5.3.1 Transition Elements

General properties of transition metals

Transition metal characteristics of elements Ti → Cu arise from an **incomplete d sub-level** in ions

these characteristics include
- **formation of coloured ions,**
- **variable oxidation state**
- **catalytic activity.**
- **Complex ion formation,**

Sc $1s^22s^22p^63s^23p^6 4s^23d^1$
Ti $1s^22s^22p^63s^23p^6 4s^23d^2$
V $1s^22s^22p^63s^23p^6 4s^23d^3$
Cr $1s^22s^22p^63s^23p^6 4s^13d^5$
Mn $1s^22s^22p^63s^23p^6 4s^23d^5$
Fe $1s^22s^22p^63s^23p^6 4s^23d^6$
Co $1s^22s^22p^63s^23p^6 4s^23d^7$
Ni $1s^22s^22p^63s^23p^6 4s^23d^8$
Cu $1s^22s^22p^63s^23p^6 4s^13d^{10}$
Zn $\mathbf{1s^22s^22p^63s^23p^6 4s^23d^{10}}$

→
When forming ions lose 4s before 3d

Sc $\mathbf{^{3+}}$ **[Ar]** $\mathbf{4s^03d^0}$
Ti $^{3+}$ [Ar] $4s^03d^1$
V $^{3+}$ [Ar] $4s^03d^2$
Cr $^{3+}$ [Ar] $4s^03d^3$
Mn $^{2+}$ [Ar] $4s^03d^5$
Fe $^{3+}$ [Ar] $4s^03d^5$
Co $^{2+}$ [Ar] $4s^03d^7$
Ni $^{2+}$ [Ar] $4s^03d^8$
Cu $^{2+}$ [Ar] $4s^03d^9$
Zn $\mathbf{^{2+}}$ **[Ar]** $\mathbf{4s^03d^{10}}$

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 ions.

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.

Typical Properties of Transition metals

The existence of more than one oxidation state for each element in its compounds
For example iron commonly forms +2 and +3, chromium commonly forms +2,+3 and +6 see page 5 of this guide for more detail.

The formation of coloured ions
There are characteristic colours for each transition metal element and the colours can vary in the different oxidation state. See the rest of the guide for many examples.

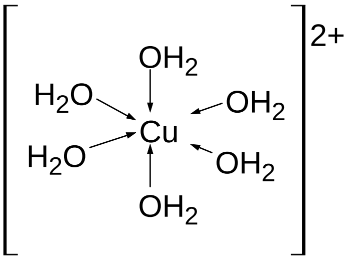
The catalytic behaviour of the elements and their compounds and their importance in the manufacture of chemicals by industry
Iron is used as a catalyst in the Haber process to produce ammonia. Manganese dioxide MnO_2 catalyses the decomposition of hydrogen peroxide. Vanadium pentoxide V_2O_5 catalyses the contact process . See 3.2.2 reaction rates for some more detail.

Complex formation

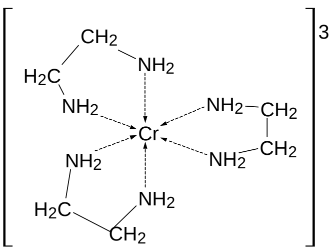
complex :is a central metal ion surrounded by ligands.

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 **unidentate** (e.g. H_2O, NH_3 and Cl^-) which can form one coordinate bond per ligand or **bidentate** (e.g. $NH_2CH_2CH_2NH_2$ and ethanedioate ion $C_2O_4^{\ 2-}$) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g. $EDTA^{4-}$ which can form six coordinate bonds per ligand).

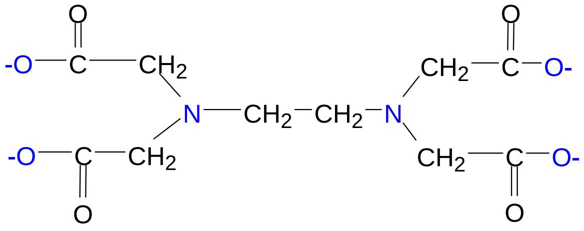


A complex with bidentate ligands e.g. $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$

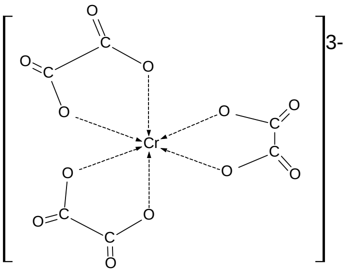
There are 3 bidentate ligands in this complex each bonding in twice to the metal ion

