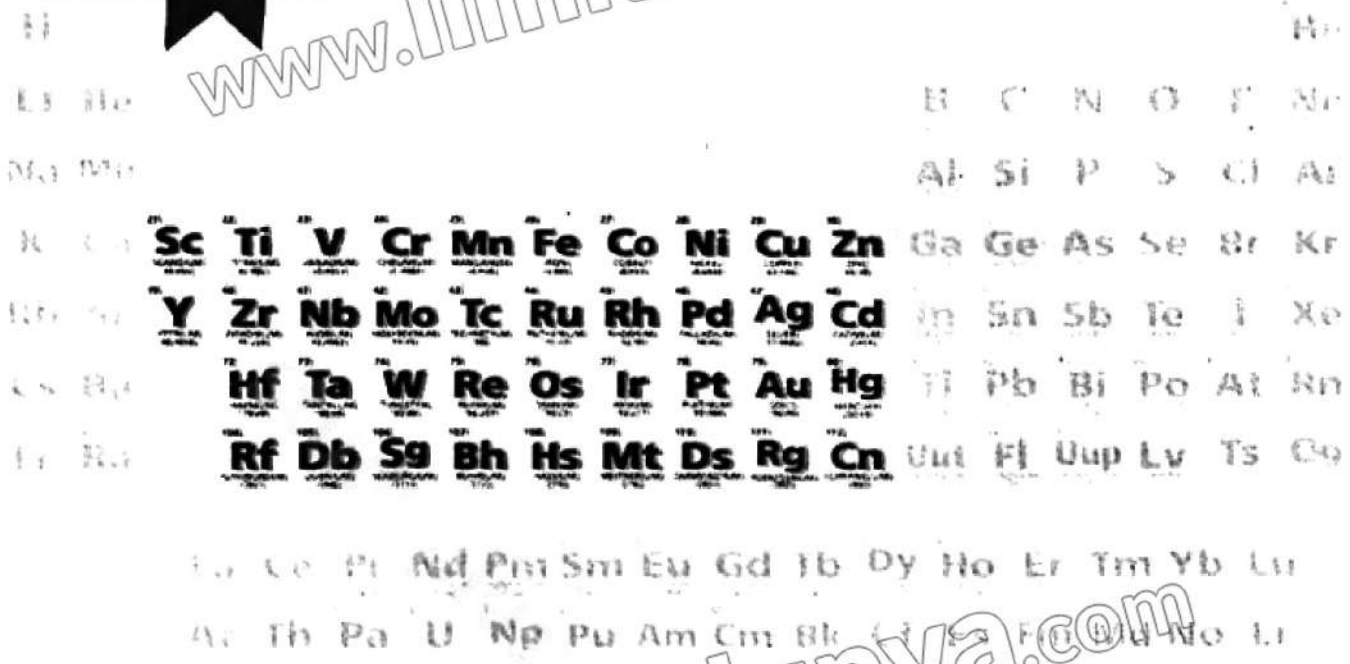
# UNIT 06



# THE TRANSITION METALS

## Student Learning Outcomes (SLOs)

- Identify the general physical and chemical properties of the first row of transition elements, titanium to copper.
- Define a transition element as a d-block element which forms one or more stable ions with incomplete d orbitals
- Sketch the shape of $3d_{xy}$ and $3_{dz^2}$ orbitals
- Identify the properties of transition elements, some examples including
  - a. They have variable oxidation states
  - b. They behave as catalysts
  - c. They form complex ions
  - d. They form coloured compounds
- Explain why transition elements have variable oxidation states in terms of similarity in energy of the 3d and 4s sub-shells.
- Explain why transition elements behave as catalysts in terms of having more than one stable oxidation states, and vacant d-orbitals that are energetically accessible and can form dative bonds with ligands.

- Explain why transition elements form complex ions in terms of vacant d-orbitals that are energetically accessible.
- Explain the reaction of transition elements with ligands to form complexes, including complexes of copper (II) and cobalt (II) ions with water and ammonia molecules and hydroxides and chloride ions.
- Define the term ligand as a species that contains a lone pair of electrons that forms a dative covalent bonds to a central metal atom/ion.
- Use the term monodentate ligand including examples water, ammonia, chloride and cyanide.
- Use the term bidentate ligand including 1,2-diaminoethane and ethanedioate ion, polydentate ligand including EDTA.
- Define the term complex as a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands.
- Describe the geometry (shape and bond angles) of transition elements complexes which are linear, square planar, tetrahedral or octahedral.
- State what is meant by coordination number.
- Predict the formula and charge of a complex ion, given the metal ion, its charge or oxidation state, the ligand and its coordination number or geometry.
- Explain qualitatively that ligand exchange can occur, including the complexes of copper (II) ions and cobalt (II) ions with water and ammonia molecules and hydroxide and chloride ions.
- Predict, using E° values, the feasibility of redox reactions, involving transition elements and their ions.
- Analyse reactions involving $MnO_4^-/C_2O_4^{2-}$ in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving $MnO_4^-/Fe^{2+}$ in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving $Cu^{2+}/I^-$ given suitable data (including describing the reaction and doing calculations).
- Perform calculations involving other colour of complexes.
- Use the terms degenerate and non-degenerate d-orbitals
- Describe the splitting of degenerate d-orbitals into two non-degenerate sets of d-orbitals of higher energy, and use ΔE in (a) octahedral complexes, two higher and three lower d-orbitals (b) tetrahedral complexes, three higher and two lower d-orbitals.
- Explain why transition elements form coloured compounds in terms of the frequency of light absorbed as an electron is promoted between two non-degenerate d-orbitals.
- Describe, in qualitative terms, the effects of different ligands on ΔE°, frequency of light absorbed, and hence the complementary colour that is observed.
- Use the complexes of copper (II) ions and cobalt (II) ions with water and ammonia molecules and hydroxide, chloride ions as examples of ligand exchange affecting the colour observed.
- Describe the types of stereoisomerism shown by complexes, including those associated with bidentate ligands:

- geometrical isomerism, e.g square planar such as $[Pt(NH_3)_2Cl_2]$ and octahedral such as $[Co(NH_3)_4(H_2O)_2]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$
- Optical isomerism, e.g $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^2$
- Deduce the overall polarity of complexes.
- Define stability constant ($K_{stab}$) of a complex as the equilibrium constant for the formation of the complex ion in a solvent (from its constituent ions or molecules).
- Write an expression for a $K_{stab}$ of a complex, $[H_2O]$ should not be included.
- Write an expression for a $K_{stab}$ of a complex, $[H_2O]$ should not be included.
- Use $K_{stab}$ expressions to perform calculations.
- Explain ligand exchanges in terms of $K_{stab}$ values and understand that a large $K_{stab}$ is due to formation of a stable complex ion.

When we come across the periodic table, we find a very important block at the centre, call transition elements. They possess unique chemical and physical properties, making them vital for daily use. Copper is used in wiring, coins, and plumbing, while iron is essential for bridges, vehicle parts, and construction. Chromium enhances plumbing fixtures; gold and silver are valuable for jewelry and electronics; platinum aids in catalytic converters; titanium is used in bicycles, aircraft, and artificial joints; and nickel, vanadium, molybdenum, and tantalum serve various industrial and medical purposes. Transition metals also form alloys, such as brass (copper and zinc) and bronze (copper and tin). In this chapter, transition metals are explored in detail.

Transition elements are those which have incomplete d-subshell in their most stable ionic states are called transition elements. They have been given the name 'transition' (which means change) because they show gradual change from much reactive group 2 elements (calcium) to much less reactive group 13 elements (gallium).

The first period of transition elements starts from scandium to zinc. However, zinc does not qualify the definition of transition elements because it forms only one colourless ion, $Zn^{2+}$, with a complete 3d sub-shell. Although, zinc can form complexes like transition metals, but this is not sufficient for it to be included in the transition elements block.

**Remember!**
Zinc is d-block element, but not transition element.

Scandium was initially controversial, as its common +3 oxidation state ($Sc^{3+}$) has an empty d sub-shell. However, it was later included in the transition metals by IUPAC system when compounds with +1 and +2 oxidation states, such as $CsScCl_3$, were synthesized.

In this chapter we will be mainly focused on the first row, the elements from titanium through to copper. To have full understanding of different properties of transition metals, we need to study their electronic configuration in detail.

## 6.1 Electron Configurations of the d-block elements

The electronic configuration of transition metals follows Aufbau principle. However, there are some exceptions to this rule. For example, chromium and copper break Aufbau principle. The reason is that atoms or ions with a half-filled 3d sub-level ($3d^5$) or a filled 3d sub-level ($3d^{10}$) are relatively stable, avoiding the inter-electronic repulsion in 4s orbital that occurs with the $4s^2$ configuration. Moreover, in both the cases, the 3d electron cloud is symmetrical which shields the nucleus relatively in a more effective way.

The electron configurations of some of the first-row d-block elements and their ions with orbital diagrams are given:

**Key Information**
When forming cations, electrons are always removed from the higher energy sub-shell, i.e 4s in first row of d block elements.

| Element | Electronic configuration | Ion | Electronic configuration |
|---|---|---|---|
| **Sc** | $[Ar]3d^1 4s^2$ | $Sc^{1+}$ | $[Ar]\ 3d^1 4s^1$ |
| | | $Sc^{2+}$ | $[Ar]\ 3d^1$ |
| **Ti** | $[Ar]3d^2 4s^2$ | $Ti^{2+}$ | $[Ar]\ 3d^2$ |
| **V** | $[Ar]3d^3 4s^2$ | $V^{4+}$ | $[Ar]\ 3d^1$ |
| **Cr** | $[Ar]\ 3d^5 4s^1$ | $Cr^{2+}$ | $[Ar]\ 3d^4$ |
| | | $Cr^{3+}$ | $[Ar]\ 3d^3$ |
| **Mn** | $[Ar]\ 3d^5 4s^2$ | $Mn^{2+}$ | $[Ar]\ 3d^5$ |
| **Fe** | $[Ar]\ 3d^6 4s^2$ | $Fe^{2+}$ | $[Ar]\ 3d^6$ |
| | | $Fe^{3+}$ | $[Ar]\ 3d^5$ |
| **Co** | $Ar]\ 3d^7 4s^2$ | $Co^{2+}$ | $[Ar]\ 3d^7$ |
| **Ni** | $Ar]\ 3d^8 4s^2$ | $Ni^{2+}$ | $[Ar]\ 3d^8$ |
| **Cu** | $Ar]\ 3d^{10} 4s^1$ | $Cu^{1+}$ | $[Ar]\ 3d^{10}$ |
| | | $Cu^{2+}$ | $[Ar]\ 3d^9$ |
| **Zinc** | $[Ar]\ 3d^{10}\ 4s^2$ | $Zn^{2+}$ | $[Ar]\ 3d^{10}$ |

**Relative Energies of 4s and 3d Sub-shells**

The energy difference between 3d and 4s orbitals changes across the period of transition metals. In calcium, the 4s orbital has lower energy than the 3d orbital because the 4s electron experience full attraction of the unscreened nucleus. This makes the 4s electrons more penetrating than the 3d electrons.

Along 3d period, after calcium, the 4s electrons are shielded by the 3d electrons, slightly decreasing their energy causing small rise in the first and second ionization energies. On the contrary, the 3d electrons faces higher effective nuclear charge due to less shielding, strongly attracted by the nucleus. This results in potential increase of 3d electrons, reflected in higher rise of third ionization energy.

