl</b> Flerovium (289)	115 <b>Mc</b> Moscovium (290)	116 <b>Lv</b> Livermorium (293)	117 <b>Ts</b> Tennessine (294)	118 <b>Og</b> Oganesson (294)						

# Electronic

# Configuration

Transition metals are **d-block elements** that form **at least one stable ion** with a **partially filled d-orbital**

A d-orbital can hold up to **10 electrons**

**Scandium** and **zinc** are **not transition metals**:

- **Scandium**: forms only **Sc<sup>3+</sup>**



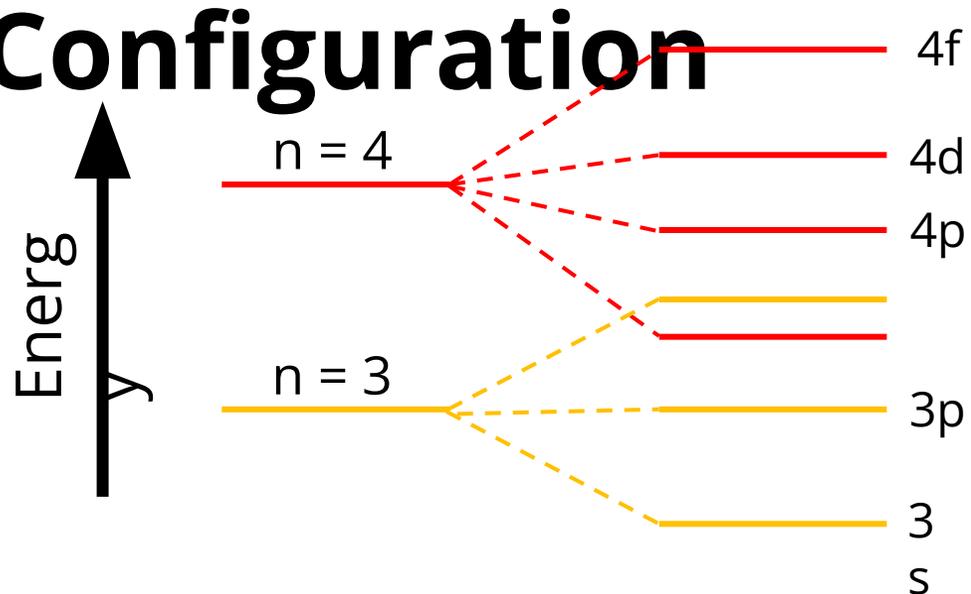
- **Zinc**: forms only **Zn<sup>2+</sup>**



1 <b>H</b> Hydrogen 1.008																	2 <b>He</b> Helium 4.0026						
3 <b>Li</b> Lithium 6.94	4 <b>Be</b> Beryllium 9.0122																	5 <b>B</b> Boron 10.81	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998	10 <b>Ne</b> Neon 20.180
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# Electronic Configuration



But **Cr** and **Cu** behave differently:



The **4s sub-shell** is **lower in energy** than the **3d sub-shell**

- **4s** will **fill up** with electrons **first** before 3d
- **4s** will **lose** electrons **first** before 3d

The electronic configuration of Cr can be written as  $1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{3d^5 4s^1}$  or  $1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{4s^1 3d^5}$  – they are the same

## Exemplar Exam Question – Long Answer

1) State the electronic configuration of nickel and zinc. Using the electronic configurations drawn, explain why nickel is a transition metal but zinc is not.

**[4 marks]**

**Command:** state - simple recall of electronic configuration, explain – give reasoning why

**Context:** definition of a transition metal, use of periodic table

**Direction:** define transition metal, write electronic configuration of Ni and Zn, compare to each other

## Exemplar Exam Question – Long Answer

1) State the electronic configuration of nickel and zinc. Using the electronic configurations drawn, explain why nickel is a transition metal but zinc is not.

**[4 marks]**

The electronic configuration of nickel is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$ . Nickel has

a partially filled d-orbital when it forms stable ions so it is a transition

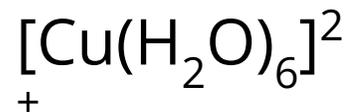
metal. The electronic configuration of zinc is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ . Zinc

does not have a partially filled d-orbital, and only forms one stable ion

( $Zn^{2+}$ ) by losing its 4s electrons and keeping the full 3d subshell.

# Ligand

**S**A **complex ion** is a **metal ion** surrounded by **ligands** through **co-ordinate/dative covalent bonding**

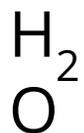


A **ligand** is an **ion** or **molecule** that **donates a pair of electrons** to a central transition metal

The **coordination number** is the **number of co-ordinate bonds** that are formed with central transition metal

# Ligand

A ligand must have **at least one pair of electrons** to form **co-ordinate/dative covalent bonds**