It has a coordination number of 6

The $EDTA^{4-}$ anion has the formula



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



A complex with bidentate ethanedioate ligands e.g. $[Cr(C_2O_4)_3]^{3-}$

Equations to show formation of bidentate and mutidentate complexes

$Cu(H_2O)_6^{2+} + 3NH_2CH_2CH_2NH_2 \rightarrow [Cu(NH_2CH_2CH_2NH_2)_3]^{2+} + 6H_2O$

$Cu(H_2O)_6^{2+} + 3C_2O_4^{2-} \rightarrow [Cu(C_2O_4)_3]^{4-} + 6H_2O$

$Cu(H_2O)_6^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-} + 6H_2O$

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

Shapes of complex ions

transition metal ions commonly form **octahedral** complexes with small ligands (e.g. H_2O and NH_3).

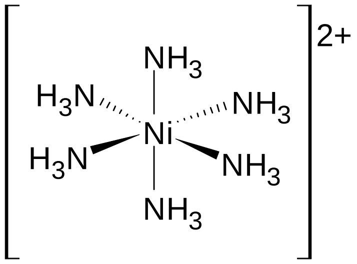
$[Co(NH_3)_6]^2$ $[Cu(H_2O)_6]^{2+}$

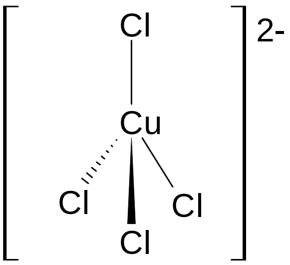
transition metal ions commonly form **tetrahedral** complexes with larger ligands (e.g.Cl^-).

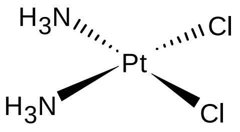
$[CoCl_4]^{2-}$

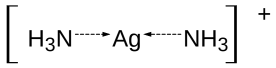
square planar complexes are also formed, e.g. cisplatin

Ag^+ commonly forms **linear** complexes e.g. $[Ag(NH_3)_2]^+$, $[Ag(S_2O_3)_2]^{3-}$ and $[Ag(CN)_2]^-$ (all colourless).





