You have come across compounds like Na[Ag(CN)₂] and Na₂[Zn(CN)₄], Such compounds are referred to as coordination compounds or complex compounds. Coordination compounds play an important role in the chemical industry and in life itself. For example, the Ziegler-Natta catalyst which is used for polymerization of ethylene, is a complex containing the metals aluminum and titanium. Metal complexes play important role in biological systems. For example, chlorophyll, which is vital for photosynthesis in plants, is a magnesium complex and hemoglobin, which carries oxygen to animal cells, is an iron complex. These are the compounds that contain a central atom or ion, usually a metal, surrounded by a number of ions or molecules. The complexes tend to retain their identity even in solution, although partial dissociation may occur. Complex ion may be cationic, anionic or nonionic, depending on the sum of the charges of the central atom and the surrounding ions and molecules.

In this lesson you will study about the complexes including their nomenclature and nature of bonding in them.

**Objectives**

After reading this lesson, the learner will be able to,

- state the postulates of Werner’s theory;
- define ligands, coordination number and coordination sphere;
- name simple complexes by IUPAC system;
- explain valance bond theory;
- apply VB theory to explain hybridization, shape and magnetic behavior of the following complexes [Fe(CN)₆]⁴⁻, [Fe(CN)₆]³⁻, [Cr(NH₃)₆]³⁺, [NiCl₂]²⁻, [Ni(CO)₄] and [Ni(CN)₄]²⁻ and
- explain the applications of coordination compounds in extraction of metals, medicine and qualitative analysis.
Coordination compounds were known in eighteenth century. It was a mystery for the chemist, of those days to understand as to why a stable salt like $\text{CoCl}_3$ reacts with varying number of stable molecules or compounds such as ammonia to give several new compounds: $\text{CoCl}_3\cdot 6\text{NH}_3$, $\text{CoCl}_3\cdot 5\text{NH}_3$ and $\text{CoCl}_3\cdot 4\text{NH}_3$; and what are their structures? These compounds differed from each other in their chloride ion reactivity. Conductivity measurements on solutions of these compounds showed that the number of ions present in solution for each compound are different. Several theories were proposed, but none could satisfactorily explain all the observable properties of these compounds and similar other series of compounds which had been prepared by then. It was only in 1893 that Werner put forward a set of ideas which are known as Werner’s coordination theory, to explain the nature of bonding in complexes. His theory has been a guiding principle in inorganic chemistry and in the concept of valence. The important postulates of Werner’s theory are:

1. Metals exhibit two types of valence:
   (a) Primary valence (ionizable)
   (b) Secondary valence (non-ionizable).

Primary or ionizable valence is satisfied by negative ions and corresponds to oxidation state of the metal. The secondary or non-ionizable valence, which is satisfied by negative, positive or neutral groups, is equal to the coordination number of metal ion.

Every metal tends to satisfy both its primary and secondary valence.

2. The secondary valence is directed toward fixed positions in space i.e. this has spatial arrangement corresponding to different coordination number.

For the complexes $\text{CoCl}_3\cdot 6\text{NH}_3$, $\text{CoCl}_3\cdot 5\text{NH}_3$ and $\text{CoCl}_3\cdot 4\text{NH}_3$, the number of ionizable ions in these complexes are three, two and one, respectively. It has been proved by precipitation reactions and conductivity measurements. On the basis of Werner’s postulate these compounds are formulated as:

$[\text{Co(NH}_3\text{)}_6]\text{Cl}_3$, $[\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2$ and $[\text{Co(NH}_3\text{)}_4\text{Cl}_2]\text{Cl}_2$, respectively, the species inside the square brackets being the complex ion and outside the square brackets the ionisable ions.

On the basis of Werner’s theory the structure of $[\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2$ is:
One of the three chloride ions satisfy both primary and secondary valence.

He also postulated that octahedral, tetrahedral and square planar shapes are more common for coordination compounds of transition elements. Six coordinated complexes such as \([\text{Ni(NH}_3\text{)}_6]^{2+}\) and \([\text{Co(NH}_3\text{)}_6]^{3+}\) are octahedral whereas four coordinated such as \([\text{NiCl}_4]^{2-}\) and \([\text{Ni(CN)}_4]^{2-}\) are tetrahedral and square planar, respectively.