## 6.2 Properties of Transition Elements

The transition elements are much more like each other than the elements across period 3. For instance, they are all metals rather *than showing* a change from metal to metalloids and non-metal. On the other hand, when we move along period 3, there come metals, then metalloids, non-metals and then noble gases. Similarly, there is not that decrease in atomic radii as in period 3 elements. Due to such similarities, transition metals show the following physical and chemical properties.

**Interesting Information**
The atomic radii of vanadium (23) and zinc (30) is same because the shielding offered by addition of 3d electrons counter the effect of increasing nuclear charge.

### 6.2.1 Physical properties

Transition metals show the following physical properties.

- They have high melting points because of strong metallic bonding in them.
- They have high density due to close packing of atoms in their lattices.
- They are good conductors of electricity because they have free electrons.
- They are good thermal conductors.
- They have a shiny metallic luster.
- They are malleable and ductile.
- They are hard and strong which makes them suitable for construction and manufacturing.
- They show magnetic properties, like paramagnetism and ferromagnetism and this property is exploited in various application, including magnetic resonance imaging (MRI).

### 6.2.2 Physical Characteristics

Some of their physical properties of first row of transition metals are given in detail.

#### 1. Density

Density of metals is the mass per unit volume expressed in the unit gram per cubic centimetre ($g/cm^3$). It is an important physical property of metals which shows how closely the metal atoms are packed in metallic lattice.

Moving through first period of transition metals, from scandium to copper, the density of transition metals generally increases. This is because of the two factors:

- The atomic mass of the metals increases, making their nuclei progressively heavier as we move to the right across the period.
- The atomic radius decreases across the period due to the increasing nuclear charge, which pulls the electron cloud closer, thereby reducing the size (volume) of the atoms.

Since density is directly related to mass and inversely related to volume, the increase in mass and decrease in volume across the period generally lead to an increase in the density of the metals.

However, there are some exceptions to the general trend. The density of manganese and copper is different from what is generally expected. The atomic radius of zinc is larger than that of copper because its full 3d sub-shell ($3d^{10}$) leads to less tight packing of zinc atoms in its metallic lattice, resulting in reduced density.

## 2. Atomic Radii

Transition metals show specific trends of atomic radii across the period. Understanding these trends require consideration of both shielding effect and electronic configuration.

In the first-row transition elements, the atomic radii decrease across the period because the nuclear charge increases, pulling electron closer to the nucleus. However, unlike main group elements, this decrease is less steep because electrons being added in 3d sub-shell do not shield one another sufficiently from the nuclear charge.

In the beginning, the atomic radii decrease because of increasing nuclear charge which overcomes the shielding effect.

**Important Information**
While discussing covalent and ionic radii, two factors are taken into consideration simultaneously, electron-electron repulsion and electron-nucleus attraction.

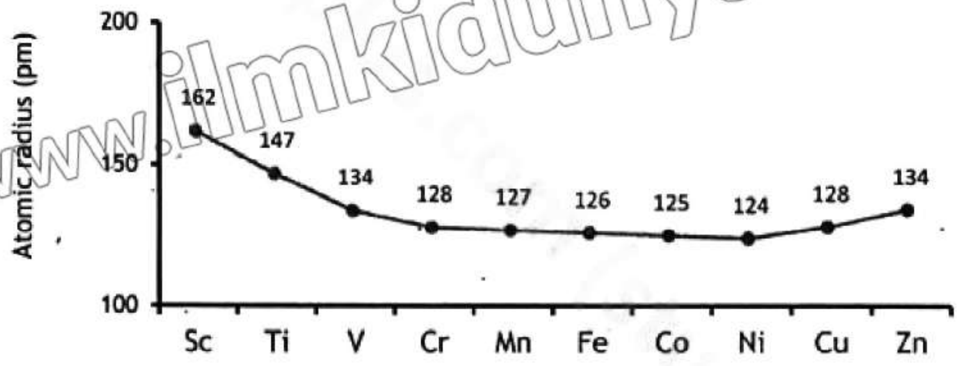


**Fig 6.1:** Atomic radii of first row transition metals

The decrease in atomic radii is not that pronounced while going through the middle of the period because of the two factors, i.e increasing nuclear charge and shielding effect, counterbalance each other. In this way, the atomic radii remain almost constant at the centre of the period.

Moving towards the end, atomic radii increase from nickel to copper and zinc. The reason is that the 3d sub-shell becomes full which causes shielding effect, pushing 4s sub-shell away from the nucleus.

Similarly, when moving from copper to zinc, we see an unexpected increase in atomic radius. The atomic radius of zinc is larger than that of copper because the additional electron in the 4s sub-shell in zinc increases the shielding effect, which outweighs the effect of the higher nuclear charge.

The melting and boiling points of the transition elements are generally much higher than those of the s- and p-block elements. They have strong metallic bonding because of involvement of electrons of both 3d and 4s sub-shells. When we plot melting and boiling points against atomic number, both graphs have some irregular behaviour. In the beginning, melting and boiling points increases as atomic number increases. Then we get two minima at manganese which reflect that the full 4s and half 3d sub-shells are much stable and not readily available for metallic bonding.

Zinc has lowest melting and boiling points because of full 3d and 4s sub-shells which cannot participate in metallic bonding. This is why mercury is liquid at room temperature as it belongs to zinc family (with full 3d and 4s sub-shells).

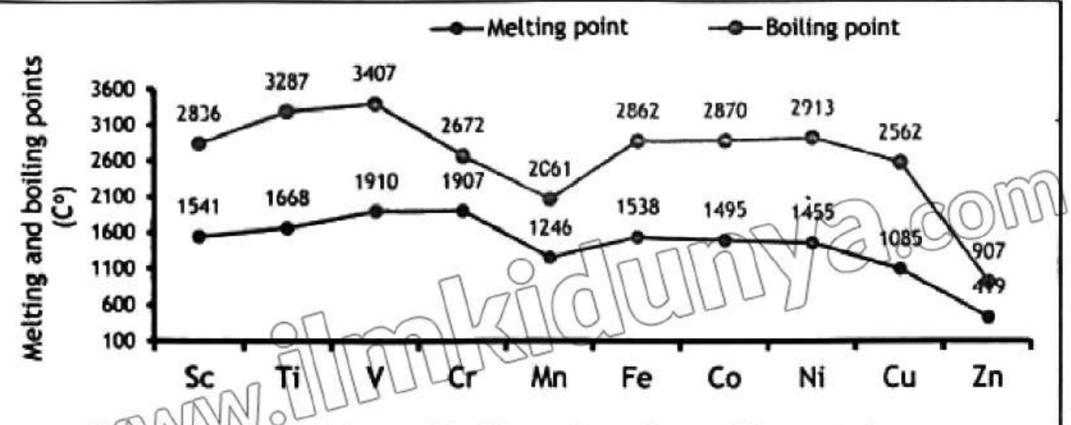


**Fig 6.2:** Melting and boiling points of transition metals

**Key Information**
Metallic bonding is directly related tp the number of unpaired electrons in outermost shells. However, the stability of sub-shells is also counted in this regard.

### Magnetic Properties

Transition metals and their compounds show magnetic properties which provide us information about chemical bonding in them and important uses in modern technology. An electron spinning around its own axis generates magnetic field just like electric current flowing through a wire does. It means that a single unpaired electron acts like a small magnet. Based on unpaired and paired electrons in outermost shells, transition metals and their compounds show different magnetic properties.

Paramagnetic substances are weakly attracted in magnetic field. For example, aluminium and sodium etc. The reason is that they have unpaired electron(s) in valence shells. The unpaired electrons on atoms or ions are not influenced by the electrons on surrounding atoms so they are directed randomly. When a paramagnetic solid is placed in magnetic field, the magnetic moments are aligned parallel to one another and a net weak attraction is observed. However, when the magnet is removed, the solid loses its paramagnetic properties.

Ferromagnetic substances are strongly attracted in magnetic field, for example iron, cobalt and nickel. They have also unpaired electrons in the valence shells of their atoms and ions in solid states. Their unpaired electrons are influenced by the electrons of surrounding atoms and ions and align in same direction. When a ferromagnetic substance is placed under magnet, a very strong attraction is observed-nearly million times more than a paramagnetic substance. Ferromagnetic substances maintain their magnetic moment even after removal of magnetic field, so they are permanent magnets.

Diamagnetic substances are those which are weakly repelled by magnet because they have paired electrons in outermost shells. For example, copper and iron etc. The paired electrons in an orbital cancel out their individual magnetic moments making net magnetic moment zero.

Alloys are the mixtures of metals which carry useful properties. Transition metals can form alloys because of their similar atomic size. They can substitute one another in their metallic lattices. Steel is an alloy of iron, chromium, nickel and manganese possessing more useful properties, like hardness; corrosion resistance and shiny. Other examples of alloys are brass (copper and zinc) and bronze (copper and tin).

## 6.2.3 Chemical Properties

While crossing first row transition metals, there is no such similarity in chemical properties as we found in physical properties. Some important chemical properties of transition metals are given here.

### 1. Variable Oxidation States

The common oxidation state for the first row of the d-block elements is +2 obtained by loss of two 4s electrons to form an $M^{2+}$ ion. The maximum stable oxidation state frequently corresponds to the maximum number of electrons (3d and 4s) available for bonding. For example, manganese, with electronic configuration, $[Ar]3d^5 4s^2$, can have a maximum oxidation state of +7.

**Do You Know?**
The simple ions of transition metal exist in low oxidation states ($Mn^{2+}$) while their complex ions ($MnO_4^{1-}$) are stable in high oxidation states.

The oxidation states of first row transition metals is shown:

| | | | | | | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | +1 | |
| | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | | | |
| | +4 | +4 | | +4 | | | | | |
| | | | | | | | | | |
| | | +5 | | | | | | | |
| | | | +6 | +6 | | | | | |
| | | | | +7 | | | | | |

The stability of +2 oxidation state compared to +3 oxidation state increases with atomic number from left to right across the first row of the d-block as it becomes increasingly difficult to remove 3d electrons. On the other hand, the stability of the higher oxidation states decrease with atomic number from left to right across the series.

The greater stability of +2 oxidation state of manganese compared to its +3 oxidation state and +3 oxidation state of iron relative to its +2 oxidation state can be explained on the basis of stability of half-filled 3d sub-shell.

### 2. Catalytic Activity

Transition elements or their compounds can be used as catalysts in various chemical reactions. They show two unique properties responsible for their catalytic activity:

- They can exist in more than one stable oxidation state.
- They have vacant d orbitals capable of forming temporary dative bonds with ligands.

First row transition metals have a unique property to change between different oxidation state, like $Fe^{2+}$ and $Fe^{3+}$ or $Cu^{+}$ to $Cu^{2+}$. They temporarily change their oxidation states by gaining or losing electrons during chemical reactions and help reactants convert to products. At the end of reaction, they regain their original oxidation state and become ready to play their role as catalysts again.

These metals possess incomplete 3d-orbitals in their valence shells. These vacant orbitals can accept electrons pairs from ligands (molecules or ions) forming temporary dative bonds between the transition metals and ligands. These dative bonds are responsible for holding reactants on the surface of transition metal and bring them closer. Resultantly, the bonds within reactant particles weaken and ultimately break. The product formation takes place on the surface of transition metal. In this way transition metals speed up the reaction to occur. After completion of reaction, the transition metal releases the products and becomes ready to bind to new reactants, continuing its role as catalyst.

