Chem Factsheet

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# Complexes

**To succeed in this topic you need to understand:**

- **coordinate bonding (covered in Factsheet 5);**
- **oxidation numbers (covered in Factsheet 11);**
- **shapes of molecules and ions (covered in Factsheet 4).**

**After working through this Factsheet you will:**

- **know that complexes are formed by the coordination of ligands to a cation, atom or molecule;**
- **know the formulae and names of common anionic and molecular ligands;**
- **understand the following aspects of complex ions:- coordination number, formulae, ionic charge, nomenclature, formation, colour, shapes and isomerism;**
- **be familiar with other types of complexes.**

The term *complex* is used to describe a great many compounds, molecules and ions resulting from coordination, i.e. the establishment of coordinate bonds.

> ***Remember -*** *A coordinate (or dative covalent) bond is a special kind of covalent bond, in which both of the bonding electrons originate from one atom. A coordinate bond, once formed, is indistinguishable from a covalent bond.*

Complex species are formed by the coordination of one or more *ligands* to a cation, atom or molecule.

> *A ligand is defined as an anion or molecule with a lone pair of electrons available for donation.*
> *Examples of anionic ligands are $F^-$, $Cl^-$, $Br^-$, $OH^-$ and $CN^-$.*
> *Examples of molecular ligands are $H_2O$, $NH_3$ and CO.*

### Complexes based on a cation

When ligands coordinate to a cation (referred to as the 'central cation'), the product is known as a *complex ion*. Compex ions include:

- hydrated metal cations, such as $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$;
- other complex cations, such as $[Co(NH_3)_6]^{2+}$;
- complex anions, such as $[Ag(CN)_2]^-$.

> *In order to attract lone pairs of electrons from ligands, the central cation needs to have a high surface charge density, i.e. a high charge (at least 2+), a low radius or, ideally, both.*
>
> - *For this reason, transition metal cations are at the centre of most complex ions.*
> - *Apart from $Al^{3+}$ and $Be^{2+}$, cations from the main group elements do not normally enter into complex ions.*
> - *Some complex ions are based on* hypothetical cations, *e.g. $B^{3+}$ and $Si^{4+}$. Such ionsare said to 'exist only in complexes', where they are 'stabilised by coordination'.*

When the central cation and ligands react together, their original properties are lost as the complex ion, with its own characteristics, is formed. For instance, the complex salt potassium hexacyanoferrate(II) shows none of the reactions of the $Fe^{2+}$ and $CN^-$ ions from which it is formed, but has entirely different properties due to the complex ion $[Fe(CN)_6]^{4-}$.

> ***Remember -*** *Iron(II) sulphate, $FeSO_4$, is used as an antidote for cyanide poisoning. As the toxic $CN^-$ ions coordinate to $Fe^{2+}$ ions, they are converted to harmless $[Fe(CN)_6]^{4-}$ ions.*
> ***Warning!*** *Do not try this.*

### Coordination number

> *The coordination number of a central cation is defined as the number of coordinate bonds which it forms. If all the ligands are 'monodentate' , i.e. if they coordinate through only one atom, coordination number is equal to the number of ligands.*
> *Coordination numbers of 2, 4 and 6 are encountered in complex ions, but 6 is by far the most common.*

Coordination number is governed by two factors.

- Available space
  Most central cations are so small that no more than six ligands can be packed around them.
- Availability of vacant orbitals
  The central cation must have vacant orbitals at a relatively low energy level to accept lone pairs of electrons. This explains why the coordination number of boron in complex ions such as $[BF_4]^-$ is restricted to 4. The central $B^{3+}$ cation has the configuration $1s^2$. Incoming electrons can enter the second shell but not the higher energy third shell. The second shell can hold four electron pairs altogether; one in the vacant 2s orbital and three in the 2p orbitals.

  Similar reasoning suggests that the maximum coordination number of aluminium shouldbe nine, because electrons enter the third shell which can hold 18 electrons (nine electron pairs), but in fact the number is six because $Al^{3+}$ is such a small cation that no more than six ligands can be accommodated.

**Formulae**

- The symbol for the central element is written first, followed by anionic ligands and molecular ligands in that order.
- Within each ligand class, the order should be alphabetical in terms of the symbol for the donor atom of the ligand.
- Polyatomic ligands (but not monoatomic ones) are enclosed in curved brackets.
- The formula of the whole complex ion is enclosed in square brackets.
- The charge on the complex ion is shown superscript outside the right hand bracket.