### Intext Questions 24.1

1. Explain primary valence.
   
2. Explain secondary valence.
   
3. What is the number of the secondary valence in the following: \([\text{Cr(H}_2\text{O)}_6] \text{Cl}_3\) and \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\)?
   
4. What is shape associated with a six-coordinated complex?

5. How many types of shapes are possible for four-coordinate complexes?

### 24.2 Definition of Some Important Terms

There are certain terms, which are normally used in dealing with coordination compounds. Some of these important terms are defined below:

**Ligand:** the molecules or ions that are attached to the metal in a complex ion are called ligands. The interaction between a metal atom and the ligands can be thought of as Lewis acid-base reaction. As you know a Lewis base is a substance capable of donating one or more electron pairs, every ligand has at least one unshared pair of valence electron. Few examples are shown below:

\[
\text{H} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{N} \quad \text{H} \quad \text{[Cl]^-}
\]

The atom in the ligand that is bound directly to the metal atom is known as the donor atom. For example, nitrogen is the donor atom and Cu\(^{2+}\) is the acceptor atom in the \([\text{Cu(NH}_3\text{)}_4]^{3+}\) complex ion.

Depending on the number of the donor atoms present, ligands are defined as monodentate, bidentate or polydentate. \(\text{H}_2\text{O}\) and \(\text{NH}_3\) are monodentate ligands with only one donor atom in each. Ethylenediamine (en) is a bidentate ligand.
The two nitrogen atoms can coordinate with a metal atom. Bidentate and polydentate ligands are also called chelating agents because of their ability to hold the metal atom like a claw (from the Greek Chele, meaning “claw”) one example is ethylenediaminetetraacetate ion (EDTA), a polydentate (hexadentate) ligand.

Coordination number: The coordination number in coordination compounds is defined as the number of ligand (donor) atoms/ions surrounding the central metal atom in a complex ion. For example, the coordination number of cobalt in \([\text{Co(NH}_3\text{)}_6]^3+\) is six. Similarly the coordination number of \(\text{Ag}^+\) in \([\text{Ag(NH}_3\text{)}_2]^+\) is 2, that of \(\text{Cu}^{2+}\) in \([\text{Cu(NH}_3\text{)}_4]^{2+}\) is 4, and that of \(\text{Fe}^{3+}\) in \([\text{Fe(CN)}_6]^{3-}\) is 6.

Coordination sphere: The central metal atom and the ligands which are directly attached to it are enclosed in a square bracket and are collectively termed as coordination sphere. The ligands and the metal atom inside the square brackets behave as single constituent unit.

Oxidation number: Another important property of coordination compounds is the oxidation number of the central metal atom. The net charge on a complex ion is the sum of the charges on the central atom and its surrounding ligands. In the \([\text{PtCl}_6]^{2-}\) ion for example, each chloride ion has an oxidation number of \(-1\), so the oxidation number of Pt must be +4. If the ligands do not bear net charges the oxidation number of the metal is equal to the charge of the complex ion. Thus in \([\text{Cu(NH}_3\text{)}_4]^{2+}\) each \(\text{NH}_3\) is neutral, so the oxidation number of copper is +2.
1. What is the coordination number of the metal ion in the following?
   (i) \([\text{Co(NH}_3\text{)}_5\text{Cl}]^+\)
   (ii) \([\text{Cr(en)}_2\text{Cl}_2]^+\)
   (iii) \([\text{NiCl}_4]^2-\)

2. What is the oxidation state of the metal ion in the following?
   (i) \([\text{MnCl}_6]^{4-}\)
   (ii) \([\text{Fe(CN)}_6]^{3-}\)
   (iii) \([\text{Cr(NH}_3\text{)}_6]^{3+}\)
   (iv) \([\text{Ni(en)}_3]^{2+}\)

3. Give an example of a chelate ligand.

4. Give one example of each monodentate, bidentate and polydentate ligand.

5. What is the oxidation and coordination number of Co in this \([\text{Co(en)}_2(\text{H}_2\text{O})\text{CN}]^{2+}\) complex ion? Which ligand is bidentate in the above complex?

24.3 Rules of Nomenclature of Coordination Compounds

We have already discussed about the ligands and oxidation number of metal, our next step is, to learn how to name these coordination compounds. The rules for naming coordination compounds as recommended by IUPAC are as follows:

1. The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in \(\text{K}_3[\text{Fe(CN)}_6]\) and \([\text{Co(NH}_3\text{)}_4\text{Cl}_2]\)Cl compound, we name the \(\text{K}^+\) and \([\text{Co(NH}_3\text{)}_4\text{Cl}_2]\)^+ first, respectively.

