Transition Element Complexes (A2)

- A transition element complex consists of a transition metal atom surrounded by ligands.
- A complex ion has a central metal ion with ligands surrounding it. The ligands attach to the central ion by co-ordinate bonds.

Ligands.

- atoms, or ions, which possess lone pair of electrons
- form co-ordinate bonds to the central ion.
- donate a lone pair into vacant orbitals on the central species.

Ligand	Formula	Name of ligand
chloride	Cl^-	chloro
cyanide	NC^-	cyano
hydroxide	HO^-	hydroxo
oxide	O^{2-}	oxo
water	H_2O	aqua
ammonia	NH_3	ammine

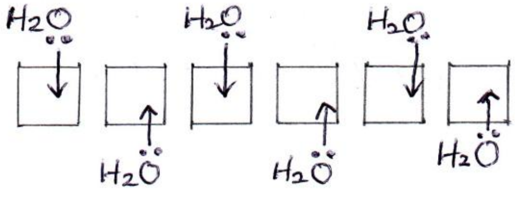
Bonding in simple complex ions

$Al(H_2O)_6^{3+}$

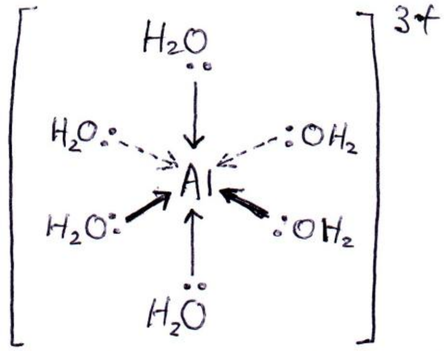
- Aluminium $1s^2 2s^2 2p^6 3s^2$
- Forming Al^{3+} ion $1s^2 2s^2 2p^6$
- Now all the 3-level orbitals are empty.
- The aluminium uses 6 of these orbitals to accept lone pairs from six water molecules.
- It re-organises (hybridises) the 3s, the three 3p and two of the 3d orbitals to produce 6 new hybrid orbitals, all with the same energy.
- Six is the maximum number of water molecules that possible to fit around an aluminium ion (and for most other metal ion).

- By making the maximum number of bonds, it releases most energy and becomes most energetically stable.

6 hybrid orbitals on the aluminium



- The resulting complex ion:



- Because the electron pairs from water molecules are shared with the centre of the ion, the 3+ charge is no longer located entirely on the aluminium, but is now spread over the whole of the ion.

- Co-ordination number of a complex ion is the number of co-ordinate (dative) bonds to the central metal ion.

- For $[Al(H_2O)_6]^{3+}$, the co-ordination number = 6

- Shape of $[Al(H_2O)_6]^{3+}$ complex ion is octahedral.

$Fe(H_2O)_6^{3+}$

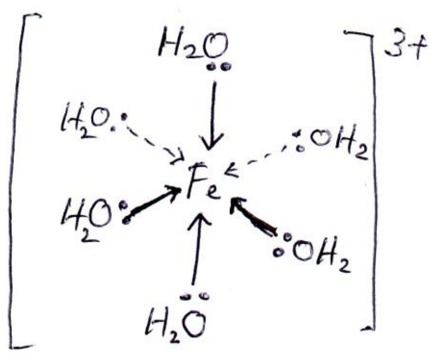
- Electronic configurations (outer shells)

	3d	4s
Fe	↑↓ ↑ ↑ ↑ ↑	↑↓
Fe^{3+}	↑ ↑ ↑ ↑ ↑	☐

↓ loses 3 electrons

- The Fe^{3+} uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules.
- The orbitals are hybridised to produce 6 orbitals of equal energy.
- Fe^{3+} 3d ↑ ↑ ↑ ↑ ↑ 4s ☐ 4p ☐ ☐ ☐ 4d ☐ ☐ ☐ ☐ ☐

these orbitals are hybridised and used to accept lone pairs from 6 water molecules

- 

- Iron is forming 6 bonds, the co-ordination number of the iron is 6
- Shape of complex ion $[Fe(H_2O)_6]^{3+}$ is octahedral