Examples are as follows,

| | |
|---|---|
| $[Cr(H_2O)_6]^{3+}$ | |
| $[Al(OH)(H_2O)_5]^{2+}$ | (Anionic ligand before the molecular ligands) |
| $[Cu(NH_3)_4(H_2O)_2]^{2+}$ | (Donor atoms are N and O; N is alphabetically before O) |
| $[CoCl(NH_3)_5]^{2+}$ | ($NH_3$ in parentheses but not Cl) |

> ***Remember -*** *Square brackets have two main uses in chemistry.*
>
> - *To denote molar concentrations; e.g. $[H^+]$ represents the concentration of hydrogen ions in mol $dm^{-3}$.*
> - *To enclose complex ions.*

### Ionic charge

> *The charge on a complex ion is the algebraic sum of that on the central cation and the total charge carried by the ligands.*

When all the ligands are neutral, the overall charge of the complex ion is simply that carried by the central cation, e.g. $Cr^{3+}$ + six neutral $H_2O$ molecules give $[Cr(H_2O)_6]$ with a charge of 3+.

In other cases, you should write down the charges of all the components and then calculate the overall charge. Examples are as follows.

$[Fe(CN)_6]^{4-}$ comprises an $Fe^{2+}$ ion and six $CN^-$ ions.

$\therefore$ overall charge = +2 -6 = -4

$[Al(OH)(H_2O)_5]^{2+}$ comprises an $Al^{3+}$ ion, one $OH^-$ ion and five $H_2O$ molecules.

$\therefore$ overall charge = +3 -1 +0 = +2

> ***Exam Hint - Do not confuse ionic charge with oxidation number.***
> - ***The ionic charge is equal to the oxidation number of the central element only if all the ligands are neutral.***
> - ***If necessary, the oxidation number of the central element can be shown by a superscript Roman numeral to the right of the symbol, e.g. $[Fe^{II}(CN)_6]^{4-}$.***

### Nomenclature

> *- Ligands are named first, followed by the central element.*

The names of some ligands are given in Tables 1 and 2.

**Table 1 Common anionic ligands with names used in complex nomenclature**

| | |
|---|---|
| $F^-$ | fluoro |
| $Cl^-$ | chloro |
| $Br^-$ | bromo |
| $I^-$ | iodo |
| $OH^-$ | hydroxo |
| $CN^-$ | cyano |
| $NO_2^-$ | nitro |
| $H^-$ | hydrido* |

* IUPAC (but not ASE) recommends that 'hydro' is used in complexes of boron.

**Table 2 Common molecular ligands with names used in complex nomenclature**

| | |
|---|---|
| $H_2O$` | aqua |
| $NH_3$ | ammine |
| CO | carbonyl |
| NO | nitrosyl |

- The number of each type of ligand is denoted by a prefix of Greek origin (Table 3). These prefixes are the same as those used in naming organic compounds. 'Mono' is not normally used.

**Table 3 Multiplying prefixes**

| | |
|---|---|
| 2 | di |
| 3 | tri |
| 4 | tetra |
| 5 | penta |
| 6 | hexa |

- Ligands are listed in alphabetical order, the multiplying prefix being ignored. For example, 'pentaaqua' would be cited before 'dicyano'.
- For all complexes, the name of the central element follows the names of the ligands. For complex cations the name of the element remains unchanged, but for complex anions thename of the element is changed from -ium to -ate, e.g. chrom*ium* to chrom*ate*. In some cases, where the symbol is of Latin origin, the name is more radically altered, e.g. 'ferrate' for anionic complexes of iron and 'cuprate' for those of copper.
- The oxidation state of the central element is indicated by a Roman numeral in parentheses after the name of the complex.

Examples are as follows.

| | |
|---|---|
| $[Cr(H_2O)_6]^{3+}$ | hexaaquachromium(III) ion |
| $[Al(OH)(H_2O)_5]^{2+}$ | pentaaquahydroxoaluminium(III) ion<br>(penta**a**qua before **h**ydroxo) |
| $[CoCl_4]^{2-}$ | tetrachlorocobaltate(II) ion |
| $[Fe(CN)_6]^{4-}$ | hexacyanoferrate(II) ion |

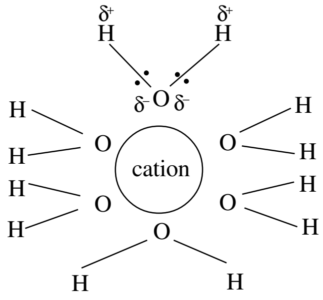
> ***Remember -*** *Complex names are written as one word, with no hyphens and no spacing between the name and the oxidation state of the central element.*

### Formation

Compex ions may be formed by two mechanisms.

