

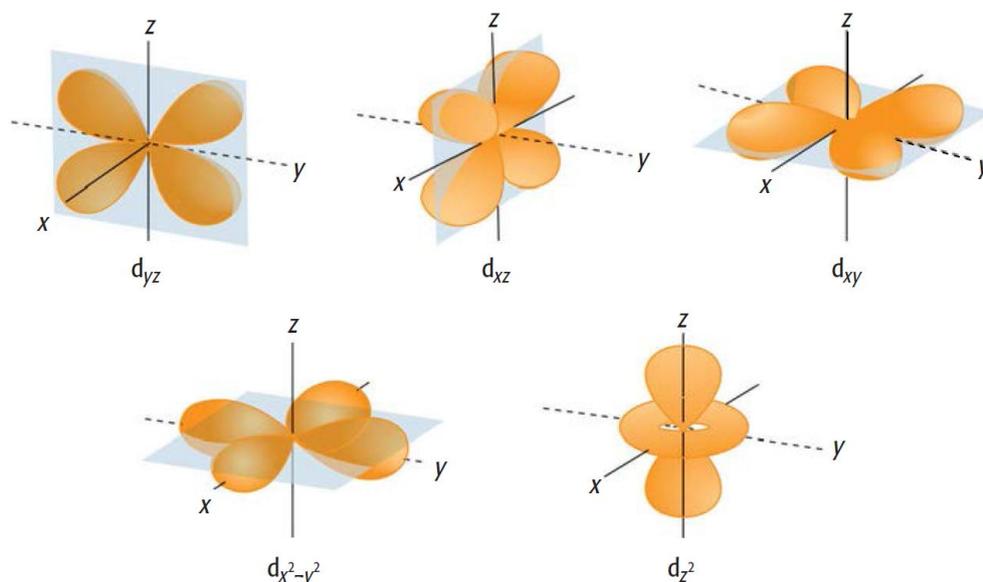
## Transition elements (Chapter 24)

- The transition elements are found in the d block of the Periodic Table, between Groups 2 and 13
- A **transition element** is a d-block element that forms one or more stable ions with an incomplete d subshell
- We do not define Sc and Zn as transition elements:
  - Scandium forms only one ion ( $\text{Sc}^{3+}$ ) which has no electrons in its 3d subshell – the electronic configuration of  $\text{Sc}^{3+}$  is  $(\text{Ar}) 3d^0 4s^0$
  - Zinc forms only one ion ( $\text{Zn}^{2+}$ ) which has a complete 3d subshell – the electronic configuration of  $\text{Zn}^{2+}$  is  $(\text{Ar}) 3d^{10} 4s^0$

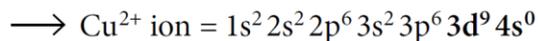
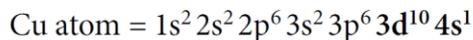
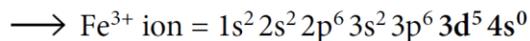
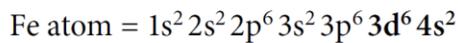
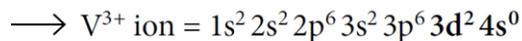
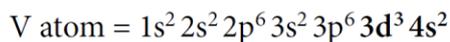
Element	Electronic configuration
titanium (Ti)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
vanadium (V)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
chromium (Cr)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
manganese (Mn)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
iron (Fe)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
cobalt (Co)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
nickel (Ni)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
copper (Cu)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

**Table 24.1** Electronic configurations of the first row of transition elements.

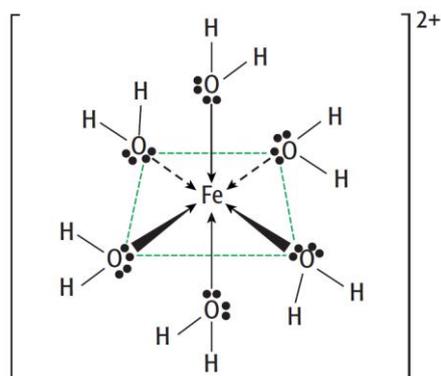
- The shape of a d orbital:



- Transition metals have **variable oxidation states**, as each transition metal can form more than one ion, e.g.  $\text{Cu}^{2+}$  and  $\text{Cu}^+$ ; the resulting ions are often of different colours, hence the names of the compounds must have their oxidation number included, e.g. manganese(IV) oxide, cobalt(II) chloride
- Transition elements forming ions:

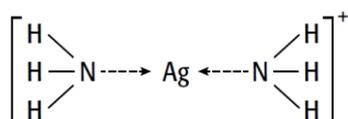


- Contrast, qualitatively, the melting points and densities of the transition elements with those of calcium as a typical s-block element:
  - Melting point of calcium < than that of transition element
  - Density of calcium < than that of transition element
  - Atomic radius of calcium > than that of transition element
  - Ionic radius of the calcium ion,  $\text{Ca}^{2+}$ , > than that of transition element
  - First ionisation energy of calcium < than that of transition element
  - The electrical conductivity of calcium > than that of transition element (with the exception of copper)

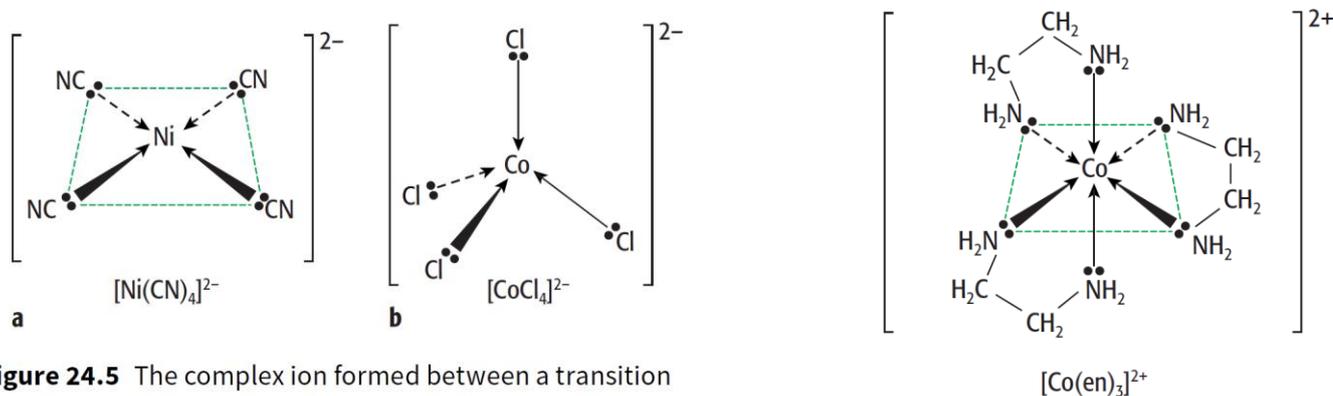


**Figure 24.4**  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ; the complex ion formed between an  $\text{Fe}^{2+}$  ion and six water molecules. It is called a hexaquairon(II) ion.

- Each water molecule bonds to the central  $\text{Fe}^{2+}$  ion by forming a dative (co-ordinate) bond from the oxygen atom into vacant orbitals on the  $\text{Fe}^{2+}$  ion; the water molecules are called **ligands** and the resulting ion is called a **complex ion**, with an octahedral shape; formula:  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- **Ligand**: a species that contains a lone pair of electrons that forms a dative bond to a central metal atom/ion including monodentate, bidentate and polydentate ligands
- **Complex**: a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands
- The **co-ordination number** of a complex is the number of co-ordinate (dative) bonds to the central metal ion
  - Some ligands can form two co-ordinate bonds from each ion or molecule to the transition metal ion (bidentate ligands), Figure 24.6
  - Most ligands, such as water and ammonia, form just one co-ordinate bond (monodentate ligands)
  - A few transition metal ions, e.g. copper(I), silver(I), gold(I), form linear complexes with ligands. The co-ordination number in these complexes is 2, Figure 24.7



**Figure 24.7** The diamminesilver(I) cation has a linear structure.



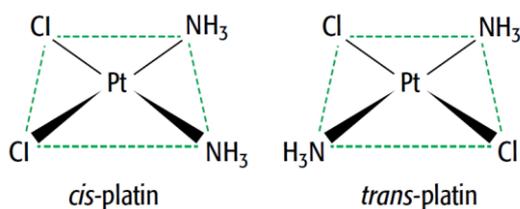
**Figure 24.5** The complex ion formed between a transition metal ion and a larger ligand can only fit four ligands around the central ion. These are arranged in either a square planar shape (as in **a**  $[\text{Ni}(\text{CN})_4]^{2-}$ ) or a tetrahedral shape (as in **b**  $[\text{CoCl}_4]^{2-}$ ).