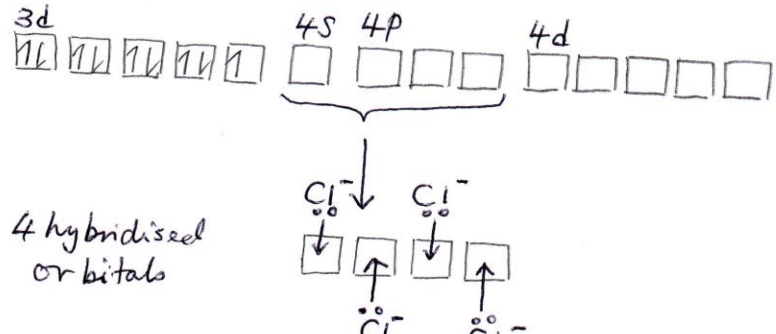
$CuCl_4^{2-}$

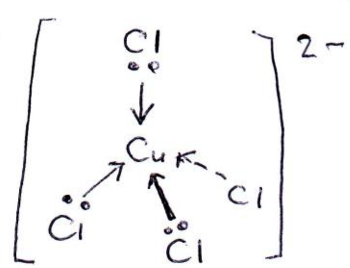
- Example of Complex ion with a negative charge
- Electronic configuration:

  Cu $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

  Cu^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

- To bond the 4 chloride ions, the empty 4s and 4p orbitals are used (in hybridised form) to accept a lone pair of electrons from each choride ion. Because chloride ions are bigger than water molecules, only 4 chloride ions can fit around the central ion.
- Cu^{2+}



- 

  shape : tetrahedral

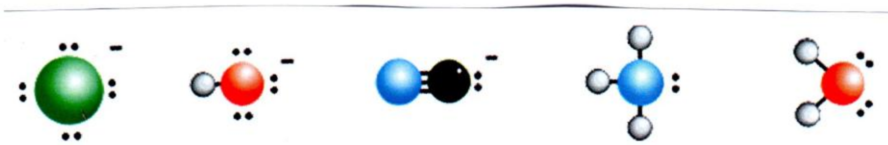
- The complex ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and 4 negative charges from the 4 Cl^- ions.
- The co-ordination number of the copper is 4.

Classification of ligands

- some ligands attach themselves using two or more lone pairs.
- classified by the number of lone pairs they use.
- multidentate and bidentate ligands lead to more stable complexes.

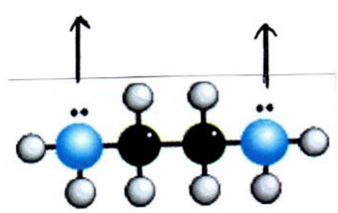
Monodentate / Unidentate

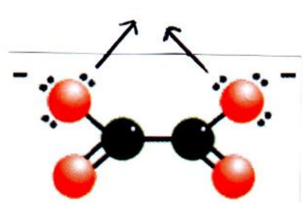
- form one co-ordinate bond.
- eg. Cl^-, OH^-, CN^-, NH_3 and H_2O



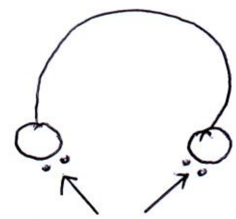
Bidentate

- form two co-ordinate bonds
- eg. $H_2NCH_2CH_2NH_2$ and $C_2O_4^{2-}$
  1,2-diaminoethane (en) ethanedioate ion (ox)



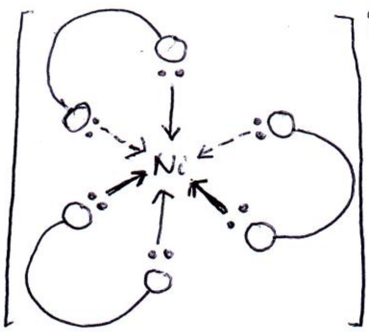


• the bidentate ligands looked like a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.

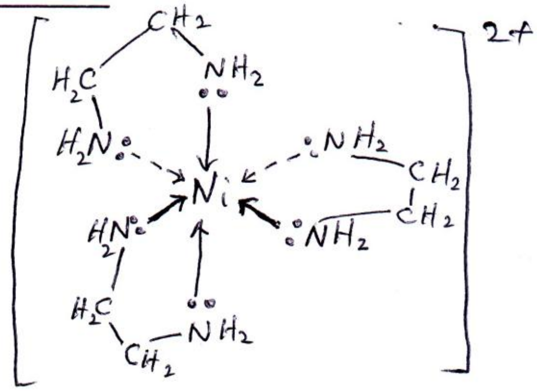


These lone pairs can both be used to form co-ordinate bonds with the same metal ion.