• *Deprotonation (acid-base reaction)*

In aqueous solution cations become *hydrated*, i.e. surrounded by shells of water molecules, which are attracted to the cations by partial negative charge on oxygen.



For $Al^{3+}$ and transition metal cations, this *ion-dipole attraction* is reinforced by coordination. Generally, six $H_2O$ molecules are involved, to give complex ions such as $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$. With hydroxide ions and certain other ligands that behave as bases (e.g. $NH_3$), new complex ions can be formed from these hydrated cations by the process of *deprotonation*, in which protons ($H^+$) break away from coordinated water molecules to join the basic ligand. If, for example, two $OH^-$ ions were to attack a hydrated aluminium ion, the reaction would be:

$$[Al(H_2O)_6]^{3+}(aq) + 2OH^-(aq) \rightarrow [Al(OH)_2(H_2O)_4]^+(aq) + 2H_2O(l)$$

Since the hydrated cation behaves as an acid (proton donor) while $OH^-$ is a base (proton acceptor), such changes are often described as *acid-base reactions.* See Factsheet 86 for more detail.

- ***Ligand substitution***

Strong ligands, i.e. those that bond strongly to the central cation, will replace weaker ligands in *ligand substitution reactions*. Some of these are reversible because it is possible for a weak ligand to replace a stronger one if the former is present in excess.

Ligand substitution may occur with or without a change in coordination number. On boiling a mixed solution of iron(II) sulphate and potassium cyanide, six $H_2O$ molecules are replaced by six $CN^-$ ions:

$$[Fe(H_2O)_6]^{2+}(aq) \;+\; 6CN^-(aq) \;\rightarrow\; [Fe(CN)_6]^{4-}(aq) \;+\; 6H_2O(l)$$

However, when concentrated hydrochloric acid is added to a solution of a cobalt(II) salt, six $H_2O$ molecules are replaced by only four $Cl^-$ ions:

$$[Co(H_2O)_6]^{2+}(aq) \;+\; 4Cl^-(aq) \;\rightleftharpoons\; [CoCl_4]^{2-}(aq) \;+\; 6H_2O(l)$$

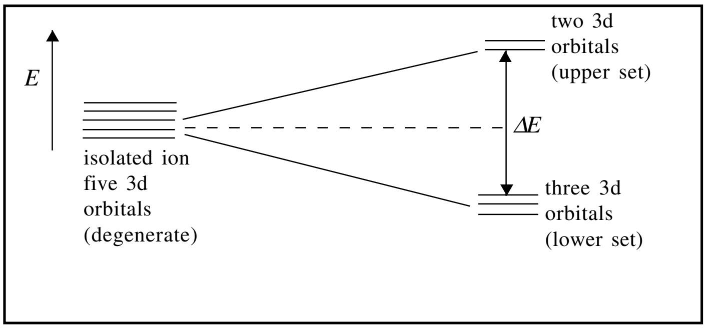
The decrease in coordination number is attributed to the relatively large size of $Cl^-$ ions compared with $H_2O$ molecules.

**Practical 1 - Preparation of tetrachlorocobaltate(II) ions.**
Add concentrated hydrochloric acid slowly, with shaking, to a few $cm^3$ of a solution of a cobalt(II) salt in a test tube and observe the colour change. Afterwards add water, until it is present in excess, and again observe the colour change.
Make sure you can write the equation for this reversible reaction.

## Colour

Most, but not all, complex ions are coloured, depending on whether or not the central cation has partially occupied d-orbitals. In a simple cation, all five 3d orbitals are *degenerate*, i.e. at exactly the same energy level, but, in the presence of ligands, this is not so. (The degeneracy is said to be 'relieved'.) Two of the orbitals are raised in energy level ('upper set') while the other three are lowered ('lower set'), an effect known as the 'splitting of d-orbitals' (Fig. 1)

**Fig. 1 Splitting of d-orbitals**



The energy difference between the upper set and the lower set can be symbolised $\Delta E$. When white light falls on a complex, the component whose frequency ($\nu$) corresponds to $\Delta E$ is absorbed in promoting an electron from the lower to the upper set. ($\Delta E$ and $\nu$ are related by Planck's equation, $\Delta E = h\nu$, where h = Planck's constant.) The other components of white light are transmitted, so that the complex appears to be coloured.

