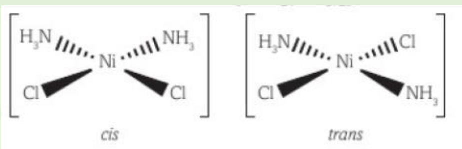
Ch 24 Transition Metals

Spec Reference: *5.3.1 Transition elements, 5.3.2 Qualitative Analysis*

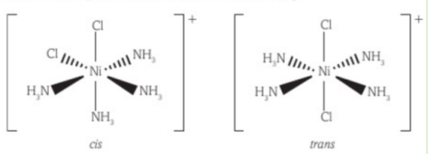
Key Vocabulary

Transition elements	A d-block element that has an incomplete d-sub-shell as a stable ion.
Complex ion	A transition metal metal ion bonded to one or more ligands by **coordinate bonds** (dative covalent bonds)
Ligand	A ligand is a molecule or ion that donates a pair of electrons to the central metal ion to form a coordinate bond.
Coordination number	The total number of coordinate bonds formed between a central metal ion and its ligands
Stereoisomer	Species with the same structural formula but with a different arrangement of the atoms in space.

Stereoisomerism – cis/trans isomerism



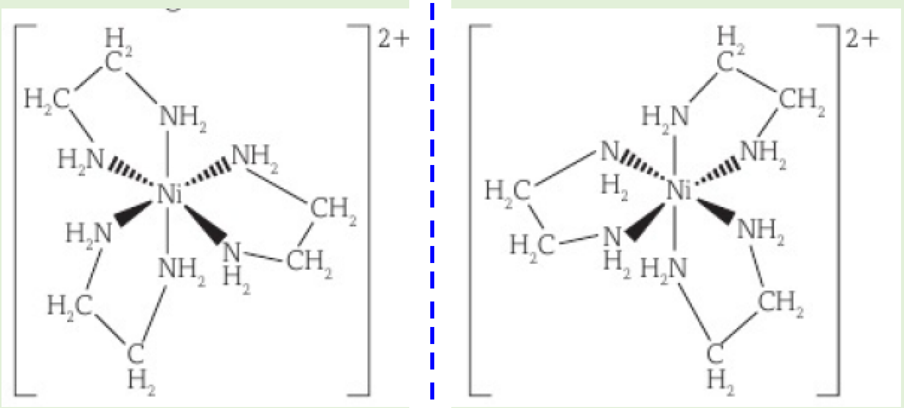
Square- planar
(Four coordinate bonds)



Octahedral
(6 coordinate bonds)

Stereoisomerism - Optical isomerism

Six coordinate bonds – octahedral (Bidentate)



Properties Part 1

Element	Z	Electron configuration	Noble gas configuration	Electron in box diagram
Scandium	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	[Ar] $4s^2 3d^1$	[↑↓] [↑][ ][ ][ ][ ]
Titanium	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	[Ar] $4s^2 3d^2$	[↑↓] [↑][↑][ ][ ][ ]
Vanadium	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	[Ar] $4s^2 3d^3$	[↑↓] [↑][↑][↑][ ][ ]
Chromium	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	[Ar] $4s^1 3d^5$	[↑] [↑][↑][↑][↑][↑]
Manganese	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	[Ar] $4s^2 3d^5$	[↑↓] [↑][↑][↑][↑][↑]
Iron	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	[Ar] $4s^2 3d^6$	[↑↓] [↑↓][↑][↑][↑][↑]
Cobalt	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	[Ar] $4s^2 3d^7$	[↑↓] [↑↓][↑↓][↑][↑][↑]
Nickel	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	[Ar] $4s^2 3d^8$	[↑↓] [↑↓][↑↓][↑↓][↑][↑]
Copper	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	[Ar] $4s^1 3d^{10}$	[↑] [↑↓][↑↓][↑↓][↑↓][↑↓]
Zinc	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	[Ar] $4s^2 3d^{10}$	[↑↓] [↑↓][↑↓][↑↓][↑↓][↑↓]

Figure 3 Electron configurations for the d-block elements of Period 4.