2. Within a complex ligands are named first, in alphabetical order, and the metal ion is named last.

3. The name of anionic ligand ends with the letter ‘O’, whereas a neutral ligand is usually called by the name of the molecule. The exceptions are \(\text{H}_2\text{O}\) (aqua), \(\text{CO}\) (carbonyl) and \(\text{NH}_3\) (ammine). The table given below lists some common ligands:
Table 24.1: Some Common Ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Name of the ligand in coordination compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride (F⁻)</td>
<td>Fluro</td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>Chloro</td>
</tr>
<tr>
<td>Bromide (Br⁻)</td>
<td>Bromo</td>
</tr>
<tr>
<td>Hydroxide (OH⁻)</td>
<td>Hydroxo</td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻)</td>
<td>Sulphato</td>
</tr>
<tr>
<td>Oxide (O²⁻)</td>
<td>Oxo</td>
</tr>
<tr>
<td>Carbonate (CO₃²⁻)</td>
<td>Carbonato</td>
</tr>
<tr>
<td>Oxalate (C₂O₄²⁻)</td>
<td>Oxalato</td>
</tr>
<tr>
<td>Thiocyanate (SCN⁻)</td>
<td>Thiocyanato</td>
</tr>
<tr>
<td>Cyanide (CN⁻)</td>
<td>Cyano</td>
</tr>
<tr>
<td>Isothiocyanate (NCS⁻)</td>
<td>Isothiocyanato</td>
</tr>
<tr>
<td>Ethylenediamine (NH₂CH₂CH₂NH₂)</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>Ammine</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>Aqua</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetato</td>
</tr>
</tbody>
</table>

4. When several ligands of a particular kind are present, we use the Greek prefix di, tri-, tetra etc to name them. Thus the ligands in cation [Co(NH₃)₄Cl₂]⁺ are named as “tetraammine dichloro” (note that prefixes are ignored when alphabetizing ligands). If the ligand itself contains a Greek prefix, we use the prefixes bis, tris and tetrakis etc to indicate the number of ligands present. For example, the ligand ethylenediamine already contains di, therefore, if two such ligands are present the name is bis(ethylenediamine).

5. The oxidation number of the metal is written in roman numerals following the name of the metal. For example, the roman numeral III is used to indicate the +3 oxidation state of chromium in [Cr(NH₃)₄Cl₂]⁺, which is named as tetraamminedichlorochromium (III) ion.

6. If the complex is an anion, its name ends in –ate. For example, in K₄[Fe(CN)₆] the anion [Fe(CN)₆]⁴⁻ is called hexacyanoferrate(II) ion. Note that the numeral (II) indicate the oxidation state of iron. Table given below gives the name of anions containing metal atoms.

7. If the complex is either a cation or is neutral, no change is required in the name of the central metal ion. For example [Co(NH₃)₆]³⁺ and [Ni(CO)₄] are named as hexaamminecobalt(III) ion and tetracarbonyl nickel(0), respectively.

Table 2.4: Some anions containing metal atoms

<table>
<thead>
<tr>
<th>Metal</th>
<th>Name of metal in anionic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Cuperate</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zincate</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Aluminate</td>
</tr>
<tr>
<td>Chromium</td>
<td>Chromate</td>
</tr>
<tr>
<td>Tin</td>
<td>Stannate</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Cobaltate</td>
</tr>
<tr>
<td>Nickel</td>
<td>Nickelate</td>
</tr>
<tr>
<td>Gold</td>
<td>Aurate</td>
</tr>
<tr>
<td>Silver</td>
<td>Argentate</td>
</tr>
<tr>
<td>Lead</td>
<td>Plumbate</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Rhodate</td>
</tr>
<tr>
<td>Iron</td>
<td>Ferrate</td>
</tr>
<tr>
<td>Manganese</td>
<td>Manganate</td>
</tr>
</tbody>
</table>
A. Few examples are given below:

[Co(H₂O)₆]Cl₃  hexaaquacobalt(III) chloride
K₂[PtCl₆]  potassium hexachloroplatinate(IV)
[Pt(NH₃)₂Cl₄]  diamminetetrachloroplatinum(IV)
[Co(en)₂Cl₂]Cl  dichlorobis(ethylenediamine)cobalt(III) chloride.