Therefore, for a complex to be coloured, there must be at least one electron in the lower set (available for promotion) and at least one vacancy in the upper set (to receive the promoted electron). This rules out complexes of $Al^{3+}$ and $Sc^{3+}$ (no electron in the lower set) and complexes of $Cu^+$ and $Zn^{2+}$ (no vacancy in the upper set). However, transition element ions in general do satisfy these conditions and their complexes are coloured (Table 4).

**Table 4 Electronic configurations and colours of some hydrated ions, $[M(H_2O)_6]^{n+}$, where n = 2 or 3**

| M | Electronic configuration | Colour |
|---|---|---|
| $Sc^{3+}$ | [Ar] $3d^0$ | none |
| $Ti^{3+}$ | $3d^1$ | violet |
| $V^{3+}$ | $3d^2$ | green |
| $Cr^{3+}$ | $3d^3$ | grey-blue |
| $Mn^{2+}$ | $3d^5$ | pale pink |
| $Fe^{3+}$ | $3d^5$ | pale violet* |
| $Fe^{2+}$ | $3d^6$ | pale gree |
| $Co^{2+}$ | $3d^7$ | pink |
| $Ni^{2+}$ | $3d^8$ | green |
| $Cu^{2+}$ | $3d^9$ | blue |
| $Zn^{2+}$ | $3d^{10}$ | none |

* The pale violet colour of $[Fe(H_2O)_6]^{3+}$ can be seen in salt hydrates, such as $Fe(NO_3)_3.9H_2O$. In aqueous solution, however, iron(III) salts are brownish yellow due to salt hydrolysis - a deprotonation reaction:

$$\underset{\text{pale violet}}{[Fe(H_2O)_6]^{3+}(aq)} \;+\; H_2O(l) \;\rightleftharpoons\; \underset{\text{brownish yellow}}{[Fe(OH)(H_2O)_5]^{2+}(aq)} \;+\; H_3O^+(aq)$$

The colour of complex ions depends on the following factors.

- Nature of the metal
  Different metals produce differently coloured ions, even when those ions have identical configurations and identical ligands. (Compare $[Mn(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$.)
- d-orbital occupation
  For a particular metal, colour depends on the number of d-electrons. (Compare $Fe^{3+}$ and $Fe^{2+}$.)
- Nature of the ligand
  For a particular cation, different ligands produce different colours. (Compare $[Co(H_2O)_6]^{2+}$ (pink) with $[CoCl_4]^{2-}$ (blue) and $[Co(NH_3)_6]^{2+}$ (red-brown).)

## Shapes

🔑 *- Shapes of complex ions*
- *Six-coordinate complexes are octahedral.*
- *Four-coordinate complexes are tetrahedral,* ***except for $[Ni(CN)_4]^{2-}$*** *which is square planar.*
- *Two-coordinate complexes are linear.*

Examples are shown in Table 5.

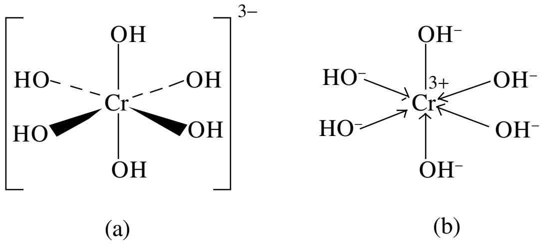
**Table 5 The geometry of some typical complex ions**

| Octahedral | Tetrahedral | Linear |
|---|---|---|
| $[Al(H_2O)_6]^{3+}$ | $[CoCl_4]^{2-}$ | $[Cu(NH_3)_2]^+$ |
| $[Ni(NH_3)_6]^{2+}$ | $[Cu(CN)_4]^{3-}$ | $[CuCl_2]^-$ |
| $[Fe(CN)_6]^{4-}$ | $[Zn(NH_3)_4]^{2+}$ | $[Ag(NH_3)_2]^+$ |
| $[Cr(OH)_6]^{3-}$ | | |

Whenever you are asked to draw the shapes of complex ions, read the question carefully!

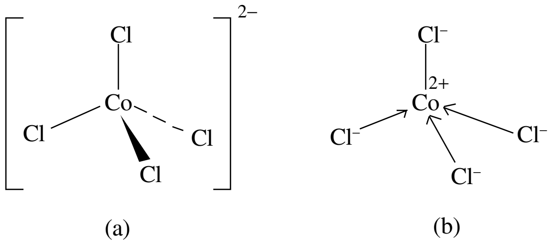
If you are asked to show the formation of a complex ion, you need diagrams such as those shown in Figs. 2(b) and 3(b), but if you are asked to show an ion once it has been formed, figures such as 2(a) and 3(a) are more appropriate because they show delocalisation of charge over the whole of the complex.