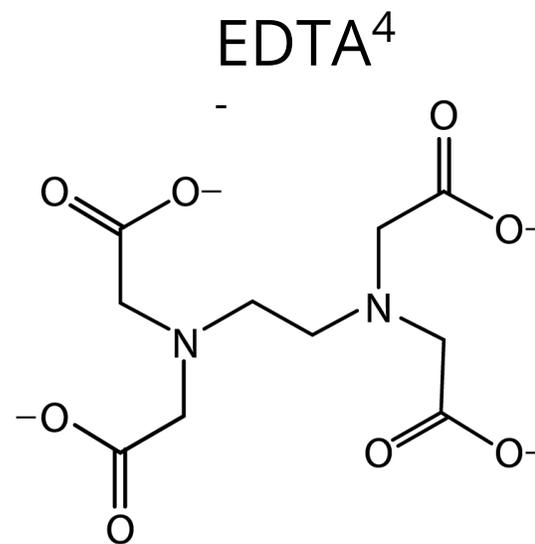
**One pair**

1,2-diaminoethane = en

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

Benzene-1,2-diol

**Two pairs**



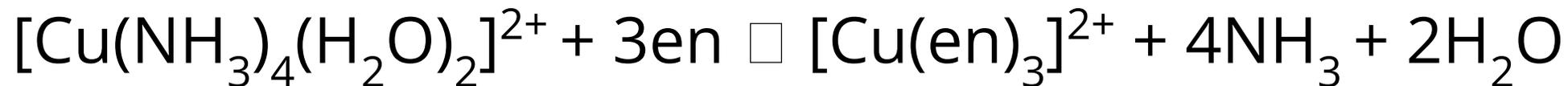
**More than two pairs**



# Ligand

Not on OCR spec

**Multidentate** ligands will **replace monodentate** ligands around TM ions due to the



This is called the chelate effect. Higher coordination numbers are **entropically favoured** as there is **an increase in the number of arrangements** molecules in solution when monodentate ligands are released.

## Exemplar Exam Question – Short Answer

2) Explain why a chloride ion is considered a ligand but methane is not.

**[2 marks]**

**Command:** give reasoning why

**Context:** structure of ligands and their bonding

**Direction:** compare  $\text{Cl}^-$  ion and a  $\text{CH}_4$  molecule

## Exemplar Exam Question – Short Answer

2) Explain why a chloride ion is considered a ligand but methane is not.

**[2 marks]**

A chloride ion has lone pairs that they can donate to a central transition

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metal forming dative covalent bonds. A methane molecule does not have

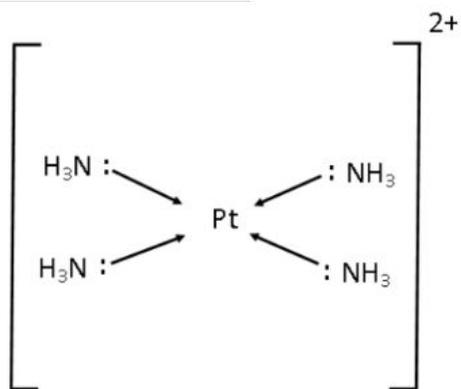
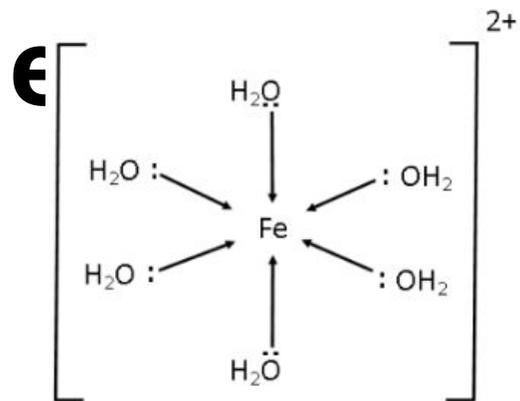
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any lone pairs so it is not considered a ligand.

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# Shape



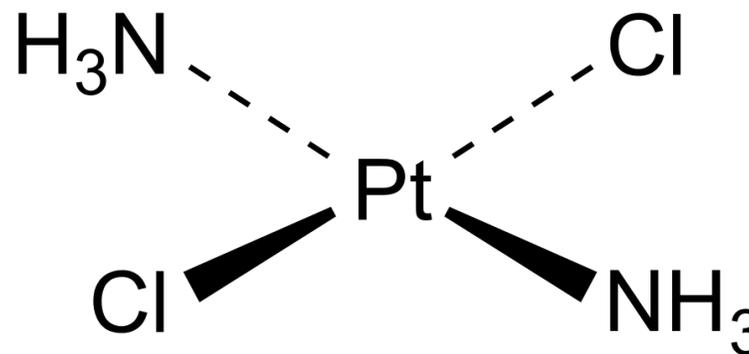
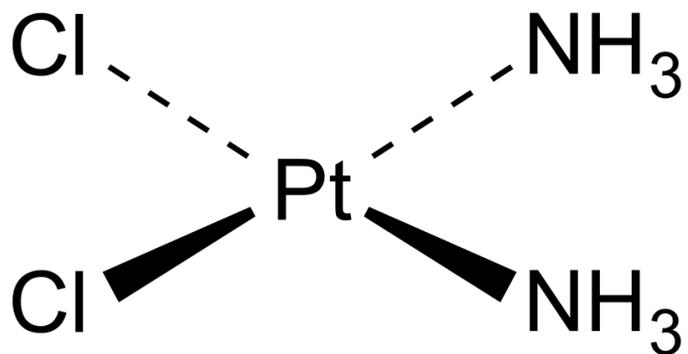
Co-ordination No.	Shape	Example
6	Octahedral	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
4	Tetrahedral (most common)	$[\text{Cu}(\text{Cl}_4)]^{2-}$
4	Square planar (less common)	$[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{2+}$
2	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$