**Intext Questions 24.3**

1. Write down the name of the following complexes:
   (a) [Co(NH₃)₄Cl₂]⁺
   (b) (NH₄)₃[Cr(NCS)₆]
   (c) Ni(CO)₄
   (d) K₄[Fe(CN)₆]
   (e) [Cr(en)₃]Cl₃

2. Write down the formula of the following:
   (a) Tetrachloronickelate(II)
   (b) Pentaamminenitrocobalt(III) ion
   (c) Potassium hexacyanoferrate(III)
   (d) Dichlorobis(ethylenediammine) chromium(III) ion

**24.4 Valence Bond Theory**

Linus Pauling of the California Institute of Technology developed the valence bond theory. He was awarded the Nobel prize in chemistry in 1954. Pauling’s ideas have had an important impact on all areas of chemistry. He applied valence bond theory to coordination compounds. This theory can account reasonably well for the structure and magnetic properties of metal complexes.

The basic principles, which are involved in the valence bond treatment of coordination compounds are:

(a) Hybridization of valance orbitals of the central metal/ ion
(b) Bonding between ligand and the metal ion/atom.
(c) Relation between the type of bond and the observed magnetic behaviour.

**Six Coordinate Complexes**

Let us explain by taking simple examples such as [CoF₆]³⁻ and [Co(NH₃)₆]³⁺. Although in
Both the complexes, the oxidation state of cobalt is +3, but \([\text{CoF}_6]^3-\) is paramagnetic and \([\text{Co(NH}_3)_6]^{3+}\) is diamagnetic, why? The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken e.g. \(\text{Co}^{3+}\). Cobalt atom has the outer electronic configuration \(3d^7 4s^2\). Thus \(\text{Co}^{3+}\) ion will have the configuration \(3d^6\) and the electrons will be arranged as:

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\end{array}
\]

\(\text{Co}^{3+}\) ion forms both paramagnetic (outer orbital) and diamagnetic (inner orbital) complexes depending upon the nature of ligands as illustrated below.

As \(\text{Co}^{3+}\) ion combines with six fluoride ligands in \([\text{CoF}_6]^3-\), empty atomic orbitals are required on the metal ion to receive the coordinated lone pair of electrons. The orbitals used are one \(4s\), three \(4p\) and two \(4d\). These are hybridized to give a set of six equivalent \(sp^3d^2\) hybrid orbitals. A ligand orbital containing a lone pair of electron forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a \(\sigma\) bond is formed with each ligand. The \(d\)-orbitals used are the \(4d_{x^2-y^2}\) and \(4d_{z^2}\). It is shown below:

\[
\begin{array}{cccc}
3d & 4s & 4p & 4d \\
\uparrow & \uparrow & \uparrow & \uparrow \\
F & F & F & F \\
\end{array}
\]

\(sp^3d^2\), outer orbital complex

Since the outer \(4d\) orbitals are used for bonding, this is called an outer orbital complex. The energy of these orbitals is quite high, so the complex will be reactive. This complex will be high-spin paramagnetic, because it has four unpaired electrons.

An alternative octahedral arrangement in \([\text{Co(NH}_3)_6]^{3+}\) is possible when the electrons on metal ion are rearranged as shown below:

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

\(\text{NH}_3\) \(\text{NH}_3\) \(\text{NH}_3\) \(\text{NH}_3\) \(\text{NH}_3\) \(\text{NH}_3\)

\(d^2sp^3\), inner orbital complex

Since inner \(d\)-orbitals are used this is called an inner orbital complex. There is no unpaired electron, the complex will be low-spin diamagnetic.

The metal ion can also form 4-coordinate complexes. For such complexes two different arrangements are possible i.e. tetrahedral \((sp^3)\) and square planar \((dsp^2)\):
About such complexes you will study later.

Let us illustrate six coordinate complexes with more examples:

1. **Cr(NH$_3$)$_6$**$^{3+}$

The electronic configuration of only 3d, 4s and 4p orbitals are taken into account. The following steps are involved. The electronic configuration of Cr atom and Cr$^{3+}$ ion are given in (i) and (ii) below:

(i) **Cr ground state:**

(ii) **Cr$^{3+}$**

(iii) **[Cr(NH$_3$)$_6$]**$^{3+}$

The 12 electrons for bond formation come from six ligands, each donating a lone pair of electrons. The resulting complex will be paramagnetic because it has three unpaired electrons. Its magnetic moment will be:

$\sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87\text{B.M}$

2. **[Fe(CN)$_6$]**$^{4-}$

(i) **Fe**

(ii) **Fe$^{2+}$**
(iii) \([\text{Fe(CN)}_6]^{3-}\):

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\end{array}
\]

The resulting complex is inner orbital, octahedral and due to the absence of unpaired electron, it will be diamagnetic.