- Scandium and Zinc are not considered to be transition metals. Scandium forms only a 3+ <u>ion</u> [Ar] $4s^0 3d^0$
- Zinc forms only a 2+ <u>ion</u> [Ar] $4s^0 3d^{10}$
- Copper is a transition metal because its +2 <u>ion</u> has an incomplete d orbital. [Ar] $4s^0 3d^9$

Properties Part 2

- **Physical:** lustrous, high density, high melting/boiling points, conductors
- **Variable Oxidation States:** Transition metals can have different oxidation states. This makes them useful **catalysts.**

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

Catalytic Behaviour:

- Catalysts reduce energy usage. Many transition metals are toxic. Transition metals provide a surface on which the reaction can take place.
- Transition metals have the ability to change their oxidation states by gaining or losing electrons.
- **Examples:**
  - iron metal in Haber process,
  - vanadium (V) oxide in the contact process
  - nickel metal in hydrogenation of alkenes
  - MnO_2 catalyses decomposition of H_2O_2.

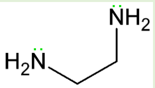
Common ligands

Monodentate Ligands

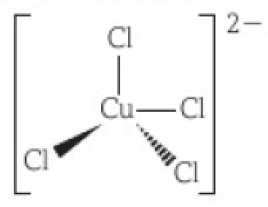
Name of ligand	Formula	Charge
Water	$:OH_2$	None – neutral ligand
Ammonia	$:NH_3$	None – neutral ligand
Thiocyanate	$:SCN^-$	–1
Cyanide	$:CN^-$	–1
Chloride	$:Cl^-$	–1
Hydroxide	$:OH^-$	–1

Bidentate Ligands

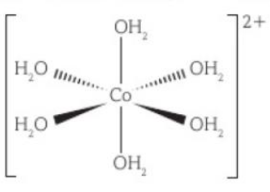
Ethane-1,2-diamine
$:NH_2CH_2CH_2NH_2:$



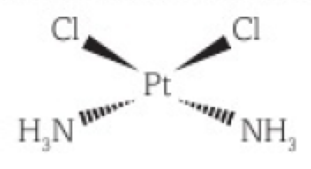
Shapes



yellow $[CuCl_4]^{2-}$
tetrahedral



blue $[Cu(H_2O)_6]^{2+}$
octahedral



cis-platin $Pt(NH_3)_2Cl_2$
square planar

*cis-platin is used as an anti-cancer drug because it binds to DNA preventing cell division

Ligand Substitutions

ligand substitution	A reaction occurs when a ligand in a complex ion is replaced by another type of ligand molecule.

Ligand substitutions – must know equations and colours!

Reaction copper sulfate (aq) with ammonia

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

pale blue solution → **deep blue solution**

Reaction of copper sulfate (aq) with hydrochloric acid

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

pale blue solute → yellow solution

Reaction of chromium (III) (aq) with ammonia

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

violet solution → purple solution

Haemoglobin

- **Haemoglobin** is the molecule that causes blood to appear red. It carries oxygen from the lungs to cells in the body.
- Haemoglobin contains an Fe^{2+} ion. One coordination site is left that can bind loosely to an **oxygen molecule**.
- Oxygen is a poor ligand that is easily released to cells, where its concentration is low.
- Ligands that can form stronger bonds with the Fe^{2+} ion, such as carbon monoxide, bind irreversibly and destroy haemoglobin's ability to carry oxygen. These substances are toxic.
- Carbon monoxide (CO) will undergo a **ligand substitution** reaction with oxygen (O_2) because it forms stronger coordinate covalent bonds.