In the Haber process of ammonia synthesis, iron is used as catalyst which adsorbs hydrogen and nitrogen gas on its surface and make them react faster. Similarly, in the Contact process, the vanadium pentoxide ($V_2O_5$) is used as catalyst involving reversible change in oxidation state of vanadium from +5 to +4. Both these examples involve reactants and catalysts with different physical states, so they are heterogeneous catalysis.

On the other hand, we may have homogeneous catalysis where reactants and catalysts are in same physical states. For example, oxidation of iodide ion ($I^-$) by peroxodisulphate (VI) ion ($S_2O_8^{2-}$).

$$2I^-_{(aq)} + S_2O_8{}^{2-}{}_{(aq)} \longrightarrow 2SO_4{}^{2-}{}_{(aq)} + I_{2(aq)}$$

The reaction is slow because the negatively charged ions of reactants repel each other. It can be catalyzed by the addition of d-block metal ions like $Fe^{2+}$ (aq) which change its oxidation states reversibly between +2 and +3 as shown.

$$2Fe^{2+}{}_{(aq)} + S_2O_8{}^{2-}{}_{(aq)} \longrightarrow 2Fe^{3+}{}_{(aq)} + 2SO_4{}^{2-}{}_{(aq)}$$

$$2Fe^{3+}{}_{(aq)} + 2I^-{}_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + I_{2(aq)}$$

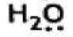
Both the steps of this mechanism involve a reaction between two oppositely charged ions making the reactions faster than the previous uncatalyzed case.

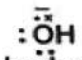
## Ligands

A ligand is an atom or group of atoms which is electron rich and can donate lone pairs of electrons to the transition metal ions, making dative covalent bonds with them. Ligands may be molecules or ions made of non-metal atoms. They are also called Lewis bases or nucleophiles because they can donate electrons. Based on the number of lone pair they can contribute to coordinate covalent bond formation, ligands have the following classes.

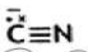
**Key Information**
The d sub-shell splitting is caused when ligands approach the central metal ion.

Monodentate Ligands: The ligand which can form one dative covalent bond with transition metal atom/ion is called monodentate (Latin word-meaning 'one-toothed'). They may have more than one lone pair of electrons but can donate only one. For example, aqua ($H_2O$), halo ($X^-$), hydroxo ($OH^-$), ammine ($NH_3$), and cyano ($CN^-$) etc.


aqua


hydroxo

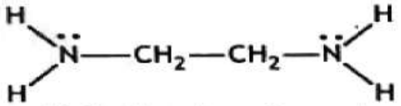

ammine


cyano

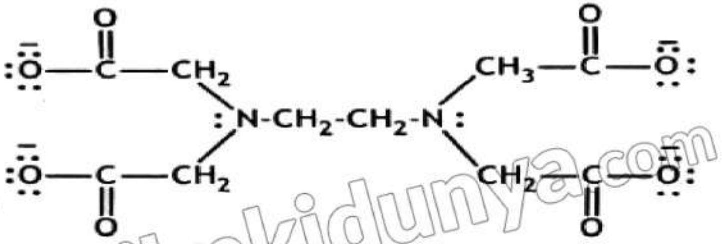

halo

The ligand that can donate more than one lone pair of electrons are called polydentate ligands (many-toothed). For example, 1,2-diamminoethane ($NH_2CH_2CH_2NH_2$) and ethanedioate $(COO^-)_2$ are bidentate ligands as they can form two coordinate covalent bonds at a time with central transition metal ions.


(ethanedioate)
oxalato


(1,2-diaminoethane)
ethylenediammine (en)

Similarly, ethanediaminetetraethanoic acid (EDTA) is hexadentate ligand because it can donate six lone pairs of electrons to the central metal atom.


ethylenediaminetetraacetate acid (EDTA)

## 6.3 Formation of Complex Compounds

A complex compound or coordination compound is formed between transition metals and ligand(s). *Ligands* donate lone pair of electrons in the vacant orbitals of transition metals while transition metals accept the electron pair making coordinate covalent bonds. Ligand is electron pair donor, so it is called Lewis base. while transition metal accepts electron pair and is called Lewis acid. Transition metal complexes may be positive, negative or neutral. Transition metals form complex ions due to the following two reasons:

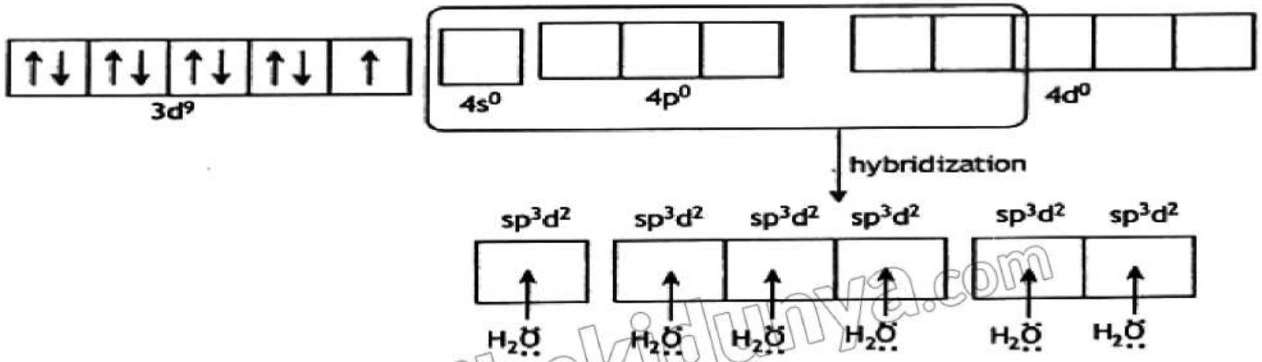
- They have a small size and high charge density, enabling them to strongly attract ligands.
- They have 3d sub-shell which has low energy and can bond to p-orbitals of ligands easily.

Transition metals lose electrons and become cations. They have vacant d orbitals that undergo hybridization to produce same number of new orbitals with equal energy. This process is followed by reaction of ligands with transition metal ion to form complex. The ligands donate electron pair to the hybridized vacant 3d orbitals of central metal ion. The vacant 3d orbitals of first row transition metals are energetically accessible because they have low energy, and ligands can easily donate lone pairs of electrons to them making dative bond with them. After this process, ligands come and donate electron pairs to those hybridized orbitals forming complex ion.

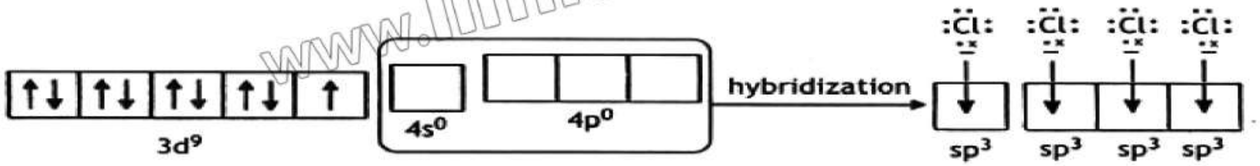
### I. Complexes of Copper (II) with Water and Chloride Ligands

Copper (II) ion ($Cu^{2+}_{(aq)}$) has electronic configuration [Ar] $3d^9$. Six water ligands approach to copper(II) ions and form six coordinate covalent bonds with copper (II) ion. However, before making bonds, the six vacant orbitals of copper (II) ion undergo hybridization, generating six $sp^3d^2$ hybrid orbitals. These orbitals are then available for six water molecules to coordinatively bond and form the given complex as reflected from the 'electrons-in-box diagram.

**Do You Know?**
The transition metal ions have high charge density, so they are highly polarizing compared to s-block metals. This is why they have higher tendency to form complexes.



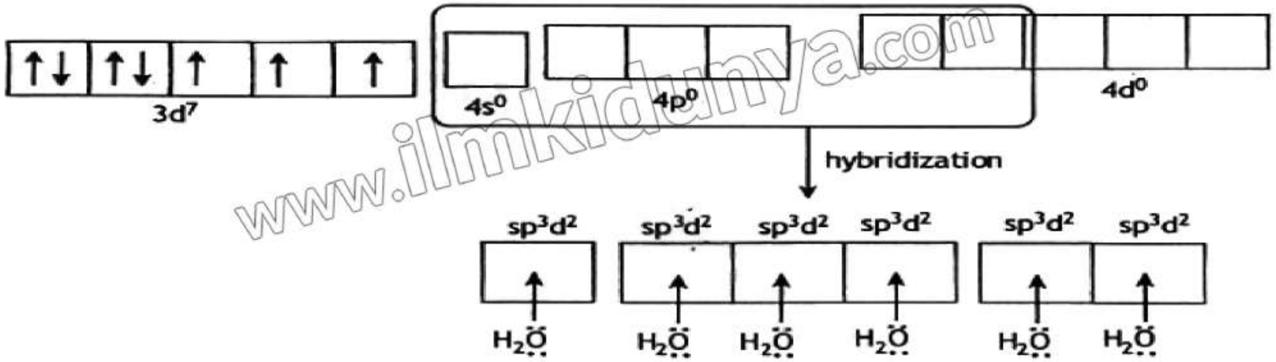
Similarly, copper (II) ions intermix four vacant orbitals (4s and 4p) giving four $sp^3$ hybrid orbitals. Then four chloride ligand coordinatively bond with those four hybrid orbitals as shown:



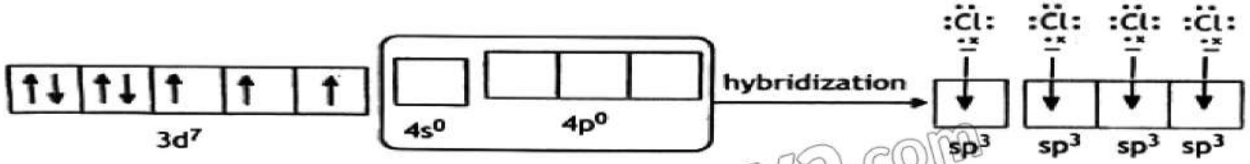
With chloride ligands, copper(II) forms tetrahedral complex, tetrachlorocuprate(II) ion, because chloride is a big ligands and six chloride ligands cannot surround a small copper(II) ion.

### ii. Complexes of Cobalt(II) ion with Water and Chloride Ligands

The condensed electronic configuration of cobalt(II) ion is $[Ar]3d^7$. It forms octahedral complex where six water ligands form dative bonds with the empty orbitals available with cobalt(II) ion. The following diagram shows the formation of octahedral complex of hexaaquacobalt(II) ion with six water ligands making six coordinate bonds with six $sp^3d^2$ hybrid orbitals.



Similarly, cobalt(II) ion reacts with four chloride ligands, making four dative bonds and give tetrahedral complex, tetrachlorocobaltate(II) ion. Before making bonds, the four vacant orbitals of cobalt (II) ions undergo hybridization as shown.



**Terminology of complex compounds**

- **Coordination Number**
  The number of coordinate covalent bonds formed by metals ions with ligands is called coordination number. The most common coordination number are 4 and 6, however, complexes with coordination number 2 can also exist. For example, the coordination number of compounds $[Cu(NH_3)_4]^{2+}$, $[Ni(CO)_4]$, $Na_4[Fe(CN)_6]$ and $[Co(NO_2)_3(NH_3)_3]$ are four, four, six and six respectively.
- **Coordination Sphere**
  The central atom or ion with ligand(s) is called coordination sphere enclosed by square bracket. The coordination sphere may be neutral, anionic and cationic. For example, $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$ and $[Ni(CO)_4]$ have anionic, cationic and neutral coordination sphere respectively.