3. \([\text{Fe(CN)}_6]^{3-}\):

(i) Fe

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\downarrow & \downarrow & \downarrow \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\end{array}
\]

(ii) \(\text{Fe}^{3+}\)

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\downarrow & \downarrow & \downarrow \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\end{array}
\]

(iii) \([\text{Fe(CN)}_6]^{3-}\):

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\downarrow & \downarrow & \downarrow \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\text{CN}^- & \text{CN}^- & \text{CN}^- \\
\end{array}
\]

The resulting complex is inner orbital, octahedral. Due to presence of one unpaired electron, it will be paramagnetic.

**Four coordinate complexes:**

1. \([\text{NiCl}_4]^{2-}\):

(i) Ni

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\downarrow & \downarrow & \downarrow \\
\text{Cl}^- & \text{Cl}^- & \text{Cl}^- \\
\text{Cl}^- & \text{Cl}^- & \text{Cl}^- \\
\end{array}
\]

(ii) \(\text{Ni}^{2+}\)

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\downarrow & \downarrow & \downarrow \\
\text{Cl}^- & \text{Cl}^- & \text{Cl}^- \\
\text{Cl}^- & \text{Cl}^- & \text{Cl}^- \\
\end{array}
\]

(iii) \([\text{NiCl}_4]^{2-}\):

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\color{red}{\downarrow} & \color{red}{\downarrow} & \color{red}{\downarrow} \\
\downarrow & \downarrow & \downarrow \\
\text{Cl}^- & \text{Cl}^- & \text{Cl}^- \\
\text{Cl}^- & \text{Cl}^- & \text{Cl}^- \\
\end{array}
\]
The resulting complex will be tetrahedral with two unpaired electrons. It will be paramagnetic.

2. \(\text{Ni(CO)}_4\)

(i) Ni

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\end{array}
\]

(ii) Ni(O)

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\end{array}
\]

(iii) \(\text{Ni(CO)}_4\)

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \downarrow & \downarrow \\
\uparrow & \uparrow & \downarrow \\
\end{array}
\]

The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.

3. \([\text{Ni(CN)}_4]^2-\)

(i) Ni

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\downarrow & \downarrow & \downarrow \\
\end{array}
\]

(ii) Ni\(^{2+}\)

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\end{array}
\]

(iii) \([\text{Ni(CN)}_4]^2-\)

\[
\begin{array}{ccc}
3d & 4s & 4p \\
\uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow \\
\end{array}
\]

The resulting complex is square planar and diamagnetic.
Intext Questions 24.4

1. Name the type of hybridization present in: \([Co(NH_3)_6]^{3+}\).

2. \([Fe(CN)_6]^{3-}\) is diamagnetic or paramagnetic?

3. \([NiCl_4]^{2-}\) and \(Ni(CO)_4\) have sp\(^3\) or dsp\(^2\) hybridization?

4. Which one is diamagnetic: \([Ni(CN)_4]^{2-}\) or \([NiCl_4]^{2-}\) ?

5. What type of hybridization is shown by (i) inner and (ii) outer orbital complexes?

24.5 Applications of Coordination Compounds

Coordination compounds are found in living systems and have many uses in the home, in industry and in medicines. A few examples are given below:

Extraction of metals: cyanide ions are used for the for the extraction of gold and silver. The crushed ore is heated with an aq. cyanide solution in the presence of air to dissolve the gold by forming the soluble complex ion \([Au(CN)_2]^+\):

\[
4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \rightarrow 4[Au(CN)_2]^{-}(aq) + 4 OH^- (aq)
\]

\[
Zn(s) + 2[Au(CN)_2]^{-}(aq) \rightarrow [Zn(CN)_4]^{2-} (aq) + 2Au(s)
\]

Complex formation is also useful for the purification of metals. Nickel is purified by converting the metal to the gaseous compound \(Ni(CO)_4\) and then decomposing the latter to pure nickel.