Most complexes with a **co-ordination number** of **4** will be **tetrahedral** – **except Ni** and **Pt** complexes

# Isomeris

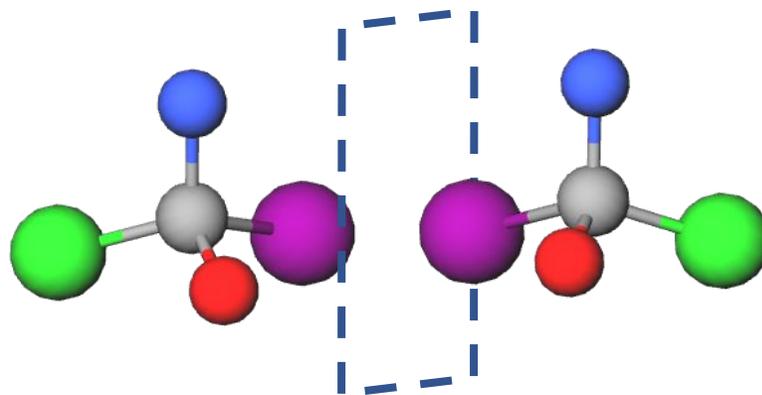
**Mer**eoisomers are molecules or complexes with the **same structural formula** but a **different arrangement** of the atoms in space

**Geometrical isomerism** can occur in **octahedral** and **square planar** complexes that have **two different ligands** around the central TM ion



# Isomeris

**m** transition metal chemistry, **optical isomerism** arises in **octahedral** complexes containing **multidentate** ligands



These isomers are

Optical isomers have **very similar physical** and **chemical** properties, but isomers will rotate **plane-polarised light** in **opposite directions**

## Exemplar Exam Question – Short Answer

3) a) Draw the isomer of platin that is used as an anti-cancer drug.

**[1 mark]**

**Command:** recall  
and sketch the  
correct isomer

**Context:** platin isomers

**Direction:** draw only  
the one that is asked

b) The  $\text{NH}_3$  ligands in this platin can be substituted for 1,2-diaminoethane (en). Suggest an equation for this and explain why this is favoured.

**Command:** suggest  
– critical thinking,  
explain – give  
reasoning

**[3 marks]**  
**Direction:** write the  
substitution equation  
and give reasons  
why it is favoured

**Context:** chelate  
effect of en

## Exemplar Exam Question – Short Answer

3) a) Draw the isomer of platin that is used as an anti-cancer drug.

**[1 mark]**

b) The  $\text{NH}_3$  ligands in this platin can be substituted for 1,2-diaminoethane (en). Suggest an equation for this and explain why this is favoured.



en is a multidentate ligand and can form 2 dative covalent bonds. In this

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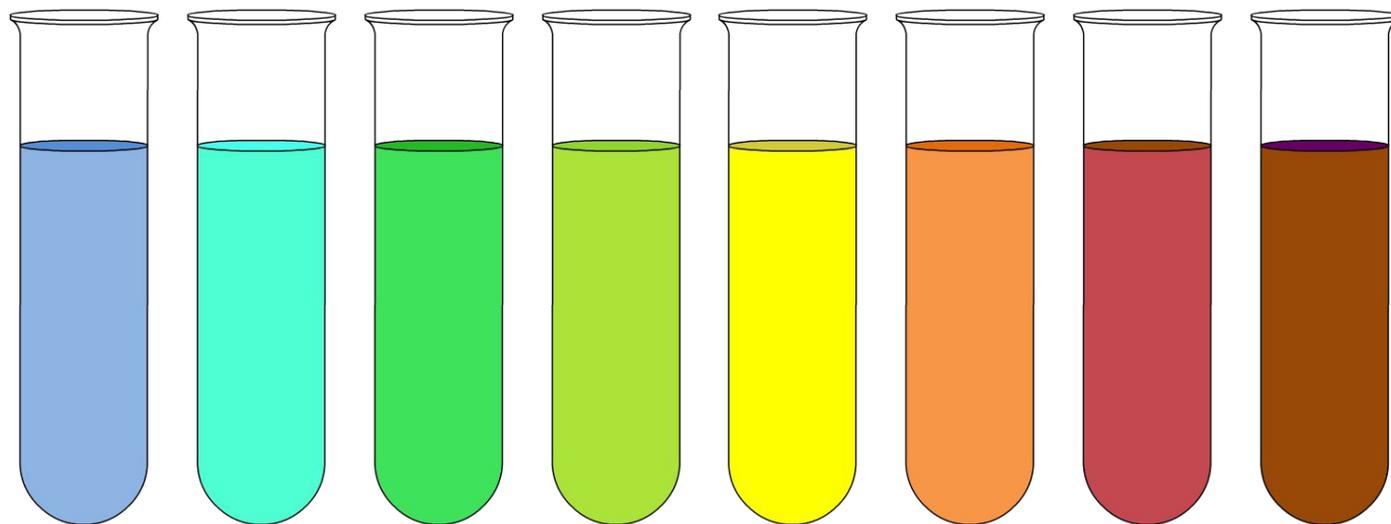
reaction there is an increase in entropy as the number of species increases

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from 2 to 3, which increases the number of possible arrangements.