- $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$ or $[Ni(en)_3]^{2+}$



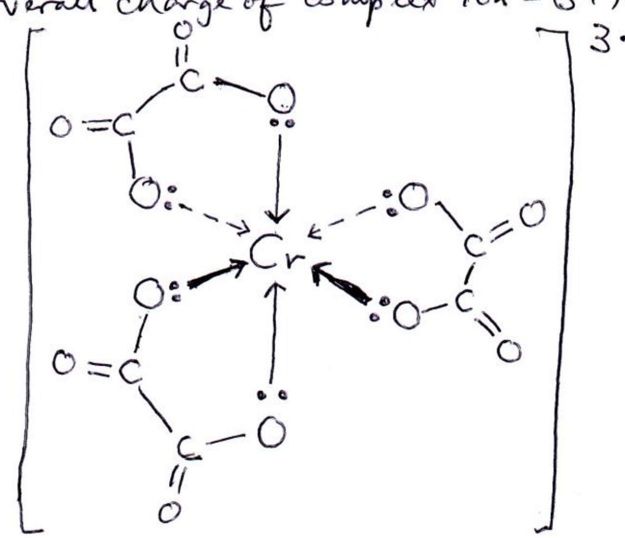
or



- the nickel is forming 6 co-ordinate bonds, the co-ordination number of this complex ion is 6.

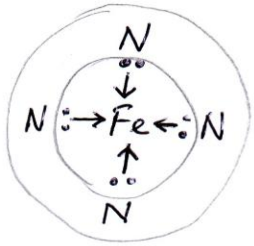
- $Cr(C_2O_4)_3^{3-}$ or $[Cr(ox)_3]^{3-}$

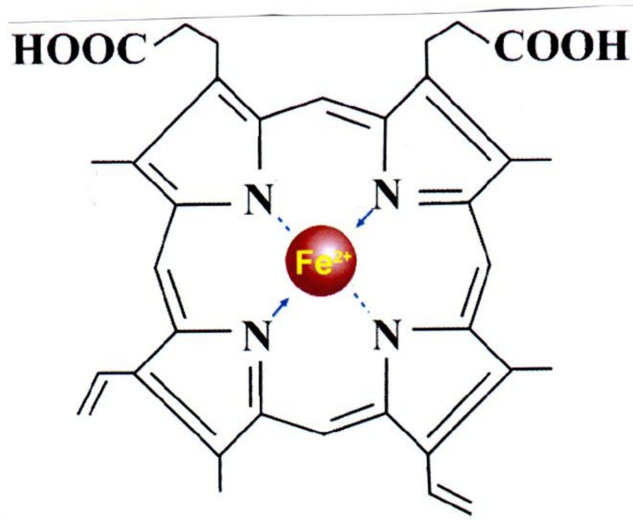
- The original chromium ion carried 3+ charges, and each ethanedioate ion carried 2−.
  The overall charge of complex ion = (3+) + 3(2−) = 3−



A quadridentate ligand.

- a quadridentate ligand has 4 lone pairs, and all of which can bond to the central metal ion.
- example in haemoglobin.
- iron ion trapped in the haem structure.



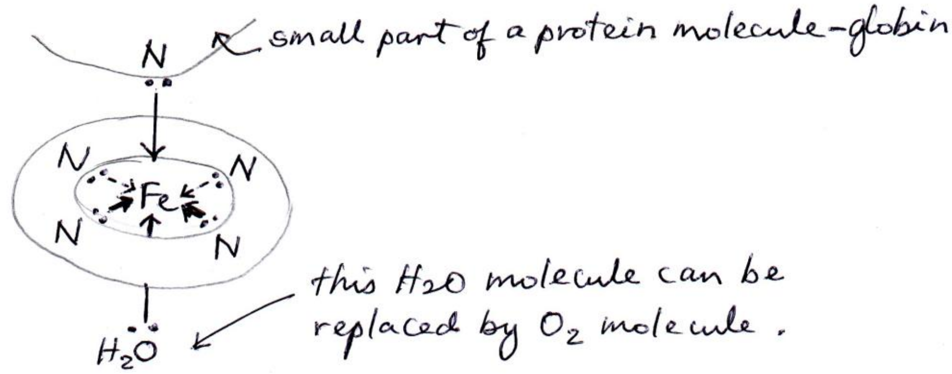


Haem

a complex containing iron(II) which is responsible for the red colour in blood and for the transport of oxygen by red blood cells.