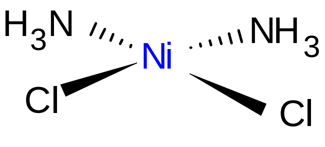




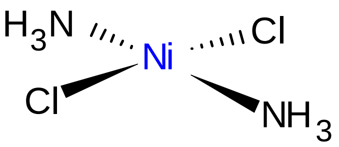
Isomerism in complex ions

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

Cis-trans isomerism in square planar complexes

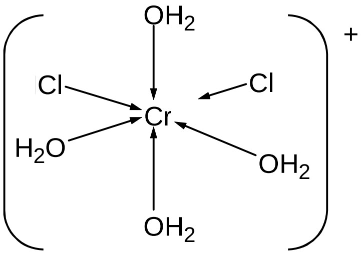


Cis-$Ni(NH_3)_2Cl_2$

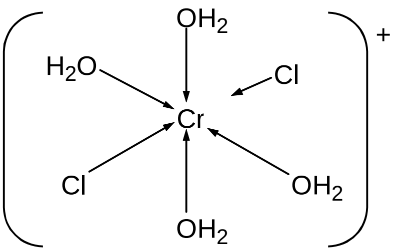


trans-$Ni(NH_3)_2Cl_2$

Cis-trans isomerism in octahedral complexes



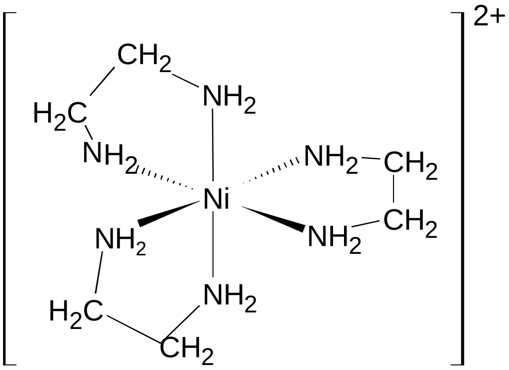
Cis-$[Cr(H_2O)_4Cl_2]^+$

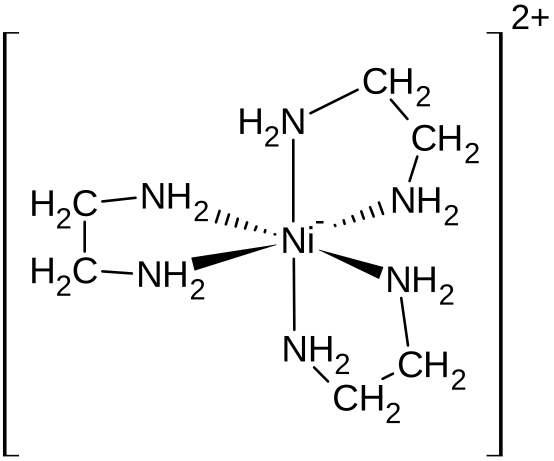


trans-$[Cr(H_2O)_4Cl_2]^+$

Optical isomerism

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





Cisplatin

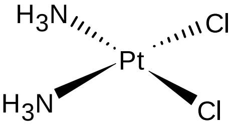
The Pt(II) complex cisplatin is used as an anticancer drug.

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.

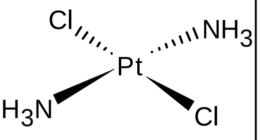
In the body one Cl ligand is subsituted by a water molecule
$Pt(NH_3)_2Cl_2 + H_2O \rightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$

Be able to apply your knowledge of bonding to given information in the question to explain how it bonds to DNA molecule- generally a combination of dative covalent bonding and hydrogen bonding.

Platin binds to DNA of cancer cells and stops cancer cells dividing.



cisplatin



transplatin

It can also prevent the replication of healthy cells by bonding on to healthy DNA which may lead to unwanted side effects like hair loss.

Ligand substitution

Reaction with excess NH_3

With **excess NH_3 ligand substitution** reactions occur with several transition aqueous ions.

$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4NH_{3\,(aq)} \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 4H_2O_{\,(l)}$

blue solution deep blue solution

Note: This substitution in the case with Cu is incomplete as not all the water molecules are substituted.

Be able to write equations for other metal ions given information about the complex formed. No need to learn colours for these other ions.

$[Co(H_2O)_6]^{2+}{}_{(aq)} + 6NH_{3\,(aq)} \rightarrow [Co(NH_3)_6]^{2+}{}_{(aq)} + 6H_2O_{\,(l)}$

The ligands NH_3 and H_2O are similar in size and are uncharged. Ligand exchange occurs without change of co-ordination number for Co and Cr

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 substitution** reaction.

The Cl^- ligand is larger than the uncharged H_2O and NH_3 ligands so therefore ligand exchange can involve a change of co-ordination number.

Be careful: If solid copper chloride (or any other metal)is **dissolved in water** it forms the **aqueous $[Cu(H_2O)_6]^{2+}$** complex and **not** the chloride $[CuCl_4]^{2-}$ complex

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

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

blue solution yellow/green solution

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

pink solution blue solution

Biological Complexes

Fe(II) in haemoglobin enables oxygen to be transported in the blood . Haem is an iron(II) complex with a multidentate ligand. O_2 bonds to Fe^{2+} ions in the haemoglobin and when required the O_2 is released.

CO is toxic to humans as CO can from a strong coordinate bond with haemoglobin. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin. With CO, the stability constant is greater than with complex in $O_{2.}$

Precipitation reactions with sodium hydroxide and ammonia

The bases OH^- and ammonia when in limited amounts form the same hydroxide precipitates.

These reactions are classed as precipitation reactions

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

Blue solution blue ppt

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

Blue solution blue ppt

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

Very pale pink solution Pale brown ppt

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

Very pale pink solution Pale brown ppt

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

green solution green ppt

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

green solution green ppt

$[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Fe(H_2O)_3(OH)_{3\,(s)} + 3H_2O_{\,(l)}$

Yellow/brown solution brown ppt

$Fe^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Fe(OH)_{3\,(s)}$

Yellow/brown solution brown ppt

$[Cr(H_2O)_6]^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Cr(H_2O)_3(OH)_{3\,(s)} + 3H_2O_{\,(l)}$

green solution green ppt

$Cr^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Cr(OH)_{3\,(s)}$

green solution green ppt

With ammonia when added in limited amounts the same hydroxide precipitates form. The ammonia acts as a base, removes a proton from the aqueous complex and becomes the ammonium ion

$[Mn(H_2O)_6]^{2+}{}_{(aq)} + 2NH_{3\,(aq)} \rightarrow Mn(H_2O)_4(OH)_{2\,(s)} + 2NH_4^+{}_{(aq)}$

$[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3NH_{3\,(aq)} \rightarrow Fe(H_2O)_3(OH)_{3\,(s)} + 3NH_4^+{}_{(aq)}$

Reaction with excess OH^-

With excess NaOH, the Cr hydroxide dissolves.
Cr becomes $[Cr(OH)_6]^{3-}$ (aq) green solution

•This hydroxide is classed as **amphoteric** because it can react with alkali to give a solution and react with acid to form the aqueous salt.