Ion	Colour of ion (aq)	Colour with small amount of NH_3 or NaOH	Equation	Colour with excess NH3 or excess OH (aq)	Equation
Cu^{2+}	Pale blue	Pale blue ppt	**Cu^{2+} (aq) + $2OH^-$ (aq) → $Cu(OH)_2$ (s)** $[Cu(H_2O)_6]^{2+}{}_{(aq)}$ + $2NH_{3\,(aq)}$ → $[Cu(OH)_2(H_2O)_4]_{(s)}$ + $2NH_4^+$ $[Cu(H_2O)_6]^{2+}{}_{(aq)}$ + $2OH^-{}_{(aq)}$ → $[Cu(OH)_2(H_2O)_4]_{(s)}$ + $2H_2O_{(l)}$	NH_3 deep blue solution (royal blue)	**$Cu(OH)_2$ (s)** + $4NH_{3\,(aq)}$ → $[Cu(NH_3)_4(H_2O)_2]^{2+}$ + 2OH- $[Cu(OH)_2(H_2O)_4]_{(s)}$ + $4NH_{3(aq)}$ → $[Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)}$ + $2H_2O_{(l)}$ + $2OH^-$
Fe^{2+}	pale green	green ppt	**Fe^{2+} (aq) + $2OH^-$ (aq) → $Fe(OH)_2$ (s)** $[Fe(H_2O)_6]^{2+}{}_{(aq)}$ + $2OH^-{}_{(aq)}$ → $[Fe(OH)_2(H_2O)_4]_{(s)}$ + $2H_2O_{(l)}$ $[Fe(H_2O)_6]^{2+}{}_{(aq)}$ + $2NH_{3\,(aq)}$ → $[Fe(OH)_2(H_2O)_4]_{(s)}$ + $2NH_4^+{}_{(aq)}$		
Fe^{3+}	pale yellow	rusty brown ppt	**Fe^{3+} (aq) + $3OH^-$ (aq) → $Fe(OH)_3$ (s)** $[Fe(H_2O)_6]^{3+}{}_{(aq)}$ + $3OH^-{}_{(aq)}$ → $[Fe(OH)_3(H_2O)_3]_{(s)}$ + $3H_2O_{(l)}$ $[Fe(H_2O)_6]^{3+}{}_{(aq)}$ + $3NH_{3\,(aq)}$ → $[Fe(OH)_3(H_2O)_3]_{(s)}$ + $3NH_4^+{}_{(aq)}$		
Mn^{2+}	Pale pink	pale brown ppt	**Mn^{2+} (aq) + $2OH^-$ (aq) → $Mn(OH)_2$ (s)** $[Mn(H_2O)_6]^{2+}{}_{(aq)}$ + $2OH^-{}_{(aq)}$ → $[Mn(OH)_2(H_2O)_4]_{(s)}$ + $2H_2O_{(l)}$ $[Mn(H_2O)_6]^{2+}{}_{(aq)}$ + $2NH_{3\,(aq)}$ → $[Mn(OH)_2(H_2O)_4]_{(s)}$ + $2NH_4^+{}_{(aq)}$		
Cr^{3+}	violet	Purple ppt	**Cr^{3+} (aq) + $3OH^-$ (aq) → $Cr(OH)_3$ (s)** $[Cr(H_2O)_6]^{3+}{}_{(aq)}$ + $3OH^-{}_{(aq)}$ → $[Cr(OH)_3(H_2O)_3]_{(s)}$ + $3H_2O_{(l)}$ $[Cr(H_2O)_6]^{3+}{}_{(aq)}$ + $3NH_{3\,(aq)}$ → $[Cr(OH)_3(H_2O)_3]_{(s)}$ + $3NH_4^+{}_{(aq)}$	OH^- green solution	**$Cr(OH)_3$ (s) + $3OH^-$ (aq) → $[Cr(OH)_6]^{3-}$ (aq)** $[Cr(OH)_3(H_2O)_3]_{(s)}$ + $6OH^-{}_{(aq)}$ → $[Cr(OH^-)_6]^{3-}{}_{(aq)}$ + $3H_2O_{(l)}$ + $3OH^-{}_{(aq)}$
				NH_3 Purple solution	**$Cr(H_2O)_6]^{3+}{}_{(aq)}$ + $3NH_{3\,(aq)}$ → $[Cr(OH)_3(H_2O)_3]_{(s)}$ + $3NH_4^+{}_{(aq)}$** $[Cr(OH)_3(H_2O)_3]_{(s)}$ + $6NH_{3(aq)}$ → $[Cr(NH_3)_6]^{3+}{}_{(aq)}$ + $3H_2O_{(l)}$ + $3OH^-{}_{(aq)}$