- the iron forms 4 co-ordinate bonds with the haem, but still has space to form two more - one above and one below the plane of the ring.

· the protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids.



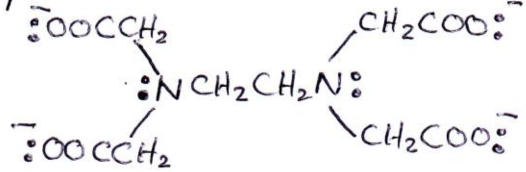
· overall, the complex ion has a co-ordination no. of 6.

· The water molecule (bottom position) is easily replaced by an oxygen molecule (via a lone pair on one of the oxygens in O_2). This allows haemoglobin carry O_2 in the blood around the body.

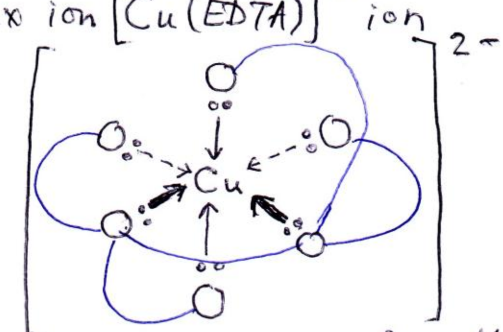
· carbon monoxide (CO) bonds to the same site and the complex formed very stable. The CO does not break away again and makes the haemoglobin molecule useless.

A hexadentate ligand.

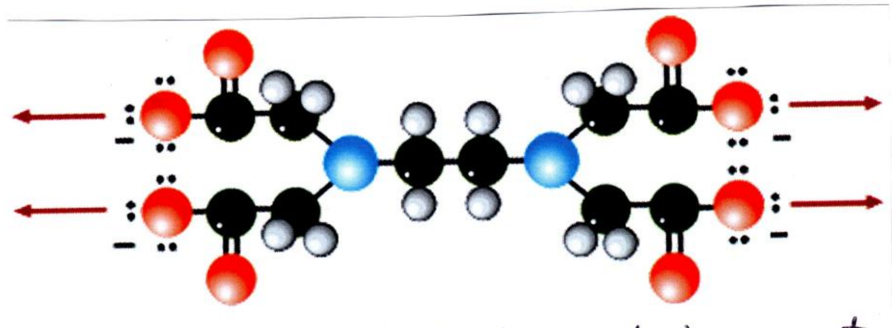
- A hexadentate ligand has 6 lone pairs of electrons and all of which can form co-ordinate bonds with the same metal ion.
- Example: $EDTA^{4-}$ (EDTA - ethylenediaminetetraacetic acid)



- Complex ion $[Cu(EDTA)]^{2-}$ ion



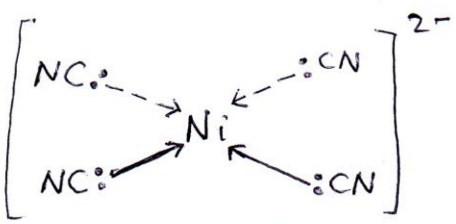
- The overall charge comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.



EDTA - an important complexing agent

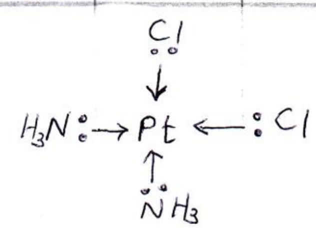
Some common ligands and their complexes

Name of ligand	Formula	Example of complex	Co-ordination no	Shape of Complex
water	H_2O	$[Fe(H_2O)_6]^{2+}$	6	octahedral
ammonia	NH_3	$[Co(NH_3)_6]^{3+}$	6	octahedral
chloride ion	Cl^-	$[CuCl_4]^{2-}$	4	tetrahedral
cyanide ion	CN^-	$[Ni(CN)_4]^{2-}$	4	square planar
hydroxide ion	OH^-	$[Cr(OH)_6]^{3-}$	6	octahedral
thiocyanate ion	SCN^-	$[FeSCN]^{2+}$ or $[Fe(SCN)(H_2O)_5]^{2+}$	6	octahedral
ethanedioate ion (ox)	$^-OOC-COO^-$	$[Mn(ox)_3]^{3-}$	6	octahedral
ethane-1,2-diamine (en)	$NH_2CH_2CH_2NH_2$	$[Co(en)_3]^{3+}$	6	octahedral