- **Charge on Coordination Sphere**
  It is the sum of total charges on transition metal ion and ligands (if any). Examples:
  i. $Na_4[Fe(CN)_6]$
  Oxidation state of iron = +2
  Total charge on six cyanide ligands = -6
  Charge on coordination sphere = +2+(-6) = -4
  ii. $[Cu(NH_3)_4]SO_4$
  Oxidation state of copper= +2
  Total charge on four ammonia ligands = 0
  Charge on coordination sphere= +2+0 = +2

The charge on coordination sphere is equal but opposite to the charge on the ions outside the coordination sphere.

## 6.3.1 Naming Complex Compounds

IUPAC nomenclature of complex compounds recommends the following rules:

i. Name cation before anion, whether it is simple ion or complex ion.
ii. While naming coordination sphere, the ligands are named first in alphabetical order, then the transition metal ion.
iii. The suffix "ate" is added to the name of the central metal atom if the coordination sphere is anionic. For example ferrate for iron, cuperate for copper and argentate for silver. Otherwise, the name of metal remains unchanged.
iv. We use the prefixes di, tri and tetra etc for ligands to show their number. For polydentate ligands, prefixes bis (two), tris (three), tetrakis (four) ligands and pentakis (five) etc are usded.
v. Naming anionic ligands, we use suffix "o", e.gchloro ($Cl^-$), hydroxo ($OH^-$) and carbonato ($CO_3^{2-}$) etc. Neutral ligands usually retain their names, like aqua/aqua ($H_2O$), ammine ($NH_3$) and carbonyl (CO) etc.
vi. The oxidation state of the central ion is represented by Roman numerals and put in parenthesis after the name of metal atom.

**Examples of Complex Compounds**

| | |
|---|---|
| $[Pt(NH_3)_4BrCl]Cl_2$ | tetraaminebromochloroplatinium(IV) chloride |
| $[Cu(NH_3)_2]^{2+}$ | Diamminecopper(II) ion |
| $K_4[Fe(CN)_6]$ | Potassium hexacyanoferrate(II) |
| $[Cr(H_2O)_6]Cl_3$ | Hexaaquachromium(III) chloride |
| $[Ni(CO)_4]$ | Tetracarbonylnickel (0) |
| $[Co(NO_2)_3(NH_3)_3]$ | Triamminetrinitrocobalt (III) |
| $[Cr(en)_2Cl_2]Cl$ | Dichlorobis(1,2-diaminoethane)chromium(III) chloride<br>[en=ethylenediamine] |
| $K_2[PtCl_6]$ | Potassium hexachloroplatinate(IV) |

While naming complex compounds, the number of counter ions is not counted.

## 6.3.2 Working Out the Charge on Complexes and Their Formulae

The total charge on a complex ion depends upon the oxidation state of metal ion and the number and nature of ligands. The oxidation state of metal ion can be calculated from the charge on the complex ion. Remember that oxidation state on transition metal ion equals to charge on the complex minus sum of charges on the ligands.

The ions outside the coordination sphere neutralizing complex ion are called counter ions.

### Worked Examples

- Deduce the charge on the tetraamminedichlorocobalt(III) complex ion. What is its formula?
- The formula has two chloride ions and four ammonia molecules, so the ligands contribute two negative charges (−2). The central cobalt cation has an oxidation number of +3, so it contributes three positive charges (+3). Hence the total or net charge on the complex ion is +1. The formula is therefore $[CoCl_2(NH_3)_4]^+$.
- Deduce the oxidation state of copper in the $[CuCl_4]^{2-}$ complex ion. What is its name?
- The complex ion is an anion with a total or net charge of −2. The formula has four chloride ions acting as ligands which contribute a total of four negative charges (−4). Hence the central copper ion must contribute two positive charge so its oxidation state is +2. This ion is the tetrachlorocuprate(II) ion.

**Concept-Assessment Exercise 6.1**

1. Determine the oxidation states of transition metals in the following complexes.
   i. $[Co(NH_3)_6]Cl_3$. ii. $Na_2[MnCl_5]$ iii. $[Co(en)_2(H_2O)_2]$
   iv. $[CuCl_4]^{2-}$ v. $Na_4[Fe(CN)_2(OH)_4]$
2. Name the following complex ions.
   i. $[Co(NH_3)_4Cl_2]Cl$ ii. $[Zn(OH)_4]^{2-}$ iii. $[CrCl_2(NH_3)_4]^+$

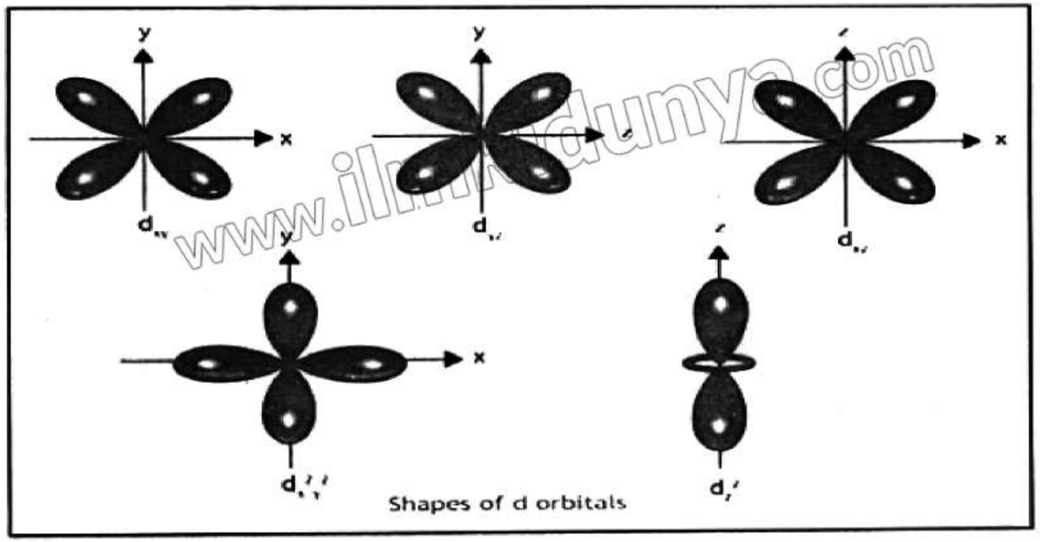
### 6.3.3 Coloured Complexes

If white light is passed on a transition metal complex, either in solid form or solution form, some light *is absorbed and some* is transmitted. There are three possibilities.

- If all the light is absorbed, the compound appears 'black'.
- If some light is absorbed, the compound will appear coloured.
- If all the light is reflected, the colour of the complex compound will appear 'white'.

Transition metal ion, in solution or solid form, are coloured because it absorbs a part of visible light and the remaining part is transmitted. Light is absorbed by those transition metal complexes which have incomplete 3d sub-shells. For example, copper (II), ([Ar]$3d^9$), complex has incomplete d sub-shell so it has coloured compounds. On the other hand, zinc (II), [Ar]$3d^{10}$) is colouless compound because it has complete d sub-shell. Before digging in the topic in detail, we must know about d orbitals.

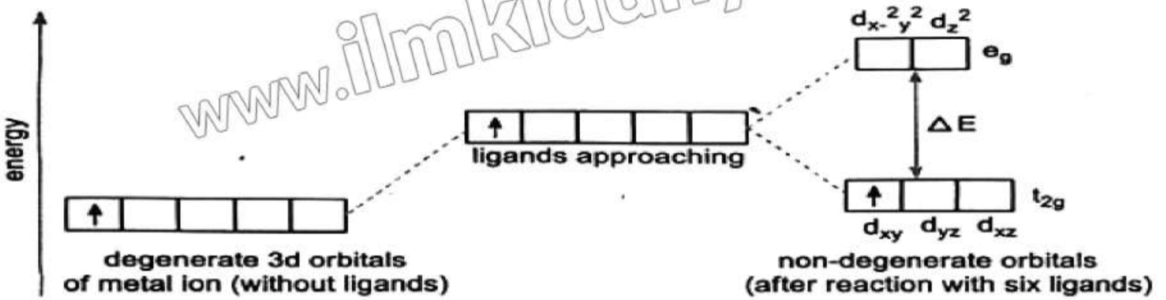
All d orbitals in d sub-shell have same energy so they are called degenerate orbitals. However, they are oriented in different directions along x, y and z axes as shown.



Shapes of d orbitals

Consider octahedral complex where six ligands approach the central metal ion along x, y and z axes. Almost all transition metals have octahedral complexes. The interaction between ligands and central metal ion caused splitting of d sub-shell into two set of orbitals. Ligands interacting with the two d orbitals lying along x, y and z axes ($d_{x^2-y^2}$ and $d_{z^2}$) experience greater repulsion than that with the d orbitals orienting in between the axes ($d_{xy}$, $d_{yz}$ and $d_{xz}$). The higher repulsion results in higher energy set of orbitals called $e_g$ whereas the lesser repulsion give rise to lower energy set of orbitals called $t_{2g}$. The overall energy of both $e_g$ and $t_{2g}$ orbitals of complex is higher than the degenerate 3d orbitals of metal ions without ligand.

The d-d splitting pattern is shown.



**Key Information**

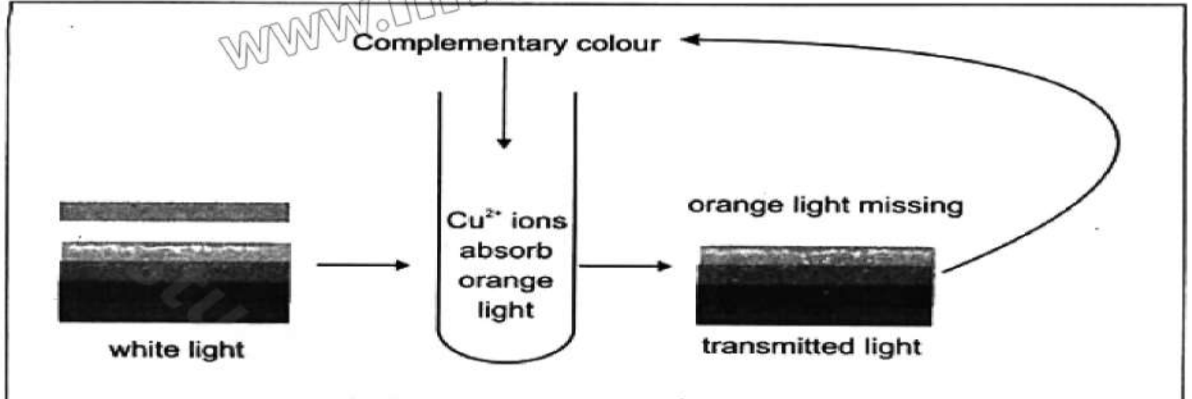
The terms $e_g$ and $t_{2g}$ stands for "doubly gerade" and "triply gerade" respectively. The subscript "g" stands for "gerade" which is a German word meaning even (degenerate).