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# Reactions of Transition Metals



# Edexcel

19. know that a ligand exchange reaction occurs when an oxygen molecule bound to haemoglobin is replaced by a carbon monoxide molecule
24. be able to record observations and write suitable equations for the reactions of $\text{Cr}^{3+}(\text{aq})$ , $\text{Fe}^{2+}(\text{aq})$ , $\text{Fe}^{3+}(\text{aq})$ , $\text{Co}^{2+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ with aqueous sodium hydroxide and aqueous ammonia, including in excess
25. be able to write ionic equations to show the difference between ligand exchange and amphoteric behaviour for the reactions in (24) above
26. understand that ligand exchange, and an accompanying colour change, occurs in the formation of: <ul style="list-style-type: none"> <li>i <math>[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}</math> from <math>[\text{Cu}(\text{H}_2\text{O})_6]^{2+}</math> via <math>\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4</math></li> <li>ii <math>[\text{CuCl}_4]^{2-}</math> from <math>[\text{Cu}(\text{H}_2\text{O})_6]^{2+}</math></li> <li>iii <math>[\text{CoCl}_4]^{2-}</math> from <math>[\text{Co}(\text{H}_2\text{O})_6]^{2+}</math></li> </ul>
27. understand that the substitution of small, uncharged ligands (such as $\text{H}_2\text{O}$ ) by larger, charged ligands (such as $\text{Cl}^-$ ) can lead to a change in coordination number

# AQA

Content	Opportunities for skills development
<p>In aqueous solution, the following metal-aqua ions are formed:</p> <p><math>[\text{M}(\text{H}_2\text{O})_6]^{2+}</math>, limited to <math>\text{M} = \text{Fe}</math> and <math>\text{Cu}</math></p> <p><math>[\text{M}(\text{H}_2\text{O})_6]^{3+}</math>, limited to <math>\text{M} = \text{Al}</math> and <math>\text{Fe}</math></p> <p>The acidity of <math>[\text{M}(\text{H}_2\text{O})_6]^{3+}</math> is greater than that of <math>[\text{M}(\text{H}_2\text{O})_6]^{2+}</math></p> <p>Some metal hydroxides show amphoteric character by dissolving in both acids and bases (eg hydroxides of <math>\text{Al}^{3+}</math>).</p> <p><b>Students should be able to:</b></p> <ul style="list-style-type: none"> <li>explain, in terms of the charge/size ratio of the metal ion, why the acidity of <math>[\text{M}(\text{H}_2\text{O})_6]^{3+}</math> is greater than that of <math>[\text{M}(\text{H}_2\text{O})_6]^{2+}</math></li> <li>describe and explain the simple test-tube reactions of: <math>\text{M}^{2+}(\text{aq})</math> ions, limited to <math>\text{M} = \text{Fe}</math> and <math>\text{Cu}</math>, and of <math>\text{M}^{3+}(\text{aq})</math> ions, limited to <math>\text{M} = \text{Al}</math> and <math>\text{Fe}</math>, with the bases <math>\text{OH}^-</math>, <math>\text{NH}_3</math> and <math>\text{CO}_3^{2-}</math></li> </ul>	<p><b>AT d and K</b></p> <p><b>PS 1.2</b></p> <p>Students could carry out test-tube reactions of metal-aqua ions with <math>\text{NaOH}</math>, <math>\text{NH}_3</math> and <math>\text{Na}_2\text{CO}_3</math></p> <p><b>AT d and k</b></p> <p><b>PS 2.2</b></p> <p>Students could carry out test-tube reactions to identify the positive and negative ions in this specification.</p> <p><b>PS 1.1</b></p> <p>Students could identify unknown substances using reagents.</p>
<p>Exchange of the ligands <math>\text{NH}_3</math> and <math>\text{H}_2\text{O}</math> occurs without change of co-ordination number (eg <math>\text{Co}^{2+}</math> and <math>\text{Cu}^{2+}</math>).</p>	
<p>Substitution may be incomplete (eg the formation of <math>[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}</math>).</p>	
<p>The <math>\text{Cl}^-</math> ligand is larger than the uncharged ligands <math>\text{NH}_3</math> and <math>\text{H}_2\text{O}</math></p>	
<p>Exchange of the ligand <math>\text{H}_2\text{O}</math> by <math>\text{Cl}^-</math> can involve a change of co-ordination number (eg <math>\text{Co}^{2+}</math>, <math>\text{Cu}^{2+}</math> and <math>\text{Fe}^{3+}</math>).</p>	