Medicines: EDTA is a chelating agent which is used in the treatment of lead poisoning. Cis platin cis \([Pt(NH_3)_2Cl_2]\) is used in the treatment of cancer. Sodium nitroprusside, \(Na_2[Fe(CN)_5NO]\) is used to lower blood pressure during surgery.

Qualitative Analyses: complex formation is useful for qualitative analyses.

(a) Separation of Ag\(^+\) from Pb\(^{2+}\) & Hg\(^{2+}\)

\[
Ag^+ + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+ \\
Soluble
\]

(b) Separation of IIA and IIB groups: The cations of IIB group form soluble complex with yellow ammonium sulphide.

(c) Cu\(^{2+}\) ion forms complex on addition of ammonia \([Cu(NH_3)_4]^{2+}\).
(d) Fe$^{2+}$ forms a blue complex with K$_3$Fe(CN)$_6$, i.e. K Fe$^{II}$[Fe$^{III}$(CN)$_6$].
(f) Cobalt(II) gives color with HCl due to the formation of complex [CoCl$_4$]$^{2-}$.
(g) Nickel forms a red complex [Ni(DMG)$_2$] with dimethylglyoxime (H$_2$DMG).

**Intext Questions 24.5**

1. Name two elements which are extracted by complexation.
   ................................................................................................................................
   2. What is the use of EDTA in medicine?
   ................................................................................................................................
   3. Name the compound of platinum which is used as anticancer agent?
   ................................................................................................................................
   4. Give two uses of complexes in qualitative analyses
   ................................................................................................................................

**What You Have Learnt**

- Coordination compounds are compound in which a central metal ion is attached to a group of surrounding ligands by coordinate covalent bond. Ligands can be monodentate or polydentate, depending upon the number of donor atoms attached to the metal. Polydentate ligands are also called chelating agents. They form complexes that have rings of atoms known as chelate rings.

- The number of donor atoms bonded to a metal is called the coordination number of the metal. Common coordination number and geometries are 2 (linear), 4 (tetrahedral and square planar), and 6 (octahedral).

- Systematic names for complexes specify the number of ligands of each particular type, the metal, and its oxidation state.

- Valence Bond Theory describes the bonding in complexes in terms of two-electron, coordinate covalent bonds resulting from the overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands; sp (linear), sp$^3$ (tetrahedral), dsp$^2$ (square planar) and d$^2$sp$^3$ or sp$^3$d$^2$ (octahedral).

- Complexes are very useful in qualitative analyses and in medicine.

**Terminal Exercise**

1. Define the following:

   (i) Coordination number

   (ii) Coordination sphere
Chemistry

(iii) Oxidation number

2. Define ligands. Give one example of each of monodentate, bidentate and polydentate ligands.

3. Write the postulates of Werner’s theory of coordination compounds.

4. Write down the name of the following complexes:
   (i) $K_3[Cr(C_2O_4)_3]$
   (ii) $[Co(NH_3)_2(H_2O)_2Cl]_+$
   (iii) $[Pt(en)_2]^{2+}$
   (iv) $[NiCl_4]^{2−}$
   (v) $[Fe(CN)_6]^{4−}$

5. Write down the formulae of the following complexes:
   i. Tris(ethylenediamine)platinum(IV)
   ii. Tetraaquadibromocobalt(III) ion
   iii. Sodium tetraiodozincate(II)
   iv. Tetracyanonickelate(II) ion
   v. Dichlorotetrathiocyanatocobalt(III) ion

6. Give the salient features of VB theory for complexes. What do you mean by inner and outer orbital complexes?

7. $[NiCl_4]^{2−}$ and Ni(CO)$_4$ are tetrahedral but differ in magnetic behaviour, explain.

8. Ni(CO)$_4$ and $[Ni(CN)_4]^{2−}$ are diamagnetic but have different geometry, explain.

9. $[NiCl_4]^{2−}$ is paramagnetic whereas $[Ni(CN)_4]^{2−}$ is diamagnetic, explain.

10. Explain the types of hybridization and magnetic behaviour of the following complexes on the basis of VB theory:
    i. $[Fe(CN)_6]^{4−}$
    ii. $[Cr(NH_3)_6]^{2+}$
    iii. $[Fe(CN)_6]^{3−}$
    iv. $[NiCl_4]^{2−}$
    v. Ni(CO)$_4$

11. Explain the application of complexes in extraction of elements, medicines and qualitative analyses.
Answers to Intext Questions

24.1

1. Primary valence corresponds to the oxidation state of the central metal ion. It is satisfied by negative ions only.

2. Secondary valence of the metal corresponds to coordination number and is satisfied by negative ions or neutral molecules.

