

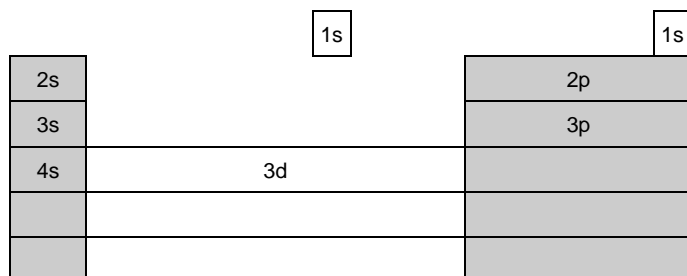


# INTRODUCTION TO TRANSITION METALS



# SECTION 1 - INTRODUCTION

## 1) ELECTRON STRUCTURE & DEFINITION OF TRANSITION METALS



4s fills before 3d.  
4s also empties before 3d.

Give the electron structure of the following atoms / ions (start from [Ar]).

Fe .....	Cu .....
Fe <sup>3+</sup> .....	Cu <sup>+</sup> .....
Sc .....	Cu <sup>2+</sup> .....
Sc <sup>3+</sup> .....	Zn .....
V .....	Zn <sup>2+</sup> .....
V <sup>2+</sup> .....	Cr .....

Definition of transition metal = **element that has an incomplete d sub-shell in either its atoms or one or more common ions**

metal	atom	Common ions	Transition metal?
Sc	Sc [Ar] .....	Sc <sup>3+</sup> [Ar] .....	
Cu	Cu [Ar] .....	Cu <sup>+</sup> [Ar] ..... Cu <sup>2+</sup> [Ar] .....	
Zn	Zn [Ar] .....	Zn <sup>2+</sup> [Ar] .....	

The incomplete d sub-shell is responsible for a number of general properties of transition elements:

- 1) variable oxidation states
- 2) catalytic action
- 3) coloured compounds
- 4) formation of complexes

## 2) COMPLEX FORMATION

### Some definitions

Ligand = molecule or ion that bonds to metals by a co-ordinate bond

Complex = metal ion with co-ordinately bonded ligands

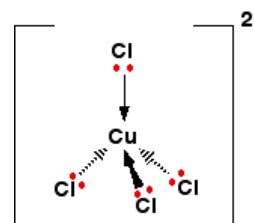
Co-ordination number = number of co-ordinate bonds from ligands to metal ion

Lewis base = lone pair donor

Lewis acid = lone pair acceptor

### Formation of complexes

Here there are 4 chloride ions ( $\text{Cl}^-$ ) each forming a single co-ordinate bond to the  $\text{Cu}^{2+}$  ion, forming the  $[\text{CuCl}_4]^{2-}$  ion.



### Type of ligands

All ligands have one (or more) lone pair(s) of electrons – these are needed to form the co-ordinate bond to the metal ion.

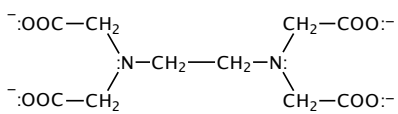
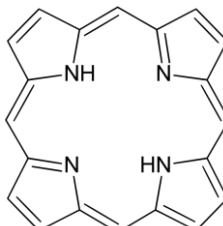
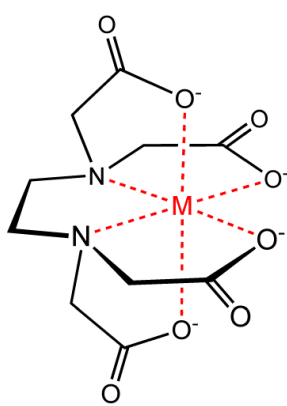
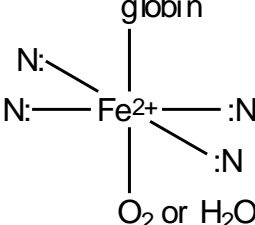
**Unidentate ligands** – ligands which form one co-ordinate bond to a metal ion

Ligand	$:\text{Cl}^-$	$:\text{OH}^-$	$:\text{CN}^-$	$\text{H}_2\text{O}:$	$:\text{NH}_3$
Example complex	$[\text{CuCl}_4]^{2-}$	$[\text{Cr}(\text{OH})_6]^{3-}$	$[\text{Ag}(\text{CN})_2]^-$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Cr}(\text{NH}_3)_6]^{3+}$