$[Ni(CN)_4]^{2-}$

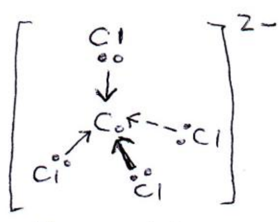
shape : square planer



Pt(II) ion

$Pt(NH_3)_2Cl_2$ - cisplatin (anticancer drug)

Shape : square planer

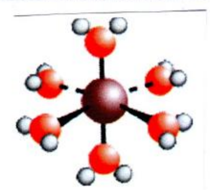
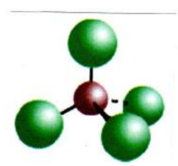
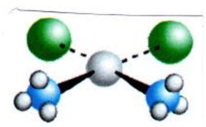
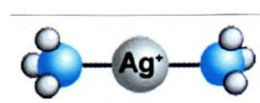


$[CoCl_4]^{2-}$

Shape : tetrahedral

Co-ordination number & shape

- the shape of a complex is governed by the number of ligands around the central ion.
- the co-ordination number gives the number of ligands around the central ion.
- a change of ligand can affect the co-ordination number.

co-ordination no.	shape	example	model
6	octahedral	$[Cu(H_2O)_6]^{2+}$	
4	tetrahedral	$[CuCl_4]^{2-}$	
4	square planar	$Pt(NH_3)_2Cl_2$	
2	linear	$[Ag(NH_3)_2]^+$	

Ligand exchange in complex ion of Copper

a) when $[Cu(H_2O)_6]^{2+}_{(aq)}$ is added with concentrated HCl,

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$

hexaaquacopper(II) ion (blue soln) shape: octahedral

tetrachlorocuprate(II) ion (yellow soln) shape: tetrahedral

- Adding water to the yellow solution, replaces the chloride ions as ligands by water molecules again, and solution returns to blue.

b) when $[Cu(H_2O)_6]^{2+}_{(aq)}$ is added with $NH_{3(aq)}$,

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Cu(OH)_2(H_2O)_4]_{(s)} + 2NH^+_{4(aq)}$$

copper(II) hydroxide (blue ppt.)

in excess NH_3,

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

blue ppt. soluble in excess NH_3

tetraamminediaquacopper(II) ion (royal blue solution) shape: octahedral

- Adding of water will not reverse much of the reaction because the ligand strength is $CN^- > NH_3 > Cl^- > H_2O$, and the solution stays deep blue.
- Equilibrium favours product side,

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

or

$$Cu(OH)_2 + 4NH_3 + 2H_2O \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 2OH^-$$

c). Adding $NaOH_{(aq)}$ to $[Cu(H_2O)_6]^{2+}_{(aq)}$,

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_2(H_2O)_{4(s)} + 2H_2O$$

(blue solution) (pale blue ppt)

- now add concentrated $NH_{3(aq)}$,

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

deep blue sol^n

d) Adding concentrated HCl to $[Cu(H_2O)_6]^{2+}_{(aq)}$

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$

(blue sol^n) (yellow sol^n)

- follow by adding concentrated NH_3 dropwise,

$$[CuCl_4]^{2-}_{(aq)} + 4NH_{3(aq)} + 2H_2O_{(l)} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 4Cl^-_{(aq)}$$

(yellow sol^n) (royal blue sol^n)

Stability Constants (K_{stab}) of Complexes

- $$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$

$$K_{stab} = \frac{[CuCl_4^{2-}]}{[Cu(H_2O)_6^{2+}][Cl^-]^4}$$

- Stability constant (K_{stab}) is the equilibrium constant for this reaction. Concentration of H_2O is ignored in the expression for Kstab.
- If Kstab is a very large equilibrium constant, implying a high tendency for chloride ions to replace the water.
-

ligand	formula of complex	stability constant, Kstab
Cl^-	$[CuCl_4]^{2-}$	4×10^5
NH_3	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	1×10^{13}
$EDTA^{4-}$	$Cu(EDTA)^{2-}$	6×10^{18}

- Kstab values tell than $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is more stable than $[CuCl_4]^{2-}$ complex. NH_3 can replace Cl^- as ligand in the complex ions.