The energy difference (ΔE) between the two sets of d orbitals in a complex ion is equal to the energy of a photon of characteristic light in visible spectrum. When white light is passed through a complex ion, whether in solution or solid form, photon of a particular energy and frequency is absorbed which will excite electron from lower energy set of d orbitals ($t_{2g}$) to higher energy set of d orbitals ($e_g$). This shift of electron between the two sets of orbitals is called d-d electronic transition.

As a result of this electronic transition, a colour from the white light is removed and the solution gives a complementary colour to the absorbed light. Different complexes give different colours depending upon the colour absorbed from white light. Each colour absorbed gives its own complementary colour as shown from the colour wheel.

The colour wheel

The nickel complex, $[Ni(H_2O)_6]^{2+}$, absorbs red light from white light and appears green, which is complementary colour to red. Similarly, the copper complex, $[Cu(H_2O)_6]^{3+}$, absorbs orange colour and appears blue (a complementary colour to orange) as shown in the diagram.



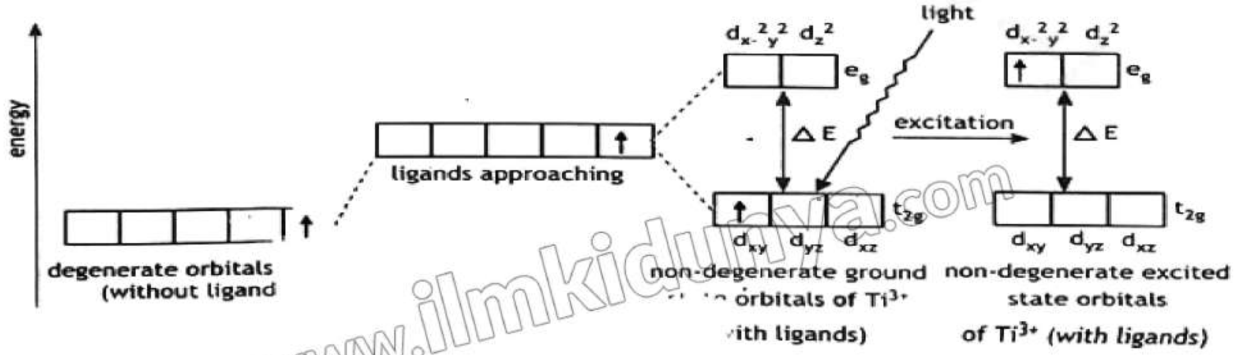
How complexes Get Colours?

## 6.3.4 The d-d Splitting Pattern in Octahedral and Tetrahedral Complexes

Let's consider the example of the aqua complex of titanium (III). This complex has an octahedral shape, with six water molecules acting as ligands around the titanium ion. In octahedral complexes, the three $t_{2g}$ orbitals (dxy, dyz, and dxz) lie between the six ligands, so they experience less repulsion from the ligands' lone pairs. In contrast, the two $e_g$ orbitals are aligned directly toward the ligands, which causes them to experience more repulsion.

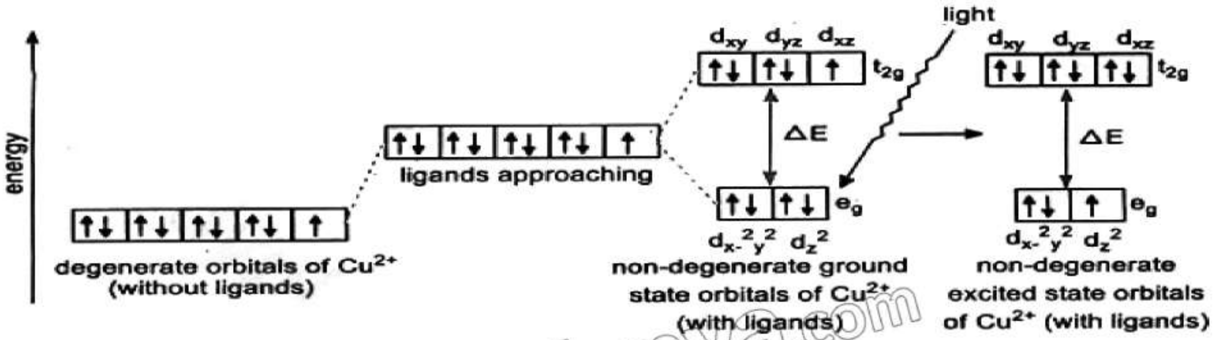
### Octahederal Complexes

Based on the extent of repulsion between the orbitals and ligands, $t_{2g}$ set of orbitals has lower energy while $e_g$ set has higher energy. When white light strikes $[Ti(H_2O)_6]^{3+}$ complex ion, in solid form or solution form, it absorbs yellow green light for excitation of electron and gives red-violet colour.



### Tetrahedral Complexes

In tetrahedral complexes, the three t2g orbitals are oriented toward the ligands, leading to more repulsion and higher energy. In contrast, the two $e_g$ orbitals are positioned between the ligands, so they experience less repulsion and have relatively lower energy. Based on the degree of repulsion between 3d orbital electrons and ligands, $t_{2g}$ set of orbitals have higher energy whereas $e_g$ has lower energy. For example, consider the tetrachlorocuprate(II) complex, $[CuCl_4]^{2-}$.

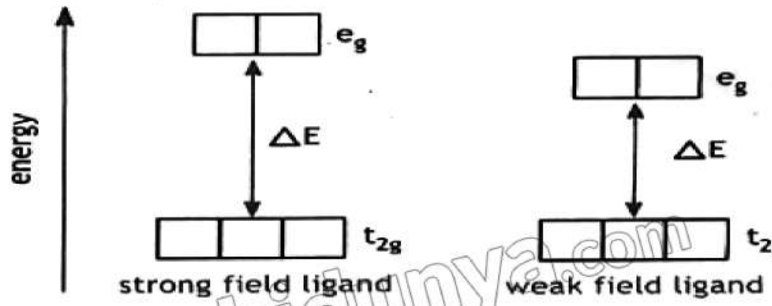


## 6.3.5 Effect of Ligands on Colour of Complexes

When ligands approach transition metal ions, their electric fields interact with the d orbitals of metal ions resulting in splitting of d orbitals into two different energy levels. On the basis of their different abilities to split d orbitals, ligands show different field strengths and follow the order:

$$CN^- > NH_3 > H_2O > OH^- > Cl^- > Br^-$$

A strong field ligand splits d orbitals to greater extent hence causes higher splitting energy (ΔE) than a weak field ligand as shown.



Consider the addition of ammonia solution to the aqueous solution of copper (II) ions and subsequent change in colour of the given complex. We know that ammonia is a strong field ligand whereas water is a weak field ligand so ammonia will replace water in the complex.

In this reactions, four ammonia molecules replace four water molecules, shifting absorption from blue to violet-blue.

$$\underset{\text{blue}}{[Cu(H_2O)_6]^{2+}(aq)} + 4NH_3(aq) \longrightarrow \underset{\text{violet-blue}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 4H_2O(l)$$

**Concept Assessment Exercise 6.2**

- What are degenerate and non-degenerate 3d orbitals?
- Why degenerate 3d orbital split into two sets of orbitals in some complexes while not in others?
- Which different ligands cause different splitting energy (ΔE) ? Give one example.

## 6.3.6 Geometries of Complexes

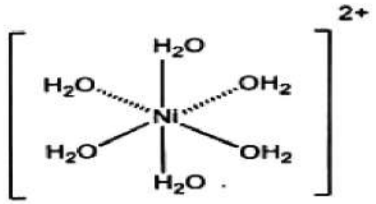
In previous class, we applied valence shell electron pair repulsion (VSEPR) theory on simple molecules to determine geometries of molecules. Similarly, we can use this theory on transition metal complexes to ensure maximum distances and minimum repulsion among dative bond pairs.

Copper (II) ion can bond to four chloride ligands, six water and six ammonia ligands. This is because the chloride ligand is bigger than water and ammonia, as chlorine belongs to period 3 while oxygen in water and nitrogen in ammonia belong to period 2. The space around copper (II) ion is not enough to surround six $Cl^-$ ions.

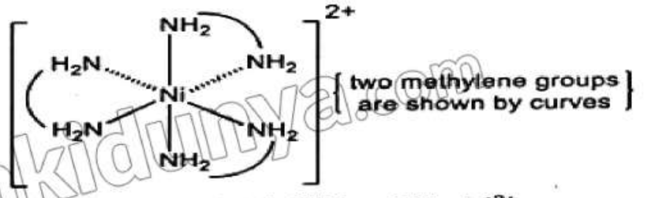
### 1. Complexes with Coordination Number 6

The complexes with coordination number 6 adopts octahedral shapes in which six donor atoms of ligands (both monodentate and polydentate) are positioned at the vertices of octahedron (oct means eight and hedron means faces). According to valence shell electron pair repulsion (VSEPR) theory, this three-dimensional arrangement of ligands experiences minimum ligand-ligand repulsion.

Octahedral complexes are the most common and stable complexes and almost all transition metals can form octahedral complexes. The octahedral complexes can have both monodentate and polydentate ligands. The angles between all ligands is 90°.



Hexaaquanickel(II) ion, $[Ni(H_2O)_6]^{2+}$



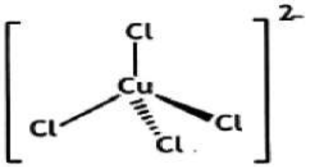
Tris(1,2-diaminoethane)nickel(II) ion, $[Ni(en)_3]^{2+}$

### 2. Complexes with Coordination Number 4

There are two possible arrangements of ligands or dative bond pairs around central metal ions in complexes with four coordination number structures. One is tetrahedral arrangement of dative bonds following VSEPR argument and the other is square planar geometry which violates VSEPR theory. We discuss the two geometries separately.

#### i. Tetrahedral Complexes

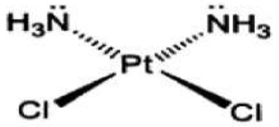
They are less common than octahedral complexes and you will often see them with chloride ligands, like tetrachlorocuprate(II), $[CuCl_4]^{2-}$. The tetrahedral geometry of $[CuCl_4]^{2-}$ complex is supported by VSEPR theory and the four chloride ligands are at maximum distances, making 109.5° angles.



Tetrahedral complexes are mostly formed by metal ions with $d^{10}$ electron configuration such as $Cu^+$ and $Zn^{2+}$. Some other examples are $[Cu(CN)_4]^{3-}$ and $[Zn(NH_3)_4]^{2+}$ etc.

#### ii. Square Planar Complexes

Square planar complexes have four ligands directed at the four corners of a square making 90° angles with one another. This arrangement of ligands in this type of complexes is against VSEPR theory. They are less common than tetrahedral complexes. Most square complexes are made by platinum, like diamminedichloroplatinum(II) complex.



cis-diaaminedichloroplatinum(II)

They are mostly formed by metal ions with $d^8$ electronic configuration such as $Ni^{2+}$ and $Pt^{2+}$ and $Au^{3+}$. Examples are $[Ni(CN)_4]^{2-}$, $[AuCl_4]^-$ and $[Pt(NH_3)_4]^{2+}$ etc.

### 3. Complexes with Coordination Number 2

Linear complexes are less stable. They have two monodentate ligands lying at 180° angle as shown.

$$\left[H_3\ddot{N}-Ag-\ddot{N}H_3\right]^+$$

Diamminesilver(I) ion

Some other examples are $[CuCl_2]^-$ and $[Au(CN)_2]^-$ etc.

