

$\psi = C_A \psi_A + C_B \psi_B$ such that $[C_A]^2 = 0.90$ and $[C_B]^2 = 0.10$

Since $[C_A]^2 = 0.90$, $C_A = \pm 0.95$ and

Since $[C_B]^2 = 0.10$, $C_B = \pm 0.32$

For the bonding orbital we take the in-phase overlap so that $\psi = 0.95 \psi_A + 0.32 \psi_B$.

Note: The squares of the coefficients determine the probabilities.

2.18 COMPARISON OF VB AND MO THEORIES

Both the VB and MO theories have been used for the purpose of describing the covalent bond, both employ quantum mechanics. The overlap criterion is predominant in both concepts. The VB theory does not provide the clear picture of the energy changes involved during bond formation. Molecular orbital approach is able to indicate even the minor energy changes during the formation of a molecule from which a lot of information may be collected, the contribution of covalent and ionic character etc. Valence bond theory is useful in predicting the symmetry of the molecules using the idea of hybridization. The most common features between the two theories are:

1. The electron distributions for a given molecule are similar.
2. In both the theories, a normal covalent bond involves the sharing of electron charge density between the nuclei.
3. In both the theories, σ and π bonds can be recognized.
4. In both the approaches, AOs of the atoms must overlap significantly and should have appropriate symmetry about the molecular axis to form a bond.
5. Variation method is used in both the treatments.
6. The variation method is a systematic effort to determine the electron distribution in a particular atom or molecule.

THE ESSENTIAL POINTS OF DIFFERENCE BETWEEN THE TWO THEORIES

1. The basic assumptions of the two theories are quite different. VB theory considers that atoms exist within molecules, and that the structure of a molecule can be interpreted in terms of its constituent atoms and the bonds between them. Whereas, the MO theory, assumes that the atomic orbitals of the original unbounded atoms become replaced by a new set of molecular energy levels, called molecular orbitals and these MOs determine the properties of the resulting molecule.
2. VB theory utilizes the concept of resonance, whereas the MO theory gives an idea of the delocalization.
3. The MO theory gives equal weight to the ionic and covalent terms, whereas, the VB theory shows hundred percent covalent character.

$$\psi_{MO} = \psi_{ionic} + \psi_{cov}$$

$$\psi_{VB} = \psi_{cov}$$

7

Chemistry of *d*-Block Elements

7.1 Introduction

The transition elements are those which as elements or as cations have partially filled $(n-1)$ *d*- or $(n-2)$ *f*-orbitals. All of them are metals and are characterized by electrons being added to $(n-1)$ *d*- or $(n-2)$ *f*-orbitals, where *n* stands for principal energy levels. In simple words, those elements which as atoms or cations have partially filled *d* or *f* orbitals in the penultimate shells are called **transition elements**. The elements in which atoms or cations have partially filled *d* orbitals are called **main transition** (also called "*d* block") **elements or *d*-transition elements**. *d* transition elements are located between Groups IIA (2) and IIIA (13) in the periodic table. Partially filled *f* orbitals are characteristic of atoms and cations of the inner transition ("*f* block") elements. The inner transition elements are sometimes known as *f*-transition elements. The inner transition elements are located between Groups IIIB (3) and IVB (4) in the periodic table, and are usually shown in separate rows below the main part of the periodic table.

1st Inner Transition Series (lanthanides) : $_{58}\text{Ce}$ through $_{71}\text{Lu}$

2nd Inner Transition Series (actinides) : $_{90}\text{Th}$ through $_{103}\text{Lr}$.

The *d*-transition elements are building an inner (next to outermost occupied) energy level from eight to 18 electrons. Filling up of $3d$, $4d$, $5d$, and $6d$ orbitals give rise to four different transition series. They are referred to as

1st Transition Series : $_{21}\text{Sc}$ through Cu

2nd Transition Series: $_{39}\text{Y}$ through $_{47}\text{Ag}$

3rd Transition Series: $_{57}\text{La}$ and $_{72}\text{Hf}$ through $_{79}\text{Au}$

4th Transition Series: (not completed) $_{89}\text{Ac}$ and elements 104 through 111

Strictly speaking, Zn, Cd and Hg (the Group IIB, i.e. group 12) elements are not *d*-transition elements since their "last" electrons go into *s* orbitals (i.e. their atoms and their cations have completely filled sets of *d* orbitals). However, they are often discussed with them because of the similarities of their properties to those of the transition metals. All of the other elements in this region have partially filled sets of orbitals, except Cu, Ag and Au (the IB elements i.e. group 11 elements) and Pd, all which have completely filled *d* orbitals. However, some of the cations of these latter elements have only partially filled sets of *d* orbitals. We commonly use the term "transition metals" to refer to only the more frequently encountered *d*-transition metals. More than half the elements belong either to a transition or inner transition series. The presence of incomplete *d* orbitals in transition elements contributes certain characteristic properties to them. One important characteristic of transition elements is the ability to form complex ion.