$Cr(H_2O)_3(OH)_{3\,(s)} + 3OH^-{}_{(aq)} \rightarrow [Cr(OH)_6]^{3-}{}_{(aq)} + 3H_2O_{(l)}$

$Cr(H_2O)_3(OH)_{3\,(s)} + 3H^+{}_{(aq)} \rightarrow [Cr(H_2O)_6]^{3+}{}_{(aq)}$

Reaction with excess NH_3

With **excess NH_3 ligand exchange** reactions occur with Cu and Cr, and their hydroxide precipitates dissolve in excess ammonia

The ligands NH_3 and H_2O are similar in size and are uncharged. Ligand exchange occurs without change of co-ordination number for Cr

Cr becomes $[Cr(NH_3)_6]^{3+}$ purple solution

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

Cu becomes $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue solution

$Cr(OH)_3(H_2O)_{3(s)} + 6NH_{3\,(aq)} \rightarrow [Cr(NH_3)_6]^{3+}{}_{(aq)} + 3H_2O_{(l)} + 3OH^-{}_{(aq)}$

$Cu(OH)_2(H_2O)_{4(s)} + 4NH_{3\,(aq)} \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 2H_2O_{\,(l)} + 2OH^-{}_{(aq)}$

Variable Oxidation States

Transition elements show variable oxidation states

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

Iron (II) Oxidation

Fe^{2+} (green solution) can be easily oxidised to Fe^{3+} (brown solution) by various oxidising agents. We commonly use potassium manganate (VII), although oxygen in the air will bring about the change

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

Purple colourless

Iron (III) Reduction

Fe^{3+} (brown solution) can be reduced to Fe^{2+} (green solution) by various reducing agents. We commonly use potassium iodide solution. The brown colour of the iodine formed can mask the colour change of the Iron.

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Reducing Chromium

Cr^{3+} (green) and then **Cr^{2+} (blue)** are formed by reduction of **$Cr_2O_7^{2-}$ (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+}**

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

Orange green

The Fe^{2+} and $Cr_2O_7^{2-}$ in acid solution reaction can be used as a quantitative redox titration. This does not need an indicator

Oxidising Chromium

When transition metals in low oxidation states are in alkaline solution they are more easily oxidised than when in acidic solution

It is easier to remove an electron from a negatively charged ion

$[Cr(H_2O)_6]^{3+}(aq) \xrightarrow{\text{Excess NaOH}} [Cr(OH)_6]^{3-}(aq)$

Acidified
Not easy to oxidise

alkaline
easier to oxidise

Alkaline chromium(III) can be oxidised by using oxidising agents such as hydrogen peroxide to the (yellow solution) chromate ion

$Cr(OH)_6^{3-}(aq) \xrightarrow{H_2O_2} CrO_4^{2-}(aq)$

Green solution

yellow solution

Reduction : $H_2O_2 + 2e^- \rightarrow 2OH^-$

Oxidation: $[Cr(OH)_6]^{3-} + 2OH^- \rightarrow CrO_4^{2-} + 3e^- + 4H_2O$

$2[Cr(OH)_6]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 2OH^- + 8H_2O$

Reduction of Cu^{2+} to Cu^+

Cu^{2+} (blue solution) can be reduced to Cu^+ by various reducing agents. We commonly use potassium iodide solution. $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow I_2(aq) + 2CuI(s)$

Brown solution White precipitate

Disproportionation of copper(I) ions

Copper(I) ions when reacting with sulfuric acid will disproportionate to Cu^{2+} and Cu metal

$2Cu^+ \rightarrow Cu + Cu^{2+}$

$Cu^+(aq) + e^- \rightarrow Cu(s)$ $E^o = +0.52$ V
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ $E^o = +0.15$ V
So $E^o_{cell} = 0.52 - 0.15 = +0.37$ V

Full Equation $Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$

As E^o Cu^+/Cu > E^o Cu^{2+}/Cu^+ and E_{cell} has a positive value of +0.37V , Cu^+ disproportionates from +1 oxidation state to 0 in Cu and +2 in Cu^{2+}