## 6.4 Ligand Substitution Reactions

Transition metals undergo many types of reactions, such as redox reactions, deprotonation reactions, and ligand substitution reactions, but we shall discuss only ligand exchange reactions in this section.

*The reaction in* which one ligand is substituted by another ligand is called ligand exchange reaction, also called ligand substitution reactions. The reactions take place if the complex formed is more stable than the reacting complex. They involve either complete or partial exchange of ligands.

We will restrict ourselves to the reactions of copper(II) complexes and cobalt(II) complexes only. The ligands participating in the reactions will be water, ammonia, hydroxide and chloride ions.

### i. Copper(II) Complexes

We add strong base, like sodium hydroxide (NaOH), to the blue solution of copper sulphate ($CuSO_4$), we observe a pale blue precipitate. In this reaction, two hydroxide ligands ($OH^-$) replaced two water ligands.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}{}_{(aq)}} + 2OH^-{}_{(aq)} \longrightarrow \underset{\text{pale blue precipitate}}{[Cu(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(l)}$$

The hydroxide ions do not substitute water ligands directly. They act as a base and take protons from water molecules forming water and leaving hydroxide ions behind. The hydroxide ions thus made act as a ligands and exchange with water molecules.

**Do You Know?**
A solution of copper(II) sulphate in water is shown by formula $[Cu(H_2O)_6]^{2+}$ or $Cu^{2+}{}_{(aq)}$.

Adding excess of ammonia solution dissolves pale blue precipitate giving deep blue solution.

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

If we add aqueous ammonia, instead of aqueous sodium hydroxide, we get the same observation. In this reaction, ammonia acts as a base and removes protons from water, leaving behind hydroxide ions which substitutes water as ligand. This reaction is specifically called deprotonation reaction.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}{}_{(aq)}} + 2NH_{3(aq)} \longrightarrow \underset{\text{pale blue precipitate}}{[Cu(H_2O)_4(OH)_2]_{(s)}} + 2NH_4^+{}_{(aq)}$$

This is a ligand exchange reaction in which four ammonia molecules replaced two water ligands and two hydroxide ligands.

Similarly, the water ligands in hexaaquacopper(II) ion can also be exchanged for chloride ligands if we add concentrated hydrochloric acid dropwise. This reaction gives yellow solution tetrachlorocuprate(II).

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

The reaction is reversible and the m[illegible]e has green colour because it contains both blue and yellow solutions.

**ii. Cobalt Complexes**

If we add strong base, like sodium hydroxide (NaOH), to the pink aqueous solution of cobalt(II) chloride, we see blue precipitate of cobalt(II) hydroxide.

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}_{(aq)}} + 2OH^-_{(aq)} \longrightarrow \underset{\text{blue precipitate}}{[Co(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(l)}$$

Adding concentrate aqueous ammonia slowly can also exchange for water in aqua complex of cobalt(II) ion.

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}_{(aq)}} + 6NH_{3\,(aq)} \longrightarrow \underset{\text{brown solution}}{[Co(NH_3)_6]^{2+}_{(aq)}} + 6H_2O_{(l)}$$

Addition of concentrated hydrochloric acid to aqueous solution of cobalt(II) ions gives blue solution of tetrachlorocobaltate(II) complex.

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}_{(aq)}} + 4Cl^-_{(aq)} \longrightarrow \underset{\text{blue solution}}{[CoCl_4]^{2-}_{(aq)}} + 6H_2O_{(l)}$$

## 6.4.1 Stability of Complexes and Stability Constant ($K_{stab}$).

The equilibrium constant obtained from ligand exchange reactions in a solvent is called stability constant ($K_{stab}$). The stability of a complex is expressed in terms of equilibrium constant for ligand exchange reactions. The ligand exchange reactions are reversible so we can derive equilibrium constant expression for such a reaction. Deriving stability constant is similar to equilibrium constant ($K_c$) we studied in chemical equilibrium.

Consider the chemical reaction:

$$\underset{\text{pink solution}}{[Co(H_2O)_6]^{2+}_{(aq)}} + 4Cl^-_{(aq)} \rightleftharpoons \underset{\text{blue solution}}{[CoCl_4]^{2-}_{(aq)}} + 6H_2O_{(l)}$$

The position of equilibrium lies in the direction of more stable complex. The strong field ligand always substitutes the weak field ligand in the complex.

If we add water to this reaction mixture, reverse reaction takes place and pink colour of hexaaquacobalt(II) appears. Similarly, when we add concentrated hydrochloric acid to the system, forward reaction is favoured and blue colour of the tetrachlorocobaltate(II) is observed. In both these observation, the chloride and water ligands compete with one another for bond to cobalt(II) ion.

Applying equilibrium constant expression:

$$K_c = \frac{[[CoCl_4]^{2-}]\,[H_2O]^6}{[[Co(H_2O)_6]^{2+}]\,[Cl^-]^4}$$

Water is solvent so it is in large excess. It is treated as constant and not shown in stability constant.

$$K_{stab} = \frac{[CoCl_4]^{2-}}{[Co(H_2O)_6]^{2+}\,[Cl^-]^4}$$

Where $K_{stab}$ is called stability constant. The units of stability constant are calculated as those of equilibrium constant ($K_c$). The values of stability constants show how firmly a ligand is bonded to the central metal ion. Generally, the ligand atoms with lower electronegativity bond firmly with central metal ion than those with higher electronegativity values. This is why ammonia form strong bond with metal ion and has higher stability constant value while water binds weakly to the metal ion and has lower value of stability constant.

The stability constant values ($K_{stab}$) of some copper(II) complexes are given.

| | [illegible] |
|---|---|
| $[CuCl_4]^{2-}$ | 5.6 |
| $[Cu(NH_3)_6]^{2+}$ | 13.1 |
| $[Cu(EDTA)]^{2-}$ | 18.8 |

The values of stability constants are so large that they are shown on $\log_{10}$ scale so they have no units.

The data show that complexes with polydentate ligands have higher stability constant values than those with monodentate ligands.

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 3en \longrightarrow [Cu(en)_3]^{2+} + 6H_2O_{(l)}$$

The values of stability constants guide us which ligands can replace one another. For example, adding excess of ammonia to tetrachlorocuprate(II) complex gives dark blue solution of hexaamminecopper(II) complex because the stability constant value of ammonia complex is more than chloride complex and position of equilibrium shifts in the direction of more stable complex (right side).

$$[CuCl_4]^{2-}{}_{(aq)} + 6NH_{3(aq)} \longrightarrow [Cu(NH_3)_6]^{2+} + 4Cl^-{}_{(aq)}$$

**Worked Example 1:** We get a mixture of aqueous solutions tetrachlorocuprate(II) and hexaaquacopper(II) ion after adding concentrated hydrochloric acid to an aqueous solution of copper(II) sulphate.

i. Write expression for the stability constant for aqueous solution of tetrachlorocuprate(II).

ii. What are the units of stability constant?

**Concept Assessment Exercise 6.3**

- Arrange the following ligands in increasing order of stability constants in ligand substitution reactions of iron (II) complexes.
  $CN^-$, $OH^-$, $NH_3$, $H_2O$, $Br^-$
- Given the stability constant, why can ammonia exchange for water in copper(II) complex? Give reason.

## 6.5 Redox Reactions

The transition elements can exist in various oxidation states. In redox reactions, the oxidation states of transition elements are changed when they undergo chemical reaction under suitable conditions. In redox reactions, transfer of electrons takes place from one atom to the other. The decrease in oxidation state is reduction (gain of electron/s) while increase in oxidation state is called oxidation (loss of electron/s).

Oxidizing agent is the species which accepts electron/s and undergoing reduction while reducing agent undergoes oxidation by losing electron/s. Here we will discuss three redox reactions with their feasibility supported by their standard electrode potential data.

### i. Reaction of Acidified Manganate(VII) ions with Ethanedioate ions

The reaction between ethanedioate ions and acidified manganate(VII) ion is analysed to find which way it will take place. The standard electrode potentials of individual reactions are taken into consideration to check feasibility of overall reaction. Both reactions are taken in reduction mode according to IUPAC recommendations and then we compare their standard reduction potentials.

$$2CO_{2(g)} + 2e^- \longrightarrow C_2O_4^{2-}{}_{(aq)} \qquad E^{\circ} = +0.49V$$

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +1.52V$$

Now the question arises whether manganate(VII) oxidizes ethanedioate to carbon dioxide or carbon dioxide oxidizes manganese(II) ion to manganate(VII)? Which one should be oxidizing agent and which one reducing agent?

This problem can be resolved by comparing the standard reduction potentials of the two reactions. The reaction with higher positive value of standard reduction potential is more likely to occur and proceed to the right and vice versa.

The given reduction potential values indicate that manganate(VII) ion must reduce to manganese(II) ion and should act oxidizing agent while oxalate should oxidize to carbon dioxide and act as reducing agent.

For writing the overall chemical equation, the reaction with lower standard electrode potential must be reversed and be taken in oxidation mode because it is oxidation reaction. The sign of its standard electrode potential is reversed while its magnitude remains the same.

The standard reduction potential values of reactions do not change with changing the co-efficients.

$$C_2O_4^{2-}{}_{(aq)} \longrightarrow 2CO_{2(g)} + 2e^- \qquad E = -0.49V$$

Before combining the two half reactions, the number of electrons lost must equals the number of electrons gained. This can be done by multiplying the two half equations with different multipliers (coefficients). In this case, oxidation half equation is multiplied by 2 and reduction half equation by 5.

$$2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 10e^- \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} \qquad E = +1.52V$$

$$5C_2O_4^{2-}{}_{(aq)} \longrightarrow 10CO_{2(g)} + 10e^- \qquad E = -0.49V$$

$$2MnO_4^-{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} + 16H^+{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 10CO_{2(g)} + 8H_2O_{(l)} \qquad E = +1.03V$$

This large positive value of standard electrode potential (+1.03V) supports the forward reaction to occur so this redox reaction is feasible. Remember that the negative value of standard electrode potential means that the reaction will not take place.

### ii. Reaction of Manganate(VII) ion with Iron(II) ion

In this redox reaction we consider two half equations, one is reduction of maganate (VII) whereas the other is reduction of iron (III).

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +1.52V$$

$$Fe^{3+}{}_{(aq)} + e^- \longrightarrow Fe^{2+}{}_{(aq)} \qquad E = +0.77V$$

To write the net redox reaction, we need to reverse the second reaction, treat it as an oxidation reaction by reversing it, and change the sign of its standard reduction potential to negative.

$$Fe^{2+}{}_{(aq)} \longrightarrow Fe^{3+}{}_{(aq)} + e^- \qquad E = -0.77V$$

Combine and balance the two equations and sum up their standard electrode potentials so that we can check the feasibility of overall equation.

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +1.52V$$

$$5Fe^{2+}{}_{(aq)} \longrightarrow 5Fe^{3+}{}_{(aq)} + 5e^- \qquad E = -0.77V$$

$$MnO_4^-{}_{(aq)} + 5Fe^{2+}{}_{(aq)} + 8H^+{}_{(aq)} \longrightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +0.75V$$

The positive value of the standard electrode potential indicates that this reaction will proceed to the right, making this reaction feasible.