**Fig. 2 (a) The hexahydroxochromate(III) ion**
**(b) Formation of the hexahydroxochromate(III) ion**



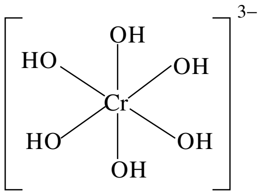
(a) (b)

**Fig. 3 (a) The tetrachlorocobaltate(II) ion**
**(b) Formation of the tetrachlorocobaltate(II) ion**



(a) (b)

***Exam Hint - 'Octahedral' does not mean star-shaped.***



*If you draw an octahedral ion like this you will lose marks!*

## Isomerism

***Remember -*** *Isomerism exists when two or more compounds have the same molecular formula but different structural formulae.*

Complexes may exhibit *ionisation isomerism* and *geometrical isomerism*. (There is also optical isomerism but this is not required at A-level.)

### Ionisation isomerism

This occurs when two or more compounds have the same composition but consist of different ions. The best known example concerns chromium(III) chloride-6-water, $CrCl_3.6H_2O$ which forms three ionisation isomers or 'hydrate isomers' as follows:

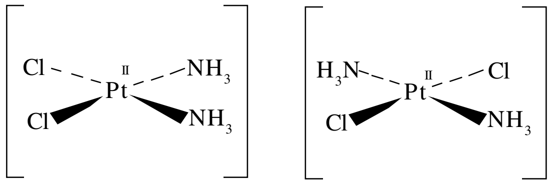
| | |
|---|---|
| $[Cr(H_2O)_6]^{3+}\ (Cl^-)_3$ | grey-blue |
| $[CrCl(H_2O)_5]^{2+}\ (Cl^-)_2.H_2O$ | light green |
| $[CrCl_2(H_2O)_4]^+\ Cl^-.2H_2O$ | dark green |

***Exam Hint -*** *If you are asked how you would distinguish between samples of each of these, bear in mind that only ionic chlorine (i.e. $Cl^-$ ions) will react with silver nitrate solution; not covalently bonded chlorine. The method therefore involves adding aqueous silver nitrate to solutions containing equal amounts of the three isomers until there is no further precipitation of silver chloride. The precipitates are then filtered off, washed, dried and weighed. Their masses will be in the ratio 3:2:1, corresponding to the numbers of $Cl^-$ ions in the formulae.*

### Geometrical isomerism

*- Sometimes known as* cis-trans isomerism*, this occurs when a complex has two sorts of ligands. If two identical ligands occupy adjoining positions on the complex an isomer is described as* cis*, but if they are across the complex from each other it is a* trans *isomer.*

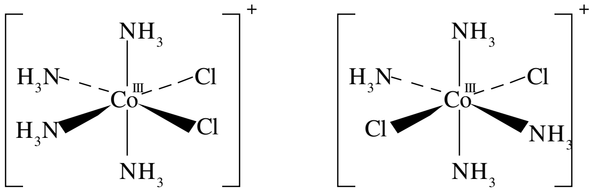
Geometrical isomerism is encountered with both square planar and octahedral complexes. The best known square planar examples are platinum(II) complexes such as the following:



*cis* isomer *trans* isomer

Note that these are complex molecules - not ions - because the overall charge is zero.

For an octahedral example, look at the tetraamminedichlorocobalt(III) ion:



*cis* isomer *trans* isomer

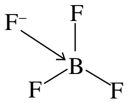
### Complexes based on an atom

Carbon monoxide is well known for coordinating to atoms of transition elements to give *metal carbonyls* such as $[Ni(CO)_4]$, tetracarbonylnickel(0), commonly called nickel tetracarbonyl. The molecule is tetrahedral.

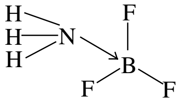
This compound has been used in the Mond process for the purification of nickel. Impure nickel will react with carbon monoxide at 80 °C to give volatile $[Ni(CO)_4]$, which is led away and decomposed at a higher temperature. This gives pure nickel because other metals will not form carbonyls at 80 °C.

### Complexes based on a molecule

Halides of boron, notably boron trifluoride, are very strong Lewis acids, forming a great many complexes by accepting a lone pair of electrons into the vacant p-orbital of the outer shell. This can result in the formation of both complex ions and complex molecules, e.g.