# OCR

## Properties

- (a) the electron configuration of atoms and ions of the d-block elements of Period 4 (Sc–Zn), given the atomic number and charge (see also 2.2.1 d)
- (b) the elements Ti–Cu as transition elements i.e. d-block elements that have an ion with an incomplete d-sub-shell
- (c) illustration, using at least two transition elements, of:
  - (i) the existence of more than one oxidation state for each element in its compounds (see also 5.3.1 k)
  - (ii) the formation of coloured ions (see also 5.3.1 h, j–k)
  - (iii) the catalytic behaviour of the elements and their compounds and their importance in the manufacture of chemicals by industry (see 3.2.2 d)

## Ligands and complex ions

- (d) explanation and use of the term *ligand* in terms of coordinate (dative covalent) bonding to a metal ion or metal, including bidentate ligands
- (e) use of the terms *complex ion* and *coordination number* and examples of complexes with:
  - (i) six-fold coordination with an octahedral shape
  - (ii) four-fold coordination with either a planar or tetrahedral shape (see also 2.2.2 g–h)

- (f) types of stereoisomerism shown by complexes, including those associated with bidentate and multidentate ligands:
  - (i) *cis–trans* isomerism e.g.  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  (see also 4.1.3 c–d)
  - (ii) optical isomerism e.g.  $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$  (see also 6.2.2 c)
- (g) use of *cis-platin* as an anti-cancer drug and its action by binding to DNA preventing cell division

## Ligand substitution

- (h) ligand substitution reactions and the accompanying colour changes in the formation of:
  - (i)  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{CuCl}_4]^{2-}$  from  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
  - (ii)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  from  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (see also 5.3.1 j)
- (i) explanation of the biochemical importance of iron in haemoglobin, including ligand substitution involving  $\text{O}_2$  and CO

## Precipitation reactions

- (j) reactions, including ionic equations, and the accompanying colour changes of aqueous  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  with aqueous sodium hydroxide and aqueous ammonia, including:
  - (i) precipitation reactions
  - (ii) complex formation with excess aqueous sodium hydroxide and aqueous ammonia

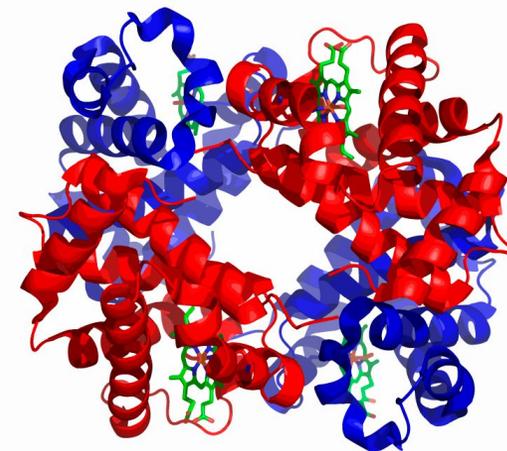
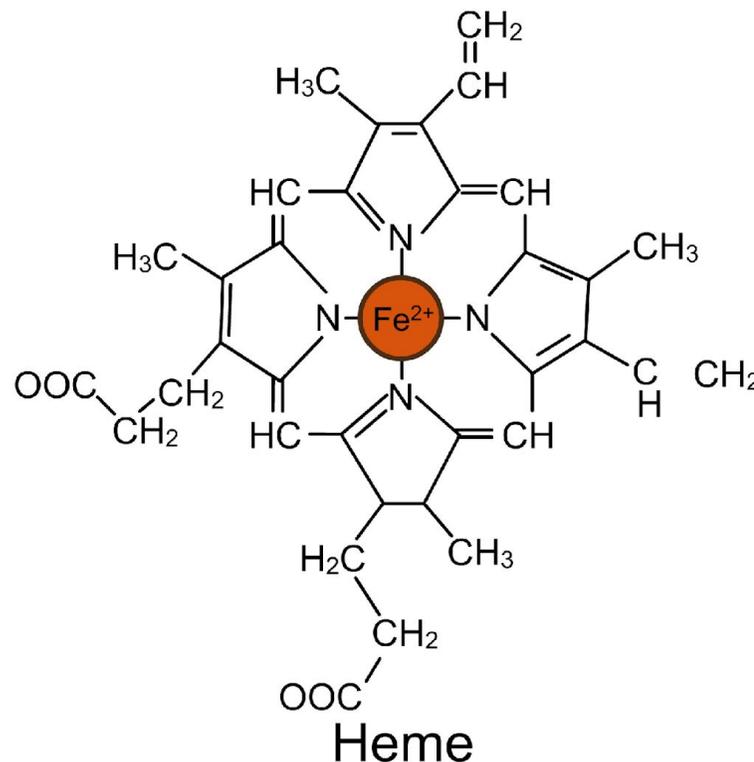
## Redox reactions

- (k) redox reactions and accompanying colour changes for:
  - (i) interconversions between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$
  - (ii) interconversions between  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$
  - (iii) reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  and disproportionation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  and Cu
- (l) interpretation and prediction of unfamiliar reactions including ligand substitution, precipitation, redox.