### iii. Reaction Between Copper(II) ion and Iodide ion

Take an aqueous solution of copper(II) sulphate in a flask and add an excess of potassium iodide to it. The following reaction takes place.

$$2Cu^{2+}{}_{(aq)} + 4I^-{}_{(aq)} \longrightarrow \underset{\text{white ppt}}{2CuI_{(s)}} + \underset{\text{red-brown solution}}{I_{2(aq)}}$$

Split the redox reaction in two half-equations.

$$\frac{1}{2}\ I_{2(aq)} + e^- \longrightarrow I^-_{(aq)} \qquad E^\ominus = +0.54V$$

$$Cu^{2+}_{(aq)} + 1e^- \longrightarrow Cu^+_{(aq)} \qquad E^\ominus = +0.15V$$

The higher standard reduction potential value of $I_2/I^-$ couple indicates that this reaction is more likely to occur.

On the contrary, the lower standard reduction potential of $Cu^{2+}/Cu^{1+}$ reaction indicates that this reaction is less inclined to proceed in the forward direction, making copper (I) a better reducing agent. However, this reaction proceeds in the forward direction because of continuous precipitation of copper (I) iodide in the reaction, although the overall standard potential value is negative as shown.

$$\begin{array}{lcll} 2I^-_{(aq)} & \longrightarrow & I_{2(aq)} + 2e^- & E^\circ = -0.54V \\ 2Cu^{2+}_{(aq)} + 2e^- & \longrightarrow & 2Cu^+_{(aq)} & E^\circ = +0.15V \\ \hline 2Cu^{2+}_{(aq)} + 2I^-_{(aq)} & \longrightarrow & 2Cu^+_{(aq)} + I_{2(aq)} & E^\circ = -0.39V \end{array}$$

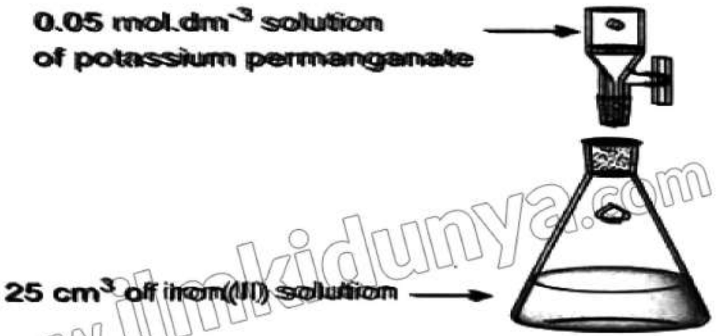
The amount of aqueous solution of iodine formed in this reaction can be determined by titrating it with sodium thiosulphate solution.

### Practical Activity 6.1: Redox titration

The above reaction can be used practically to calculate the amount of iron ($Fe^{2+}$ ions) in a sample, such as an iron tablet, by carrying out a titration. As this is redox reaction so the titration involved is called redox titration.

We take a known volume (e.g. 25 $cm^3$) of an unknown concentration of $Fe^{2+}(aq)$ is placed in a conical flask. A solution of a known concentration (0.05 $mol.dm^3$) of potassium manganate(VII) solution is put in a burette.

The potassium manganate(VII) solution is titrated against the solution containing $Fe^{2+}(aq)$ in the conical flask. During the reaction of $MnO_4^-$ (aq) with $Fe^{2+}(aq)$ in the flask, the purple colour of the manganate(VII) ions is diappears. The end-point is reached when the $Fe^{2+}(aq)$ ions have all reacted and the first permanent purple colour appears in the conical flask. This is when the $MnO_4^-$ (aq) ions become in excess in the reaction mixture



### Worked Example 6.1

**An excess of potassium iodide solution was added to a 30.00 cm³ of copper(II) sulphate solution in a flask. The solution was then titrated against 0.05 mol dm⁻³ sodium thiosulphate solution, *using starch solution* as indicator. The volume of sodium thiosulphate solution added from the burette was 10 cm³ when the endpoint reached. Calculate the concentration of the copper(II) sulphate solution.**

### Solution

Volume of copper(II) sulphate solution = 30 cm³ = 30/1000 = 0.03 dm³
Volume of sodium thiosulphate solution = 10 cm³ = 10/1000 = 0.01 dm³
Concentration of sodium thiosulphate solution = 0.05 mol.dm⁻³
Concentration of copper(II) sulphate solution = ?
For solving concentration related problems of solutions, we use the following formulae.

$$\text{concentration} = \frac{\text{moles}}{\text{volume (dm}^3\text{)}}$$

$$\text{moles} = \text{concentration} \times \text{volume (dm}^3\text{)}$$

The following two chemical equations are involved in this titration.

$$2Cu^{2+}{}_{(aq)} + 4I^-{}_{(aq)} \longrightarrow 2CuI_{(s)} + I_{2(aq)}$$

$$I_{2(aq)} + 2S_2O_3{}^{2-}{}_{(aq)} \longrightarrow 2I^-{}_{(aq)} + S_4O_6{}^{2-}{}_{(aq)}$$

First, we calculate the number of moles of thiosulphate ions used in the reaction.

$$\text{concentration} = \frac{\text{moles}}{\text{volume (dm}^3\text{)}}$$

$$\text{moles} = \text{concentration} \times \text{volume (dm}^3\text{)}$$

$$\text{moles} = 10/1000 \times 0.05 = 0.0005 \text{ mol thiosulfate ions}$$

From the above two chemical equations, we can deduce that the number of moles of copper(II) ions in the flask is equal to the number of moles of thiosulphate ions in the titre used.

Concentration of copper(II) ions = 0.0005/0.030 = 0.016 mol.dm⁻³

## 6.6 Stereoisomerism in Coordination Compounds

We have already discussed isomerism in organic compounds in the previous class. In this topic we shall focus on isomerism exhibited by coordination compounds.

Stereoisomerism stems from different arrangements of atoms/ligands of complexes in the space. Stereoisomers are divided into two types, geometric isomers and optical isomers.

### i. Geometric isomerism

Geometric isomerism is shown by those complexes that have ligands arranged differently in space relative to the central metal ion. Such isomers are also called cis-trans isomers or diastereomers. Take the example of diamminedichloroplatinum(II), $[Pt(NH_3)_2Cl_2]$, which is square planar complex.

**Do You Know?**
Tetrahedral complexes cannot show geometric isomerism because all four ligands are adjacent to each other.

The isomer having identical ligands next to each other is called cis-isomer while the one with identical ligands opposite to each other is called trans-isomer. Remember that their biological behaviours are remarkably different from one another.

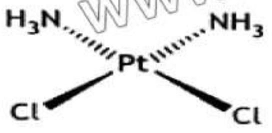
### Fighting Cancer

In 1965, Barnett Rosenberg was the first who found that cis-platin had inhibiting cell division property and could be used as anticancer drug. On the other hand, trans-platin had no such medicinal properties.

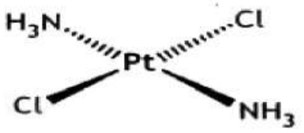
Cancer is mostly caused by abnormal DNA replication where the double helix 'unwinds' to form the template for a new strand. When replication process follows the wrong way, it either causes mutation or can grow with uncontrollable speed, resulting in cancerous tumors.

The cancer patient is administered cis-platin in solution which passes through the cell membranes into the nucleus of the cancerous cells. The cis-platin complex forms a bridge within a DNA strand of the nucleus where the donor atoms of the strands replace chloride ligands and bind themselves strongly to the platin atoms. This new platin complex disrupts the replication process of DNA and consequently the cancerous cells die. In the case of fast-growing tumor cells, the cis-platin complex shrinks the cancerous cells, leading to remission of cancer.

However, cis-platin discontinues DNA replication in both cancerous and healthy fast-growing cells, like white blood cells, leading to side effects (increased infection, hair loss and kidney damage). Despite this, it remains effective in treating many types of cancers.



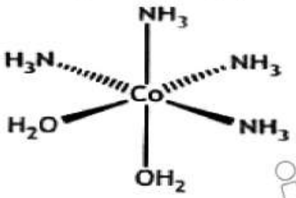
cis-diaaminedichloroplatinum(II)



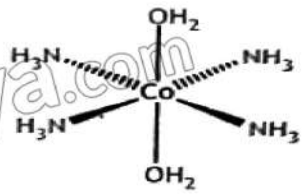
trans-diaaminedichloroplatinum(II)

In cis-complex, the two chloride ligands and two ammonia ligands are next to each other whereas in trans-complex, the two chloride and two ammonia ligands are opposite to one another. These isomers of platinum have different biological behaviours.

Similarly, octahedral complexes can also show geometric isomerism. For example tetraamminediaquacobalt(II) complex has both cis and trans isomers as shown.



cis-tetraamminediaquacobalt(III)

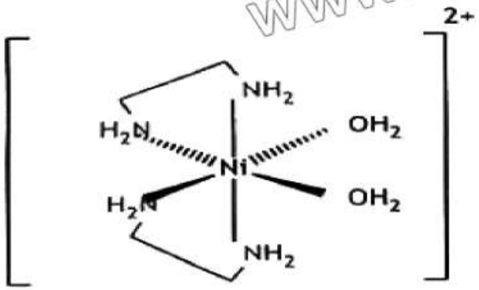


trans-tetraamminediaquacobalt(III)

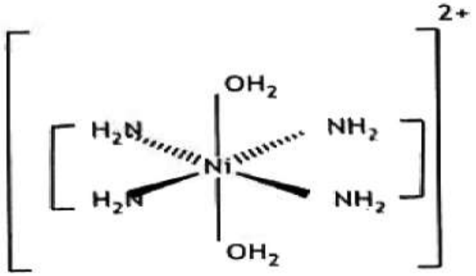
The cis-isomer of this complex has water ligands next to each other while its trans-isomer has water ligands lying on opposite side. To make cis-isomers of octahedral complexes with monodentate ligands, look the following three-dimensional diagrams.

On the other hand, trans-isomers are shown below.

Similarly, bis(1,2-diaminoethane)diaquanickel(II) ion shows geometric isomerism.



cis-bis(1,2-diaminoethane)di-aquanickel(II) ion



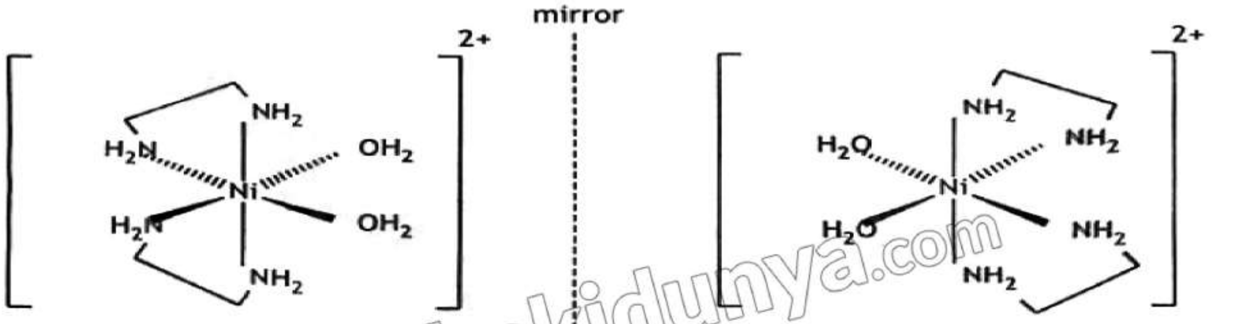
trans-bis(1,2-diaminoethane)di-aquanickel(II) ion

We have already discussed that geometric isomers show different properties because of their different symmetry and polarity. The cis-isomers are polar as they have imbalance of electron cloud and lack of symmetry. The end where water is the ligand is partial negative while the other end where ammonia is bonded gets partial positive charge, The reason is that oxygen of water has higher electronegativity than nitrogen of ammonia causing electron flow towards water. The two individual dipoles created by two water ligands result into net dipole making the complex polar.