→ $[BF_4]^-$
Tetrafluoroborate(III) ion



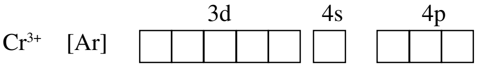
→ $H_3N{\rightarrow}BF_3$
Ammonia-boron trifluoride(1/1)

## Practice questions

1 Write down the formulae of the following.
   (a) Hexaamminecobalt(III) ion
   (b) Tetraamminediaquacopper(II) ion
   (c) Diaquatetrahydroxoaluminate(III) ion

2 Calculate the oxidation number of iron in each of the following complexes.
   (a) $[Fe(CN)_6]^{3-}$
   (b) $Fe(CO)_5$
   (c) $[Fe(OH)(H_2O)_5]^+$

3 Draw appropriate arrows in the following 'boxes' to represent orbital occupation in thehydrated chromium(III) ion. Label the diagram so as to distinguish between electrons possessed by the simple $Cr^{3+}$ ion and those originating from the ligands.



4 Copper(II) sulphate was dissolved in water to give a blue solution **A**. When **A** was treated with concentrated hydrochloric acid it gave a yellow solution **B** and when it was treated with concentrated aqueous sodium hydroxide it gave a blue solution **C**. The complex ions in solutions **B** and **C** both have a coordination number of 4.

   (a) Write down the formulae and names of the complex ions in **A**, **B** and **C** and state their shapes.

   (b) Write an ionic equation for the conversion of **A** to **B** and state the type of reaction.

   (c) Write an ionic equation for the conversion of **A** to **C** and state the type of reaction.

5 The square planar compound $[NiCl_2(NH_3)_2]$ can occur as two geometric isomers. Draw their structures and label each as *cis* or *trans.*

6 Ammonia and boron trifluoride combine together readily to give a white solid called ammonmia-boron trifluoride(1/1).

   (a) What features of the $NH_3$ and $BF_3$ molecules make this reaction possible?

   (b) What type of bond is formed?

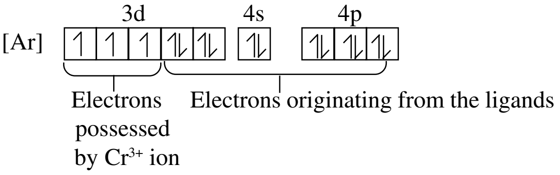
   (c) State and explain how the bond angles around both the N and B atoms are changed as a result of this combination.

## Answers

1 (a) $[Co(NH_3)_6]^{3+}$
   (b) $[Cu(NH_3)_4(H_2O)_2]^{2+}$
   (c) $[Al(OH)_4(H_2O)_2]^-$

2 (a) +3
   (b) 0
   (c) +2

3



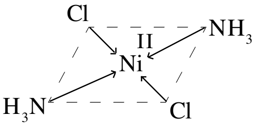
4 (a)

| | | | |
|---|---|---|---|
| **A** = | $[Cu(H_2O)_6]^{2+}$ | Hexaaquacopper(II) ion | Octahedral |
| **B** = | $[CuCl_4]^{2-}$ | Tetrachlorocuprate(II) ion | Tetrahedral |
| **C** = | $[Cu(OH)_4]^{2-}$ | Tetrahydroxocuprate(II) ion | Tetrahedral |

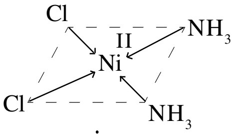
   (b) $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$
   Ligand substitution

   (c) $[Cu(H_2O)_6]^{2+}(aq) + 4OH^-(aq) \rightarrow [Cu(OH)_4]^{2-}(aq) + 6H_2O(l)$
   Deprotonation (acid-base reaction)

5



*trans*



*cis*

6 (a) $NH_3$: lone pair of electrons on N available for donation.
   $BF_3$: B has a vacant p-orbital.

   (b) Coordinate / dative covalent bond

   (c) Bond angles around N are increased from 106.7° to 109.5°, while those around B are decreased from 120° to 109.5°.

   *Reason* The bond angle in $NH_3$ (trigonal pyramidal) is governed by repulsion between three bond pairs of electrons and one lone pair: repulsion between lone pair and bond pair is greater than that between two bond pairs. In $BF_3$ (trigonal planar) the bond angle is the result of equal repulsion between three bond pairs. In the complex, the distribution of bonds about both N and B is tetrahedral due to equal repulsion between four bond pairs of electrons.

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