Qualitative Analysis

Ion	Test	Observation	Ionic Equation
CO_3^{2-}	Nitric acid test Add nitric acid	Bubbles of CO_2	$CO_3^{2-} + H^+ \rightarrow H_2O + CO_2(g)$
SO_4^{2-}	Barium test* Add barium nitrate	White ppte	$SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4(s)$
Cl-, Br-, I-	Silver nitrate test** Add silver nitrate	White ppte – chloride Cream ppte - bromide Yellow ppte - iodide	$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$
NH_4^+	Add NaOH and gently heat with litmus paper at the mouth of the test tube	Litmus paper turns blue *The ammonia gas produced is alkali*	$NH_4^+ + OH^- \rightarrow NH_3(g) + H_2O$

*barium nitrate will make a ppte with CO_3^{2-} so the carbonate test is performed first. Nitric acid is added until there is no more carbonate.
**silver nitrate will make a ppte with CO_3^{2-} so the carbonate test is performed first. Nitric acid is added until there is no more carbonate.

Halide Tests

Halide ion	Name	With $AgNO_3(aq)$	Solubility of precipitate formed
Cl^-	Chloride	White precipitate	Soluble in dilute $NH_3(aq)$
Br^-	Bromide	Cream precipitate	Soluble in concen-trated $NH_3(aq)$ only
I^-	Iodide	Yellow precipitate	Insoluble in dilute and concentrated $NH_3(aq)$

Qualitative Analysis

The equations you need to to know are the same as the ligand substitution reactions on the previous slide.

Ion	Name	Compound before addition	With $NH_3(aq)$ or $OH^-(aq)$	Excess $NH_3(aq)$	Excess $OH^-(aq)$
Cu^{2+}	Copper(II) ion	Blue solution	Blue precipitate	Precipitate re-dissolves to give a blue solution	No change
Fe^{2+}	Iron(II) ion	Green solution	Green precipitate	No change	No change
Mn^{2+}	Manganese(II) ion	Pink solution	Brown precipitate	No change	No change
Cr^{3+}	Chromium(III) ion	Violet solution	Green precipitate	Precipitate dissolves to give a purple solution	Precipitate dissolves to give a green solution
Fe^{3+}	Iron(III) ion	Yellow/brown solution	Brown precipitate	No change	No change

Interconversions between Fe(II) and Fe(III)

Iron (II) reacts with H^+/MnO_4

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

- Manganese is reduced since the oxidation number decreases from +7 in MnO_4^- to +2 in Mn^{2+}
- Iron is oxidised since the oxidation number increases from +2 in Fe^{2+} to +3 in Fe^{3+}
- The colour change is **purple** to **pale pink**.