# Ligand Substitution Reactions

Ligands can be **swapped** for another ligand in a **ligand substitution/exchange reaction**

- **Most ligands** can be replaced by other ligands which are in **higher concentration** or when **stronger co-ordinate bonds** are formed



# Ligand Substitution Reactions

**Haemoglobin** contains a **Fe<sup>2+</sup>** ion co-ordinately bonded to **4 N** lone pairs (part of the **haem**), **1 N** lone pair from a **protein (globin)**, and **1 H<sub>2</sub>O**

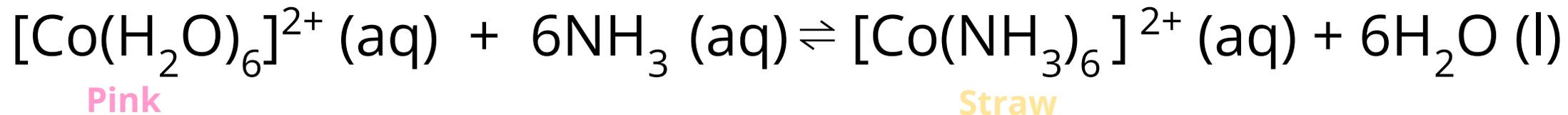
In **high O<sub>2</sub> concentration** the H<sub>2</sub>O molecule will be **substituted for O<sub>2</sub>** to be **carried around the body** where it is needed



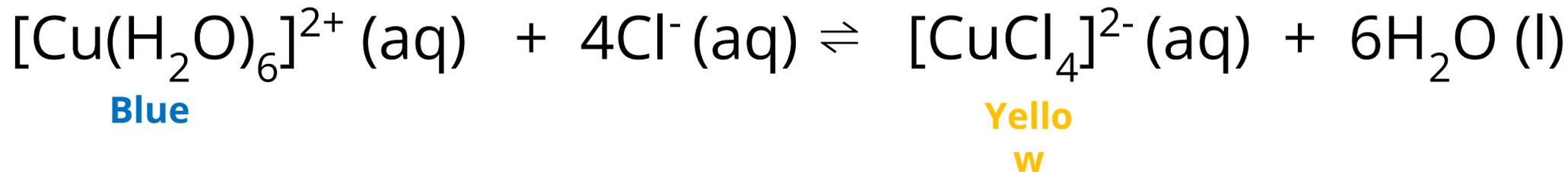
# Ligand Substitution

## Reactions

When ligands are displaced by **ligands** of similar size (e.g.  $\text{NH}_3$ ), the **coordination number** and **shape**

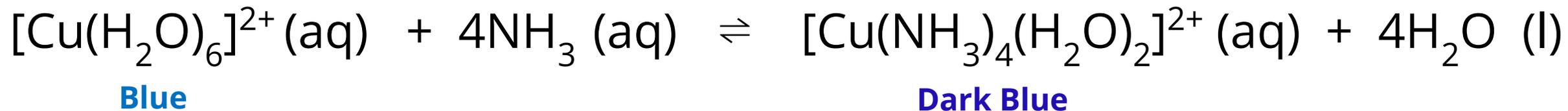


If water ligands are displaced by **ligands** with a different size (e.g.  $\text{Cl}^-$ ), then the **coordination number** and **shape**

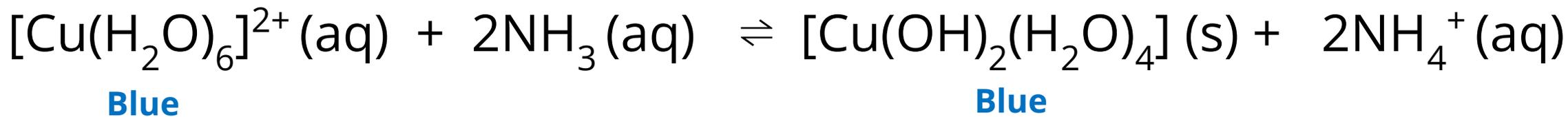


# Ligand Substitution Reactions

Substitution can also be



When only a **small amount** of ligand is added, a **precipitate** will form.  $\text{NH}_3$  is a **better ligand** than water but it can act as a **base** at first.



## Exemplar Exam Question – Short Answer

4) An excess of KCN is added to a solution of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  exists as an octahedral complex.

a) Using the table, state the coordination number and shape of the complex ion formed, and explain why this is formed.

Ligand	Size (Å)
$\text{H}_2\text{O}$	1.45
$\text{CN}^-$	1.60

**[2 marks]**

**Command:** state – simple answer, explain – give reasoning

**Direction:** give C.N. and shape using equation and table, give reasons why we see this

**Context:** effects of ligand substitution

## Exemplar Exam Question – Short Answer

4) An excess of KCN is added to a solution of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  exists as an octahedral complex.

b) State an equation for the ligand substitution that occurs, given that water is poor ligand.