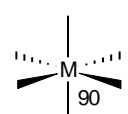
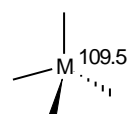
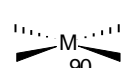
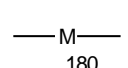
**Bidentate ligands** – ligands which form two co-ordinate bonds to a metal ion

Ligand	<p><b>1,2-diaminoethane (en)</b></p>	<p><b>ethanedioate ion (<math>\text{C}_2\text{O}_4^{2-}</math>)</b></p>
Example complex	<p><math>[\text{Cr}(\text{en})_3]^{3+}</math></p>	<p><math>[\text{Cr}(\text{C}_2\text{O}_4)]^{3-}</math></p>

**Multidentate ligands** – ligands which form more than two co-ordinate bonds to a metal ion

Ligand	<p style="text-align: center;"><b>EDTA<sup>4-</sup></b></p>  <p style="text-align: center;">forms 6 bonds</p>	<p style="text-align: center;"><b>porphyrin</b></p>  <p style="text-align: center;">forms 4 bonds</p>
How it bonds		<p style="text-align: center;">globin</p> 
Example	[Cu(EDTA)] <sup>2-</sup>	haemoglobin

### 3) SHAPES OF COMPLEXES

	octahedral	tetrahedral	square planar	linear
co-ordination number	6	4	4	2
shape				
occurrence	Most complexes	Often with Cl <sup>-</sup> ligands	Pt <sup>2+</sup> and Ni <sup>2+</sup> complexes	Ag <sup>+</sup> complexes
example	[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	[CuCl <sub>4</sub> ] <sup>2-</sup>	[PtCl <sub>4</sub> ] <sup>2-</sup>	[Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>

**✓ TASK 1 – Drawing complexes**

Formula	$[\text{Ag}(\text{CN})_2]^-$	$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$[\text{Ni}(\text{en})_3]^{3+}$
Sketch			
Shape			
Bond angles			
Metal oxidation state			
Co-ordination number			

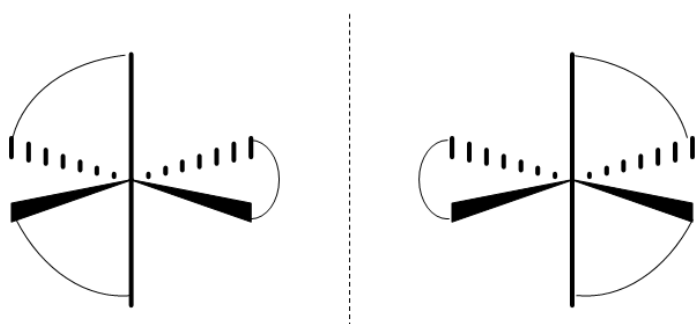
Formula	$[\text{Co}(\text{en})_2\text{Cl}_2]^+$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
Sketch			
Shape			
Bond angles			
Metal oxidation state			
Co-ordination number			

## Stereoisomerism in complexes

**Geometric** – common occurrence where there are two ligands of one type different to the other ligands.

		cis	trans
Square planar	e.g. $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$		
Octahedral	e.g. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$		

**Optical** – occurs where there are three bidentate ligands in an octahedral complex.



### **TASK 2 – Drawing stereoisomers**

- 1) Draw the two geometric isomers of square planar complex  $\text{PdCl}_2(\text{CN})_2$ .

2) Draw the two geometric isomers of octahedral complex  $[\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4]^+$

3) Draw the two optical isomers of octahedral complex  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

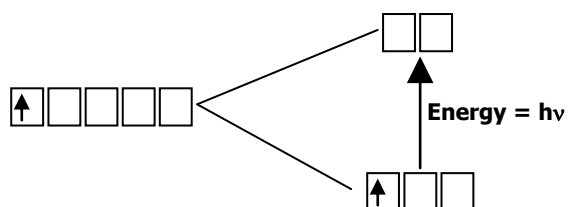
4) Draw the two optical isomers of octahedral complex  $[\text{Cu}(\text{en})_3]^{2+}$