Iron (III) reacts with I^-

$2Fe^{3+}{}_{(aq)}$	+	$2I^-{}_{(aq)}$	$\rightarrow$	$2Fe^{2+}{}_{(aq)}$	+	$I_{2(aq/s)}$
rusty brown solution				*green solution*		*brown solution*

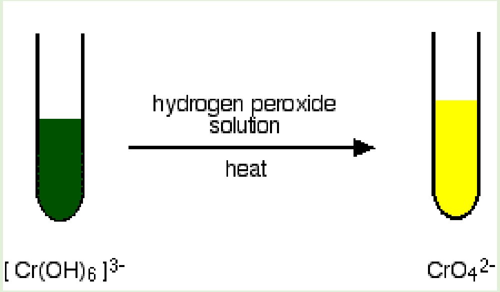
- Fe^{3+} is sufficient in oxidising power to oxidise an iodide ion to iodine, so FeI_2 is formed, not FeI_3.
- In the presence of I^- Fe^{3+} can be reduced to Fe^{2+}. The overriding colour change is **rusty brown** to **dark brown**

Interconversions between Cr(III) and Cr(VI)

Chromium (III) reacts with H_2O_2/OH^-

$$2Cr^{3+}{}_{(aq)} + 3H_2O_{2(l)} + 10OH^-{}_{(aq)} \rightarrow 2CrO_4^{2-}{}_{(aq)} + 8H_2O_{(l)}$$

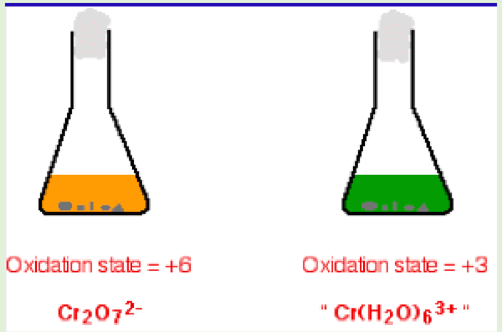
- Oxygen is reduced since the oxidation number decreases from -1 in H_2O_2 to -2 in CrO_4^{2-}
- Chromium is oxidised since the oxidation number increases from +3 in Cr^{3+} to +6 in CrO_4^{2-}
- When heated in the presence of H_2O_2/OH^- Cr^{3+} can be oxidised to Cr^{6+}. The colour change is **green** to **yellow.** (alkali conditions)



Chromium (VI) reacts with Zn/H^+

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

- Dichromate(VI) ions ($Cr_2O_7^{2-}$) can be reduced to chromium(III) ions using zinc and either sulphuric acid or hydrochloric acid.
- In the presence of Zn/H^+ $Cr_2O_7^{2-}$ can be reduced to Cr^{3+}. The colour change is orange to green. (acidic conditions)

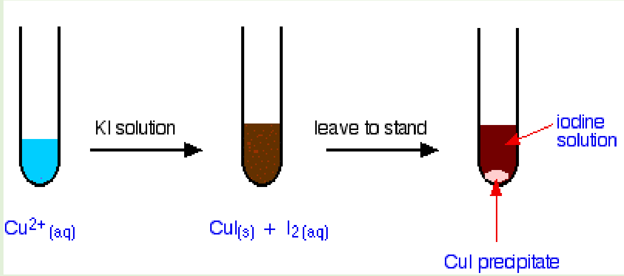


Reduction of Cu(II) to Cu(I)

Copper (II) reacts with I^-

$2Cu^{2+}{}_{(aq)}$	+	$4I^-$	$\rightarrow$	$2CuI_{(s)}$	+	$I_{2\,(aq)}$
blue solution				*off-white solid*		*brown solution*

- Cu^{2+} can be reduced to Cu^+ with I^-
- The colour change is a **blue solution** to a white **precipitate** ($CuI(s)$) and a **dark brown solution** (I_2).



Disproportionation of Cu(I) to Cu and Cu(II)

Copper (I) reacts with

$2Cu^+{}_{(aq)}$	$\rightarrow$	$Cu_{(s)}$	+	$Cu^{2+}{}_{(aq)}$
colourless		*brown solid*		*blue solution*

- In the aqueous conditions Cu^+ readily disproportionates to Cu(s) and Cu^{2+}. The colour change is colourless to brown ppt (Cu) and blue solution (Cu^{2+})