**[1 mark]**

**Command:**  
simple answer

**Context:** ligand  
substitution equations

**Direction:** write the  
equation of the reaction

## Exemplar Exam Question – Short Answer

4) An excess of KCN is added to a solution of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  exists as an octahedral complex.

a) Using the table, state the coordination number and shape of the complex ion formed, and explain why this is formed. **[2 marks]**

Ligand	Size (Å)
$\text{H}_2\text{O}$	1.45
$\text{CN}^-$	1.60

The coordination number remains as 6 because as KCN is in excess. The

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starting complex is octahedral so the new complex will be octahedral. This is

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because  $\text{H}_2\text{O}$  and  $\text{CN}^-$  are similar in size so the coordination number and

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shape do not change.

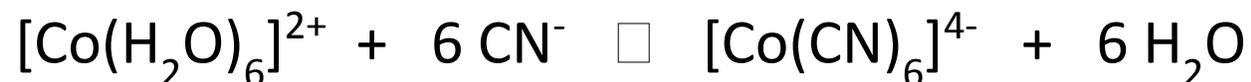
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## Exemplar Exam Question – Short Answer

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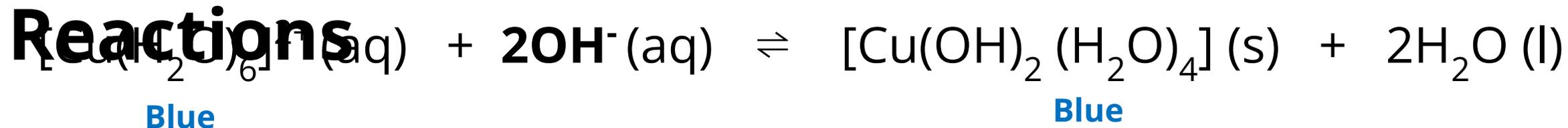
b) State an equation for the ligand substitution that occurs, given that water is poor ligand.

**[1 mark]**



# Acid-Base

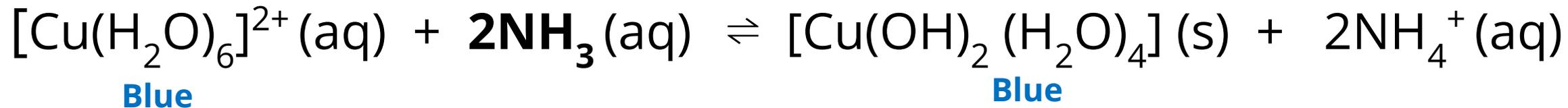
## Reactions



In this **acid-base reaction**, two **OH<sup>-</sup>** ions act as a **base accepting H<sup>+</sup> ions** from the complex, whilst the **complex** acts as an **acid donating H<sup>+</sup> ions**.

These **acid-base reactions** are **reversible** so can be termed

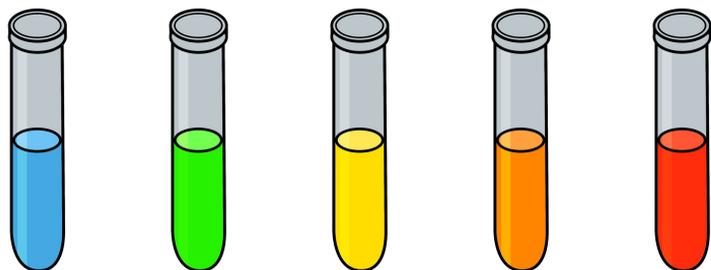
The **same reaction** is observed on the **careful addition** of **NH<sub>3</sub>**.



# Acid-Base

## Reactions

Most transition metal complexes reacting with **aqueous NaOH** or **aqueous NH<sub>3</sub>** form a **coloured hydroxide precipitate**



Ion	Solution Colour	Precipitate Colour
Cu <sup>2+</sup>	Pale blue	Dark blue
Fe <sup>2+</sup>	Pale green	Dark green
Fe <sup>3+</sup>	Yellow	Orange
Mn <sup>2+</sup>	Pale pink	Pink
Cr <sup>3+</sup>	Blue-Purple	Grey-green

Precipitate not for edexcel

Not for AQA



## Exemplar Exam Question – Statement

5) Hexaaquachromium(III) ions are blue-purple in colour. When aqueous sodium hydroxide is added to this solution a grey-green precipitate forms.

a) State the formula of the complex ion which gives the initial green solution. **[1 mark]**

b) State the formula of the grey-green precipitate and state the reaction type that forms it. **[1 mark]**

**Command:**  
simple answer

**Direction:** state  
the formulas and  
reaction type

**Context:** TMs, their  
unique colours, and  
reaction types

## Exemplar Exam Question – Statement

5) Hexaaquachromium(III) ions are blue-purple in colour. When aqueous sodium hydroxide is added to this solution a grey-green precipitate forms.

c) Suggest which complex ion would be formed when excess aqueous ammonia is added to the initial blue-purple solution and state the reaction type.

**[1 mark]**

**Command:**  
critical thinking  
and knowledge  
required

**Direction:** state the  
complex and reaction  
type

**Context:** ligand  
substitution occurs when  
excess is added

## Exemplar Exam Question – Statement

5) Hexaaquairon(II) ions are green in colour. When aqueous sodium hydroxide is added to this solution a green precipitate forms.