**Figure 24.6**  $[\text{Co}(\text{en})_3]^{2+}$  is an example of a complex ion containing the bidentate ligand  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (abbreviated to 'en').

Name of ligand	Formula	Example of complex	Co-ordination number	Shape of complex
water	$\text{H}_2\text{O}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	6	octahedral (see Figure 24.4)
ammonia	$\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+}$	6	octahedral
chloride ion	$\text{Cl}^-$	$[\text{CuCl}_4]^{2-}$	4	tetrahedral (see Figure 24.5b)
cyanide ion	$\text{CN}^-$	$[\text{Ni}(\text{CN})_4]^{2-}$	4	square planar (see Figure 24.5a)
hydroxide ion	$\text{OH}^-$	$[\text{Cr}(\text{OH})_6]^{3-}$	6	octahedral
thiocyanate ion	$\text{SCN}^-$	$[\text{FeSCN}]^{2+}$ or $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$	6	octahedral
ethanedioate ion (abbreviated as 'ox' in the formulae of complexes)	$^-\text{OOC}-\text{COO}^-$	$[\text{Mn}(\text{ox})_3]^{3-}$	6	octahedral
1,2-diaminoethane (abbreviated as 'en' in the formulae of complexes)	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	$[\text{Co}(\text{en})_3]^{3+}$	6	octahedral (see Figure 24.6)

**Table 24.4** Some common ligands and their complexes.

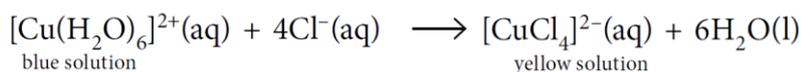
- Stereoisomerism in transition metal complexes:
  - ❖ **Geometric isomerism:** complexes with the same molecular formula but different geometrical arrangements of their atoms
    - *cis-trans* isomerism, e.g. *cis-* and *trans-*platin  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



**Figure 24.8** The geometrical isomers, *cis*-platin and *trans*-platin.

- *Cis*-platin used as an anti-cancer drug, by binding to sections of the DNA in cancer cells, preventing cell division
- ❖ **Optical isomerism** is commonly shown by octahedral (six co-ordinate) complexes associated with bidentate ligands





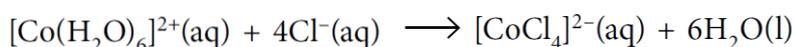
- Yellow solution forms, containing the complex ion  $[\text{CuCl}_4]^{2-}$

❖ E.g. the complexes of cobalt(II) ions:

- $\text{Co}^{2+}(\text{aq})$  refers to the complex ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  which gives a solution of cobalt(II) sulfate its pink colour; on addition with sodium hydroxide solution, blue precipitate of cobalt(II) hydroxide forms, which turns red when warmed with excess alkali
- Addition of concentrated ammonia drop by drop, with an intermediate of  $[\text{Co}(\text{OH})_2(\text{H}_2\text{O})_4]$ :



- Addition of concentrated HCl drop by drop results to a blue solution containing the tetrahedral complex  $[\text{CoCl}_4]^{2-}(\text{aq})$ :



- Different ligands form complexes with different stabilities, for example:



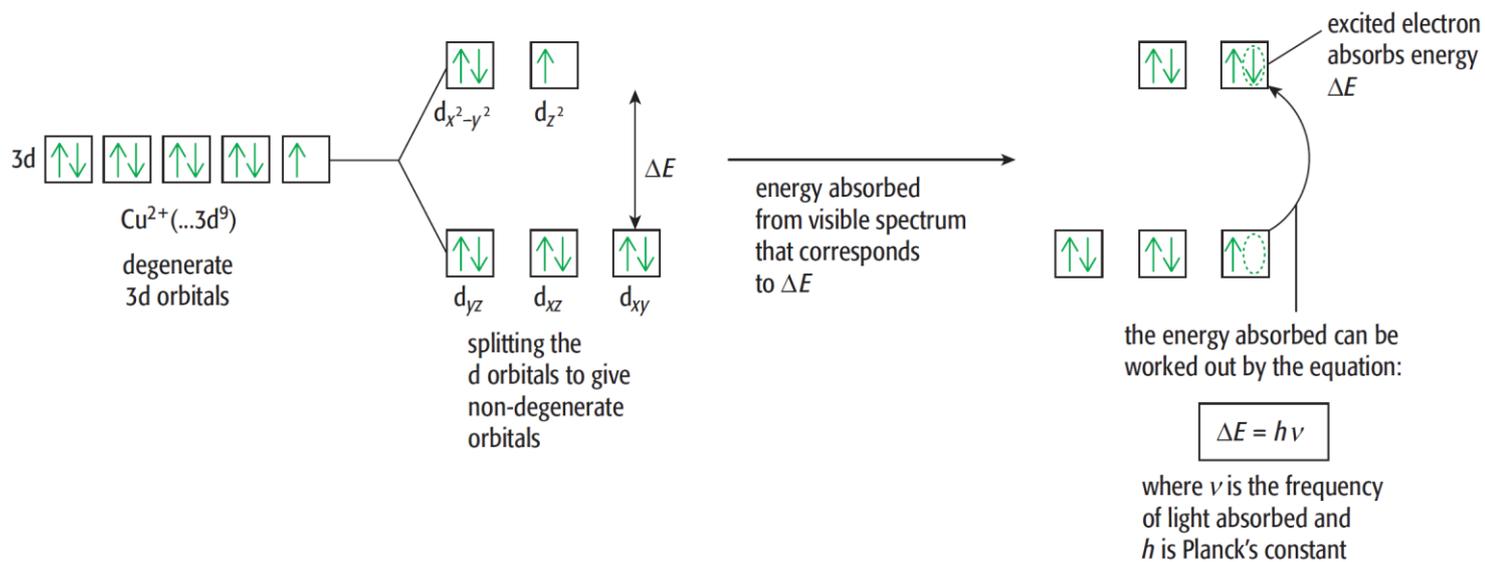
- Ligand exchanges can be explained in terms of competing equilibria of the forward and backwards reaction, where the direction of equilibria lies in the direction of the more stable complex ( $\text{NH}_3$  ligand); in addition of more water, the equilibrium shifts to the left and more complex with water molecules as ligands form
- Stability constant,  $K_{\text{stab}}$ , of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules
- For the equilibrium:



$$K_{\text{stab}} = \frac{[[\text{CuCl}_4]^{2-}(\text{aq})]}{[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}] [\text{Cl}^-(\text{aq})]^4}$$

- A large  $K_{\text{stab}}$  is due to the formation of a stable complex ion
  - For example, the addition of excess ammonia to the complex  $[\text{CuCl}_4]^{2-}(\text{aq})$  should result in the formation of a dark blue solution of the ammonia complex because the stability constant of the ammonia complex is higher than that of the chloride complex; the position of equilibrium is shifted to the right in the direction of the more stable complex
- The five d orbitals in an isolated transition metal atom or ion are described as **degenerate**, meaning they are all at the same energy level
- In the presence of ligands, a transition metal ion is not isolated; the co-ordinate bonding from the ligands causes the five d orbitals in the transition metal ion to split into two sets of **non-degenerate** orbitals at slightly different energy levels (lower and upper energy levels), hence when photon energy is absorbed in the visible light region, electrons jumps from the lower to the upper energy level (excitation); so transition metal complexes are coloured

- $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  is a pale blue, whereas a solution containing  $\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_2^{2+}$  is deep purple-blue, due to the different size of  $\Delta E$  (energy gap) between the non-degenerate d orbitals, and the different frequency of light absorbed by the two complexes



**Figure 24.14** The splitting of the 3d orbitals in a  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  complex ion.