7.2 Electronic Configuration of Transition Elements

The specific way in which the orbitals of an atom are occupied by electrons is called the *electronic configuration* of that atom. Electronic structure is central to any discussion of the transition elements. In order to determine ground-state configurations we follow the building-up principle. For the most part, the electronic configurations of transition elements are predicted by the building-up principle. Following the building-up principle, the 3d subshell begins to fill after calcium ($Z=20$) has an $[\text{Ar}]4s^2$ configuration. Thus, scandium ($Z=21$), the first transition metal in first transition series (or 3d series), has the configuration $[\text{Ar}]3d^14s^2$, and, as we go across the period, additional electrons go into 3d subshells. We get the configuration $[\text{Ar}]3d^24s^2$ for titanium, and $[\text{Ar}]3d^34s^2$ for vanadium. Then in chromium the configuration predicted by building-up principle is $[\text{Ar}]3d^44s^2$, but the actual configuration is $[\text{Ar}]3d^54s^1$. The configurations for the rest of the elements are those predicted by the building-up principle, until we reach to copper. Here, the predicted configuration of copper is $[\text{Ar}]3d^94s^2$, but the actual configuration is $[\text{Ar}]3d^{10}4s^1$. This transition from an empty 3d subshell to a filled one occurs with only two irregularities, one at chromium ($Z = 24$), and the other at copper ($Z = 29$). The $3d^54s^1$ configuration of chromium and the $3d^{10}4s^1$ configuration of copper reflect the fact that the 3d and 4s energies are very close together across the series and that an exactly half-filled (for Cr) or filled (for Cu) d - subshell provides enough extra stability to produce these configurations.

Table 7.1 Electronic Configuration of *d*-Block Elements

1st series or 3d series

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
No.	21	22	23	24	25	26	27	28	29	30
Configuration	$[\text{Ar}]3d^14s^2$	$[\text{Ar}]3d^24s^2$	$[\text{Ar}]3d^34s^2$	$[\text{Ar}]3d^54s^1$	$[\text{Ar}]3d^54s^2$	$[\text{Ar}]3d^64s^2$	$[\text{Ar}]3d^74s^2$	$[\text{Ar}]3d^84s^2$	$[\text{Ar}]3d^{10}4s^1$	$[\text{Ar}]3d^{10}4s^2$

2nd Series or 4d series

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
No.	39	40	41	42	43	44	45	46	47	48
Configuration	$[\text{Kr}]4d^15s^2$	$[\text{Kr}]4d^25s^2$	$[\text{Kr}]4d^45s^1$	$[\text{Kr}]4d^55s^1$	$[\text{Kr}]4d^55s^2$	$[\text{Kr}]4d^75s^1$	$[\text{Kr}]4d^85s^1$	$[\text{Kr}]4d^{10}5s^0$	$[\text{Kr}]4d^{10}5s^1$	$[\text{Kr}]4d^{10}5s^2$

3rd Series or 5d series

Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
No.	57	72	73	74	75	76	77	78	79	80
Configuration	$[\text{Xe}]5d^16s^2$	$[\text{Xe}]5d^26s^2$	$[\text{Xe}]5d^36s^2$	$[\text{Xe}]5d^46s^2$	$[\text{Xe}]5d^56s^2$	$[\text{Xe}]5d^66s^2$	$[\text{Xe}]5d^76s^2$	$[\text{Xe}]5d^96s^1$	$[\text{Xe}]5d^{10}6s^1$	$[\text{Xe}]5d^{10}6s^2$

The second, third and fourth transition-metal series correspond to the filling of

the 4d, 5d, and 6d subshells of (n-1)th main shell, respectively. With the exception of Nb, Mo, Ru, Rh, Pd, Ag, Pt and Au in the atoms of these elements the ns-orbital is completely filled (ns^2 configuration) and the differentiating electron enters (n-1)d subshell. It may be noted that in the elements Nb, Mo, Ru, Rh, Pd, Ag, Pt and Au one or both the electrons from ns orbital get shifted to (n-1)d orbital and hence such elements have one or no electron in ns orbital (instead of two electrons in ns orbital). This type of shifting makes the (n-1)d subshell half-filled or completely filled and such (n-1)d subshells are more stable than other (n-1)d subshells. The general valence shell configurations of the atoms of d-block elements may be written as $(n-1)d^{1-10} ns^{0,1,2}$. Note that the third and fourth series include the *lanthanoids* and *actinoids*, respectively. Which are often counted with group IIIB (Group 3). The electronic configurations of the 1st, 2nd and 3rd series elements are given in the table 7.1.