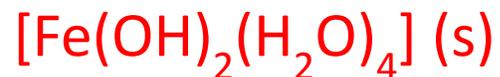
a) State the formula of the complex ion which gives the initial green solution.

**[1 mark]**



b) State the formula of the green precipitate and state the reaction type that forms it.

**[1 mark]**



Acid-base reaction

c) Suggest which complex ion would be formed when excess aqueous ammonia is added to the initial green solution.

**[1 mark]**

No visible change as no reaction.



# Mini Mock Paper

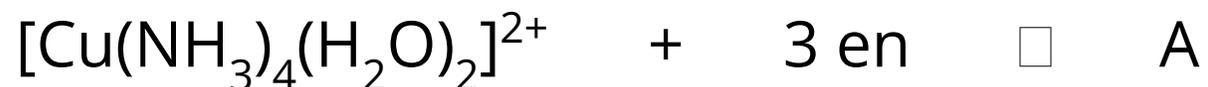


## Mini Mock Paper



- 1) Adding 3 equivalents of ethane-1,2-diamine (en) to  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  forms molecule A.
- a) Write the formula for molecule A and draw its structure. **[2 marks]**
- b) State which type of isomerism occurs in  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  and draw the isomers. **[2 marks]**

## Mini Mock Paper



- 1) Adding 3 equivalents of ethane-1,2-diamine (en) to  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  forms molecule A.
- c) State which type of isomerism occurs in molecule A and draw the isomers.  
**[2 marks]**

## Mini Mock Paper

2) The sizes of two ligands when bonded to a transition metal ion are given below.

Ligand	Size (pm)
$\text{Cl}^-$	120
$\text{Br}^-$	186

a) Explain how the differences in size may alter the coordination number of any ligand complexes. **[2 marks]**

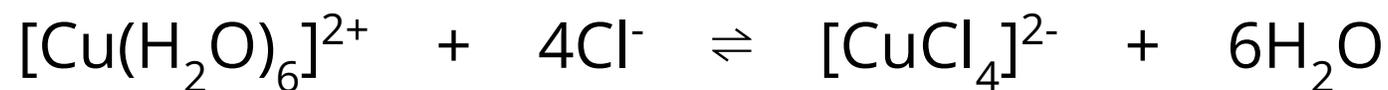
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## Mini Mock Paper

3)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ions with have an octahedral shape. Hydrochloric acid is added to aqueous copper(II) sulfate and the following reaction takes place:



a) Describe the bonding within the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion complex. **[2 marks]**

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b) State the type of reaction that takes place to form  $[\text{CuCl}_4]^{2-}$  ions and explain their likely shape. **[3 marks]**

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# Mini Mock Paper Answers



## Mini Mock Paper



- 1) Adding 3 equivalents of ethane-1,2-diamine (en) to  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  forms molecule A.
- a) Write the formula of molecule A and draw its structure. **[2 marks]**



## Mini Mock Paper



- 1) Adding 3 equivalents of ethane-1,2-diamine (en) to  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  forms molecule A.
- b) State which type of isomerism occurs in  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  and draw the isomers.  
**[2 marks]**

Geometric Isomerism

## Mini Mock Paper



- 1) Adding 3 equivalents of ethane-1,2-diamine (en) to  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  forms molecule A.
- c) State which type of isomerism occurs in molecule A and draw the isomers.

**[2 marks]**

Optical Isomerism

## Mini Mock Paper

2) The sizes of two ligands when bonded to a transition metal ion are given below.

Ligand	Size (pm)
$\text{Cl}^-$	120
$\text{Br}^-$	186

a) Explain how the differences in size may alter the coordination number of any ligand complexes. **[2 marks]**

$\text{Br}^-$  is a bigger ligand than  $\text{Cl}^-$  so fewer ligands can fit around the transition metal ion,

lowering the coordination number.

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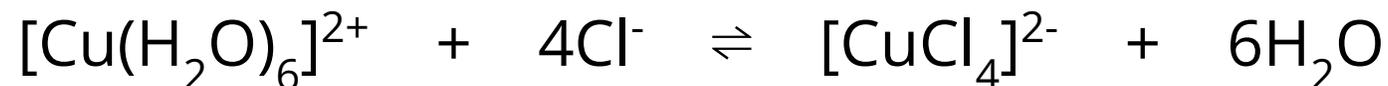
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## Mini Mock Paper

3)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ions with have an octahedral shape. Hydrochloric acid is added to aqueous copper(II) sulfate in the following reaction:



a) Describe the bonding within the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion complex. **[2 marks]**

The lone pair on the oxygen atom of the water ligands is donated to the  $\text{Cu}^{2+}$  ions in a dative  

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covalent/coordinate bond.  

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b) State the type of reaction that takes place to form  $[\text{CuCl}_4]^{2-}$  ions and explain their likely shape. **[3 marks]**

The reaction that takes place is a ligand substitution reaction.  $\text{Cl}^-$  ions are a different size  

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compared to the  $\text{H}_2\text{O}$  ligands so the coordination number and shape changes. The coordination  

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number changes from 6 to 4, and the shape changes from octahedral to tetrahedral.  

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