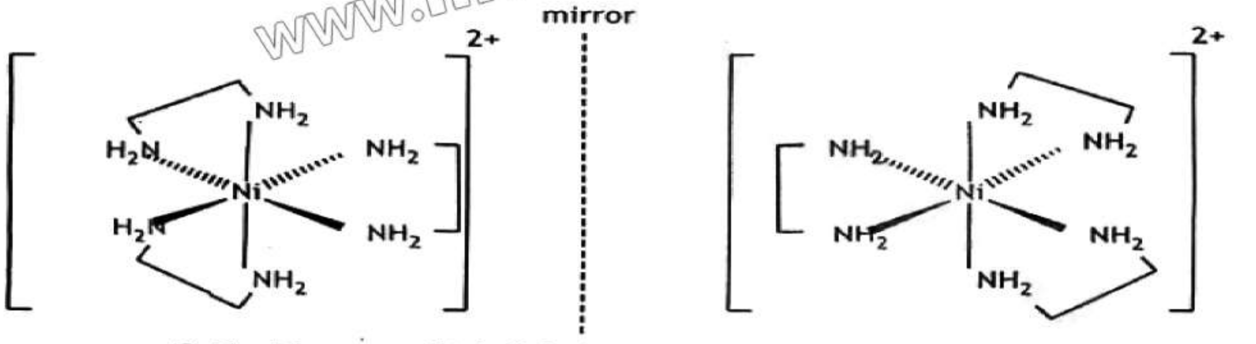
Conversely, the trans-isomers have symmetric shapes and even distribution of electron cloud making them non-polar. This is because the individual dipoles created by two water ligands work against each other cancelling the overall dipole of the complex.

### ii. Optical Isomerism

Optical isomers are molecules that have non-superimposable mirror images. They are also called enantiomers. They have identical physical properties except for their ability to rotate the plane of polarized light, either clockwise or counterclockwise. Optical isomerism is exhibited by octahedral complexes. In the case of octahedral complexes with two monodentate ligands and two bidentate ligands, only the cis-isomer can show optical isomerism.



Optical isomers of cis-bis(1,2-diaminoethane)diaquanickel(II) ion



Optical isomers of tris(1,2-diaminoethane)nickel(II) ion

Similarly, octahedral complexes of three bidentate ligands can exhibit optical isomerism. They are mirror images but not superimposable on one another.

# KEY POINTS

- Transition metals are those elements that have incomplete d sub-shell.
- The elements of the 3d block have high melting points, boiling points and densities.
- The first and second ionisation energies increase only slightly across the block from scandium to zinc, as 4s electrons are being removed which are shielded from the nuclear attraction by the inner 3d electrons.
- A ligand is a molecule or ion with one or more lone pairs of electrons available to donate to a transition metal ion.
- Transition elements form complexes by combining with ligands. Ligands bond to transition metal ions by one or more dative (co-ordinate) bonds.
- Most transition elements form $M^{2+}$ ions by loss of the 4s electrons.
- The elements vanadium, chromium and manganese have a maximum oxidation number equal to the sum of the numbers of 3d and 4s electrons.
- Transition metal ions accept electrons from ligands so metal ions act as Lewis acid while ligands as Lewis bases.
- The colours of complexes are due to d-d electronic transitions. The type of colour depends upon the nature of ligand.
- The colour of complex observed depend on the colour absorbed.
- The complexes of d block elements which have complete or empty d sub-shell are colourless.
- Transition elements can exist in several oxidation states because of the involvement of both 4s and 3d orbitals.
- Ligand exchange reactions involve exchange of ligands in a complex resulting in change in colours of complexes.
- A strong ligand can displace a weak ligand
- Ligand exchange can be described in terms of competing equilibria.
- The stability constant, Kstab, of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules.
- The higher the value of the stability constant, the more stable is the complex ion formed.
- The splitting pattern is different in octahedral and tetrahedral complexes. Different ligands will split the d orbitals by different amounts of ΔE, resulting in differently coloured complexes.

## References for Further Information

- Chemistry by Brain Ratcliff, Helen Eccles, John Raffan, John Nicholson, David Johnson and John Newman.
- Chemistry by George Facer
- Chemistry-The molecular nature of matter and change by Silberberg.
- Chemistry by Peter Cann and Peter Hughes.
- Chemistry by Blackman, Bottle, Schmid, Mocerino and Wille.
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- Chemistry by Christopher Talbot, Richard Harwood and Christopher Coates.

## EXERCISE

### 1. Multiple Choice Questions (MCQs)

i. Which one of the following species has $d^{10}$ sub-shell?

a) $Cu^{2+}$ b) $zn^{2+}$ c) Mn d) Cr

ii. Which one is correct statement about zinc element?

1. It has complete 3d sub-shell
2. It is transition metal
3. It forms colourless complexes
4. It can exist in one stable oxidation state

a) 1and 2 only b) 1,3 and 4 only

c) 1 and 4 only d) all are correct

iii. The electronic configuration of iron cation in the complex, $[Fe(CN)_6]^{3-}$, is

a) $[Ar]3d^6$ b) $[Ar]3d^5$

b) $[Ar]3d^6 4s^1$ d) $[Ar]3d^6 4s^2$

iv. Why is the hexaaquacopper(II) ion blue in colour?

a) The d-d electronic transition absorbs blue wavelength of visible spectrum

b) The d-d electronic transition absorbs all wavelengths except blue

c) The d-d electronic transition transmits all wavelengths of white light except blue

d) The d-d electronic transition absorbs red wavelength and transmit the remaining light

v. The cyanide ligand ($CN^-$) can form two complexes with iron with formulae, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. What is the oxidation state of iron in them ?

a) +2 and +3 respectively b) +4 and -2 respectively

c) +2 and +4 respectively d) +3 and +2 respectively

vi. Transition metals are different from alkali metals and alkaline earth metals in many ways. Which one is incorrect statement about transition metal when compared with group 1 and group 2 metals?

a) they form coloured compounds b) they show variable oxidation states

c) they have high melting points d) they are more reactive

vii. The species that can act as ligand in transition metal complex is

a) $CH_4$ b) $C_6H_6$ c) Na d) $C_6H_4(OH)_2$

viii. Transition metals can show different oxidation states. Which one is the most common oxidation state in first row transition elements?

a) +2 b) +3 c) +4 d) +7

ix. Which one of the following properties of transition metals is held responsible for their catalytic behaviour?

a) they form coloured complexes b) they show variable oxidation states

c) they have high melting points d) they have high density

x. The coordination number of nickel in the complex $[Ni(en)_2(OH_2)_2]^{2+}$ is

a) 2 b) 4 c) 6 d) 8

xi. Which one of the following complexes cannot show stereoisomerism?

1. $[Cu(H_2O)_6]^{2+}$ 2. $[CuCl_4]^{2-}$ 3. $[Cu(NH_3)_4(OH_2)_2]^{2}$ 4. $[Ni(en)_3]^{2+}$

a) 1,2 and 3 only b) 1,3 and 4 only
c) 1 and 2 only d) 1 and 4 only

xii. The weakest field ligand among the following is

a) $H_2O$ b) $CN^-$ c) $NH_3$ d) $OH^-$

xiii. The highest oxidation state shown by first row transition metals is shown by

a) copper b) manganese c) nickel d) cobalt

## 2. Short Answer Questions

i. The melting point of titanium is higher than calcium in the same period. Justify this statement?

ii. The first-row elements of d-block exist in more than one oxidation states. However, zinc shows only +2 oxidation state in its complexes. Why?

iii. Define the terms

a. ligand b. coordination number c. complex ion

iv. Explain why hydrated $Ti^{4+}$ complexes are colourless and hydrated $Ti^{3+}$ complexes are coloured?

v. Why do the melting points of first row transition metals increase upto the middle and then decrease? Comment

vi. Why are transition metals used as catalysts in industries for performing different reactions? Give one example.

vii. The blue cobalt chloride paper is used to test the presence of water. If water is present, the paper turns pink. This is because six water ligands exchange for four chloride ligands present in cobalt chloride, $[CoCl_4]^{2-}$. Write the equation to show the ligand substitution reaction when the test is positive.

viii. Octahedral complexes of copper(II) ion have different colours. Explain why?

## 3. Long Answer Questions

i. The reduction potential for $Cr^{2+}$ ions being reduced to chromium metal is -0.91V and that for $Cr^{3+}$ ions being reduced to $Cr^{2+}$ ions in -0.41V as shown:

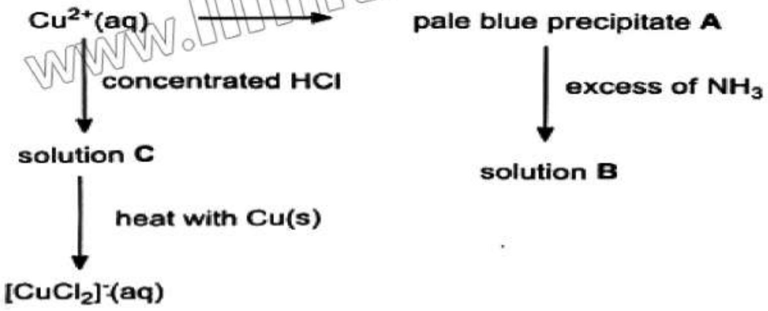
$$Cr^{2+} + e^- \rightleftharpoons Cr \quad E^\circ = -0.91V$$

$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \quad E^\circ = -0.41V$$

Predict whether the chromium(II) ion will disproportionate to chromium(III) ion and chromium metal. If yes, then write the possible ionic equation.

ii. Explain the difference in the splitting pattern of the 3d atomic orbitals in the two copper(II) complexes, $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$.

iii. The following scheme shows some reactions of copper(II) ion.



a. Suggest the formulae of A, B and C.
b. State the colours of solutions B and C.
c. Name the type of reactions occurring when C is heated with copper. Also state the role of copper in this reaction.
d. When the solution of complex $[CuCl_2]^-$ is poured into water, which colour precipitate is formed? Justify its colour.

iv. Transition metal complexes such as $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and $Pt(NH_3)_2Cl_2$ show same type of stereoisomerism.
a. Name the type of isomerism.
b. Draw three-dimensional structures for the given two isomers, two for each.

v. Aqueous copper(II) ion can form complexes with the ligands, ammonia and 1,2-diaminonethane as shown.

$$[Cu(H_2O)_6]_2^{+}{}_{(aq)} + en_{(aq)} \rightleftharpoons [Cu(H_2O)_4(en)]^{2+}{}_{(aq)} + 2H_2O_{(l)} \quad K_{stab} = 3.98\times10^{10}$$

$$[Cu(H_2O)_6]_2^{+}{}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2+}{}_{(aq)} + 2H_2O_{(l)} \quad K_{stab} = 5.01\times10^{7}$$

a. Write an expression for the stability constant for both equations and state their units.
b. Of the three complexes in the above two equations, state the formula of the complex that is the most stable. Give a reason also.

## PROJECT

Students can research the environmental challenges associated with transition metal extraction and usage. They can create awareness campaigns or projects proposing sustainable practices.