The existence of these d - electrons is partially responsible for several characteristics of transition metals.

7.3 Magnetism

Transition metals and their compounds exhibit interesting magnetic properties. Measurements of magnetic properties provide information about chemical bonding. In addition, many important uses are made of magnetic properties in modern technology.

An electron revolves round the nucleus and it also spins around its own axis to produce magnetic field like the magnetic field produced by electric current flowing through a loop of wire. Each electron behaves like a tiny magnet having a definite value of magnetic moment. Diamagnetic substances have no unpaired electrons, so they have zero magnetic moment. The external magnetic field however, induces in them a small magnetic moment which is opposed to the external magnetic field. Thus, diamagnetic substances repel lines of force and show a slight decrease in weight.

When an atom or ion possesses one or more unpaired electrons, the substance is *paramagnetic*. In a paramagnetic solid the unpaired electrons on the atoms or ions of the solid are not influenced by the electrons on adjacent atoms or ions. The magnetic moments on the individual atoms or ions are randomly oriented. When a paramagnetic substance is placed in a magnetic field, however, the magnetic moments become aligned roughly parallel to one another, producing a net attractive interaction with the magnet. Thus a paramagnetic substance is drawn into a magnetic field.

A much stronger form of magnetism called **ferromagnetism**, arises when the unpaired electrons of the atoms or ions in a solid are influenced by the orientation of the electrons of their neighbours. The most stable (lowest-energy) arrangement

results when the spins of electrons on adjacent atoms or ions are aligned in the same direction. When a ferromagnetic solid is placed in a magnetic field that results may be as much as 1 million times stronger than that for a simple paramagnetic substance. When the external magnetic field is removed, the interactions between the electrons cause the solid as a whole to maintain a magnetic moment. We then refer to it as a permanent magnet. The most common examples of ferromagnetic solids are the elements Fe, Co, and Ni.

Diamagnetic substances are those which are slightly repelled by the magnetic field and this property is associated with the paired electrons in a atom or a compound.

Paramagnetic Substances are those which are weakly attracted by the magnetic field and this property is associated with the unpaired electrons in an atom or a compound.

Ferromagnetic Substances are those which are strongly attracted in the magnetic field and this property is associated with the substances which retain their magnetism even after the removal of magnetic fields. (Due to this property ferromagnetic substances differ from paramagnetic substances which lose their paramagnetism after removing the magnetic field).

7.4 Colour

Most of the transition-metal salts and their solutions are coloured. In general, the colour of a complex depends on the particular metal, its oxidation state and the ligands bound to the metal.

The presence of a partially filled $(n-1)d$ subshell on the metal is usually necessary for a complex to exhibit colour, i.e. it is a property of unpaired d-electrons. Most transition-metal ions have a partially filled d-subshell.

In order for a compound to have colour, it must absorb visible light. Visible light consists of electromagnetic radiation with wavelengths ranging from approximately 400nm to 700nm. White light contains all wavelengths in this visible region. It can be dispersed into a spectrum of colours, each of which has a characteristic range of wavelengths.

A compound will absorb visible radiation when that radiation possesses the energy needed to move an electron from its lower energy state or ground state to some excited state. Thus, the particular energies of radiation that a substance absorbs dictate the colour that it exhibit.

When sample absorbs visible light, the colour we perceive is the sum of the remaining colours that are reflected or transmitted by an object and strike our eyes. A white object reflects light, whereas a clear one transmits it. If an object absorbs all visible light, none reaches our eyes from that object. Consequently, it

appears black. If it absorbs no visible light, it is white or colourless. If it absorbs all except orange, the material appears orange. We also perceive an orange colour, however, when visible light of all colours except blue strikes our eyes. Orange and blue are **complementary colours**. Thus, an object has a particular colour for one of two reasons. (1) It reflects or transmits light of that colour. (2) It absorbs light of the complementary colour. For example, the complex ion $\text{trans}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ absorbs red light from the visible region, its colour will be complementary to red and this is green.