3. In both secondary valance is 6.

4. Octahedral.

5. Two i.e. Tetrahedral or square planar.

24.2

1. (i) 6
   (ii) 6
   (iii) 4

2. (i) +2
   (ii) +3
   (iii) +3
   (iv) +2

3. EDTA

4. NH₃, ethylenediammine and EDTA

5. +3, 6, Ethylenediammine.

24.3

1. (i) Tetraamminedichlorocobalt(III) ion
   (ii) Ammonium-hexaisothiocyanoatocromate(III)
   (iii) Tetracarbonylnickel(0)
   (iv) Potassium-hexacyanoferrate(II)
   (v) Tris(ethylenediamine)chromium(III) chloride

2. (i) [NiCl₄]²⁻
   (ii) [Co(NH₃)₆NO₂]³⁺
   (iii) K₃[Fe(CN)₆]⁻
   (iv) [Cr(en)₂Cl₂]⁺
24.4
1. d²sp³
2. [Fe(CN)₆]³⁻ is paramagnetic because it has one unpaired electron.
3. Both the complexes have sp³ (tetrahedral) hybridization.
4. [Ni(CN)₄]²⁻ is diamagnetic because it is square planar (dsp² hybridization). It has no unpaired electron.
5. Inner – d²sp³, outer – sp³d²

24.5
1. Gold and silver are extracted by cyanide process.
2. EDTA forms soluble complex with elements. It is used in the treatment of lead poisoning.
3. Cis-platin
4. [Cu(NH₃)₄]²⁺ & [Ni(DMG)₂]
1. (a) Name the components of Bordeaux mixture.
    (b) Define an ore.
    (c) How is Flux related to Gangue and Slag?
    (d) Define interstitial compounds.
    (e) Define paramagnetism.
    (f) State two uses of sodium bicarbonate.
    (g) What are Fullerenes?
    (h) Name three isotopes of hydrogen.
    (i) Write a chemical reaction showing the strong dehydrating property of sulphuric acid.
    (j) Write a chemical reaction showing the formation of nitroglycerine from glycerine.

2. (a) Name the oxides of phosphorus and draw the structure of anyone of them.
    (b) List four characteristics of p-block elements.
    (c) Differentiate roasting from calcination.
    (d) Differentiate Electron affinity from Electronegativity.
    (e) Despite being in different group lithium shows similarities with Magnesium. Explain.
    (f) Hydrated ions of some transition elements appear coloured. Explain.
(g) Elements bearing atomic numbers from 21 to 30 are d-block elements which of them is not a transition element and why?

(h) List 4 characteristics of Transition Metals.

(i) How is heavy water different from ordinary water?

(j) Draw angular resonance structure of nitric oxide. (2 × 10 = 20)

3. (a) Assign the geometry to the following molecules using the VSEPR theory. State reasons for your answers.
   (i) Phosphorus (V) Chloride (PCl₅)
   (ii) Sulphur (VI) Flouride (SF₆)
   (iii) Boron (III) Flouride (BF₃).

(b) Potassium permanganate shows different chemical reactions in alkaline, neutral and acidic solutions. Write one chemical each, showing the difference in behaviour.

(c) How purified Haemetite is converted into iron using the process of smelting. Write the chemical equations involved.

(d) Write the sequence of chemical reactions involved in the production of washing soda using solvay process. (3 × 4 = 12)

4. (a) In the table given below the ionization energy (in kJ mol⁻¹) of some elements is shows against their symbol with atomic number

<table>
<thead>
<tr>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>900</td>
<td>800</td>
<td>1090</td>
<td>1400</td>
<td>1310</td>
<td>1680</td>
<td>2080</td>
</tr>
</tbody>
</table>

Study the table carefully and explain why the increase in ionization potential is not steady as we move from left to right.

(b) On the basis of the electronic configuration classify elements bearing atomic number 18, 26, 35 and 27 into the following groups.
   (i) Alkaline earth metals
   (ii) Noble gases
   (iii) Halogens
   (iv) Transition elements (4 × 2 = 8)