## 4) SOME EXAMPLES OF USES OF TRANSITION METAL COMPLEXES

Name	Structure	Uses
Tollen's reagent	$[\text{Ag}(\text{NH}_3)_2]^+$	<ul style="list-style-type: none"> <li>Testing for aldehydes</li> <li>Formed when adding <math>\text{NH}_3</math> to silver halides to distinguish the silver halides</li> </ul>
Cisplatin		<ul style="list-style-type: none"> <li>Anti-cancer drug (i.e. a chemotherapy drug)</li> <li>Very effective against testicular cancer</li> </ul>
Haemoglobin		<ul style="list-style-type: none"> <li><math>\text{Fe}^{2+}</math> with porphyrin attached (4 bonds), attachment to globin protein (1 bond) and bond to either <math>\text{O}_2</math> or <math>\text{H}_2\text{O}</math> (1 bond).</li> <li>Carries <math>\text{O}_2</math> around the body.</li> <li><math>\text{CN}^-</math> and <math>\text{CO}</math> are better ligands than <math>\text{O}_2</math> and so form stronger bonds to the iron, and so kill you by starving you of the oxygen your cells need to respire.</li> </ul>

## 5) FORMATION OF COLOURED IONS

### Why complexes are coloured



- In compounds, the d orbitals do not all have the same energy.
- The gap in energy between the d orbitals corresponds to the energy of UV/visible light.
- The electrons absorb UV/visible light to provide the energy to promote (excite) electrons to the higher energy level.
- The frequency of the light absorbed is linked to the energy by the equation:

$$\text{Energy} = hf$$

$h$  = Planck's constant

$f$  = frequency of light

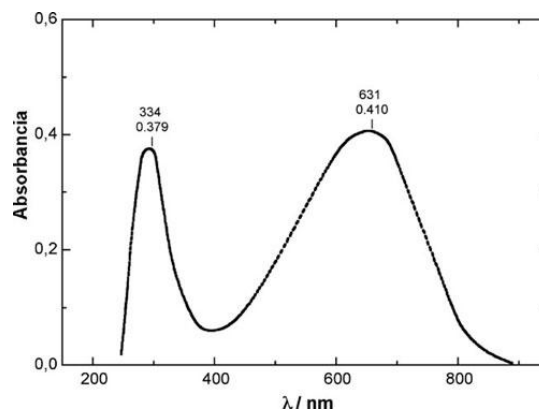
### Factors that affect the colour

Factor	Complex 1	Complex 2
Identify of metal	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , blue	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , green
Oxidation state of metal	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , pale violet	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , green
Identify of ligands	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , blue	$[\text{Cu}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$ , deep blue
Co-ordination number	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , blue	$[\text{CuCl}_4]^{2-}$ , yellow



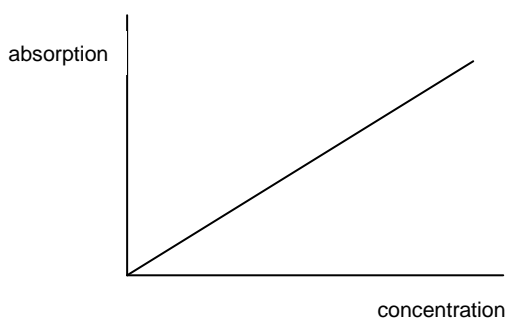
## Ultraviolet/visible spectroscopy

- The frequencies at which a complex absorbs uv/visible light can be measured with a uv/visible spectrometer.
- Uv/visible light is passed through the complex, and the frequencies of uv/vis light passing through detected – those that do not pass through are absorbed.
- The more concentrated the solution the more light that is absorbed, so uv/vis can be used to measure the concentration of the solution.



## Colorimetry

- The more concentrated the solution, the more it absorbs.
- This can be used to find the concentration of solutions – this is done in colorimeters.
- For some ions, a ligand is added to intensify the colour (e.g. SCN<sup>-</sup>).
- A colour of light is chosen that the compound absorbs (e.g. blue compounds absorb orange-red light).
- The strength of absorption of a range of solutions of known concentration is measured and a graph (calibration curve) produced.



- The concentration of a solution of unknown concentration can be found by measuring the absorption and using the graph.