7.5 The Structure of Complexes-Important Terms in Coordination Chemistry

Species such as $[\text{Ag}(\text{NH}_3)_2]^+$ that are assemblies of a central metal ion bonded to a group of surrounding molecules or ions are called metal complexes or simply **complexes**. If the complex carries a net electric charge, it is generally called a **complex ion**. A **complex ion** is a metal ion with Lewis bases attached to it through coordinate covalent bonds. A **complex** (or **coordination compound**) is a compound consisting either of complex ions and other ions of opposite charge or of a neutral complex species.

Ligands are the Lewis bases attached to the metal atom in a complex. "An ion or molecule that coordinates to a metal atom or to a metal ion to form a complex is called a **ligand**." Ligands are normally either anions or polar molecules. Furthermore, they have at least one unshared pair of valence electrons. For example, in the complexes, $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, CN^- and NH_3 are the anionic and neutral ligands respectively.

A metal or ion (usually a transition metal) surrounded by a number of ligands is called a **central metal atom or ion**, e.g., in $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ complexes, Fe and Ag are the central metal ions.

In forming a complex, the ligands are said to *coordinate* to the metal. The central metal and the ligands bound to it constitute the **coordination sphere** of the complex. In writing the chemical formula for a coordination compound, we use square brackets to set off the groups within the coordination sphere from other parts of the compound. For example, the formula $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ represents a compound containing the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ cation and the SO_4^{2-} anion. The four NH_3 ligands in the complex cation are bound directly to the Cu (II) ion and are in the coordination sphere of the copper.

The **coordination number** of a metal atom in complex is the total number of bonds the metal atom forms with ligands. In $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, the iron atom bonds to each oxygen atom in the six water molecules. Therefore, the coordination number of iron in this ion is 6.

A metal complex is a distinct chemical species with its own characteristic

physical and chemical properties. Thus, it has different properties than the metal ion or the ligands from which it is formed. Complex formation can also dramatically change the properties of metal ions such as their ease of oxidation or reduction.

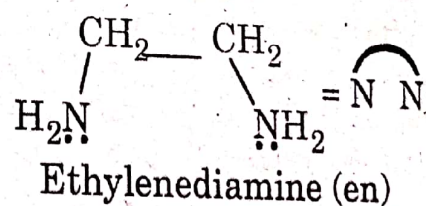
7.6 Chelates

The ligands which have a single donor atom and are able to occupy only one site in a coordination sphere are called **monodentate ligands** (from the Latin, meaning "one-toothed"). Such ligands are coordinated to the central metal ion at one site or by one metal-ligand bond only. Some ligands have two or more donor atoms that can simultaneously coordinate to a metal ion, thereby occupying two or more coordinate sites. They are called **polydentate ligands** ("many-toothed" ligands). Of the polydentate ligands, those that bond through two, three, four, five or six donor atoms are called bidentate-, tridentate-, tetradentate-, (quadridentate-), pentadentate- (quinquedentate-) and hexadentate (sexidentate) ligands, respectively. Because polydentate ligands appear to grasp the metal between two or more donor atoms, polydentate ligands are also known as **chelating agents** (from the Greek word chele, "claw").

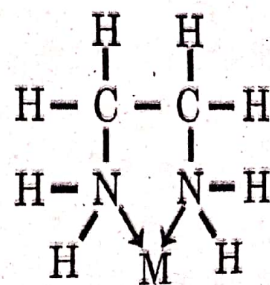
When all the donor atoms of a polydentate ligand get coordinated with the same metal ion, we get a complex compound which contains one or more rings in its structure and hence is called a **chelated** (or cyclic) **complex** or **chelate**. The process of the formation of a chelated complex or chelate is called **chelation**. The word chelating ligand does not apply to a bidentate ligand which forms a bridge system with its two donor atoms bonded to separate metal ions. A chelate ligand must have two or more lone pairs which should be at such a distance from each other that the ligand may form suitable strain-free rings at the metal ion.

Chelates are the special types of coordination compounds containing one or more rings in their structure. The ring structures are formed linking metal ion with polydentate ligands. The polydentate ligands are called **chelating agents** and the process of formation of a chelated complex or chelate is called **chelation**.

Ethylenediamine molecule, which is abbreviated en, has two nitrogen atom each carrying a lone pair of electrons and is capable of donation to the transition metals, is an example of bidentate (two teeth) ligand.

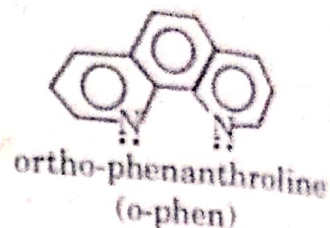
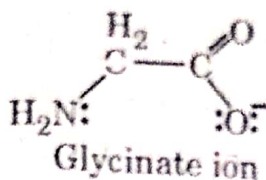
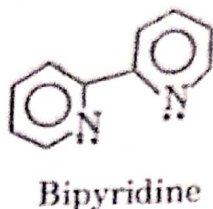
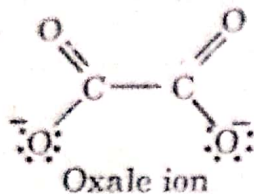
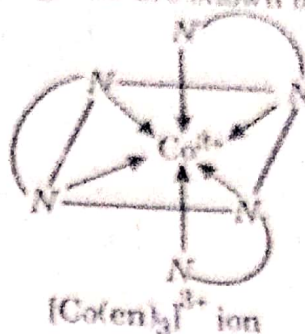
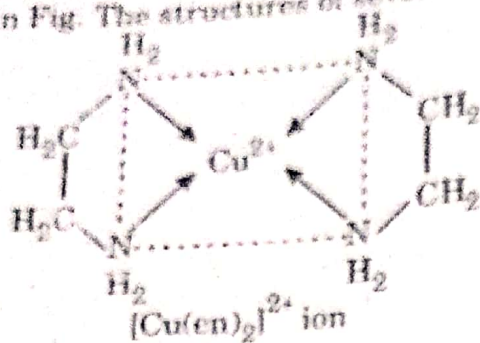


In forming a complex, the ethylenediamine molecule bonds around so that both nitrogen atoms coordinate to the metal atoms, M. Note that $\overset{\curvearrowright}{\text{N}} \text{N}$ represents ethylenediamine.

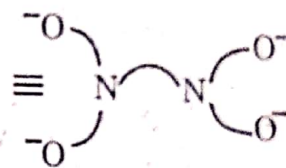
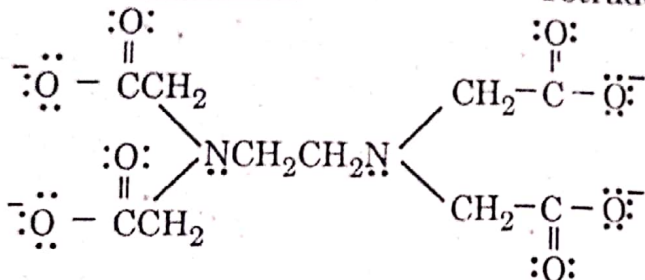
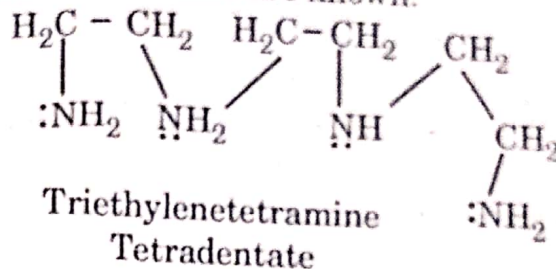
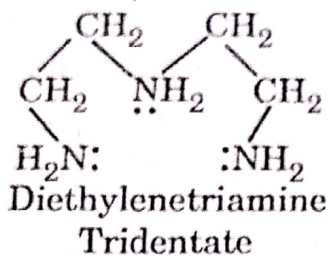


Ethylenediamine forms stable compounds with large number of metal ions through chelation. For example, two ethylenediamine ligands combine with Cu^{2+} to form $[\text{Cu}(\text{en})_2]^{2+}$ ion. The $[\text{Co}(\text{en})_3]^{3+}$ ion, which contains three

shown in Fig. The structures of several other bidentate ligands are shown below



Many tridentate, tetradentate and hexadentate are known:



Ethylenediaminetetraacetate ion abbreviated $[\text{EDTA}]^{4-}$ Hexadentate

The ethylenediaminetetraacetate ion, has six donor atoms. It can wrap around a metal ion using all six of these six donor atoms as shown in Fig. However, it often acts as a pentadentate ligand, that is, occupying five coordination positions, with one of the acetate groups dangling free.

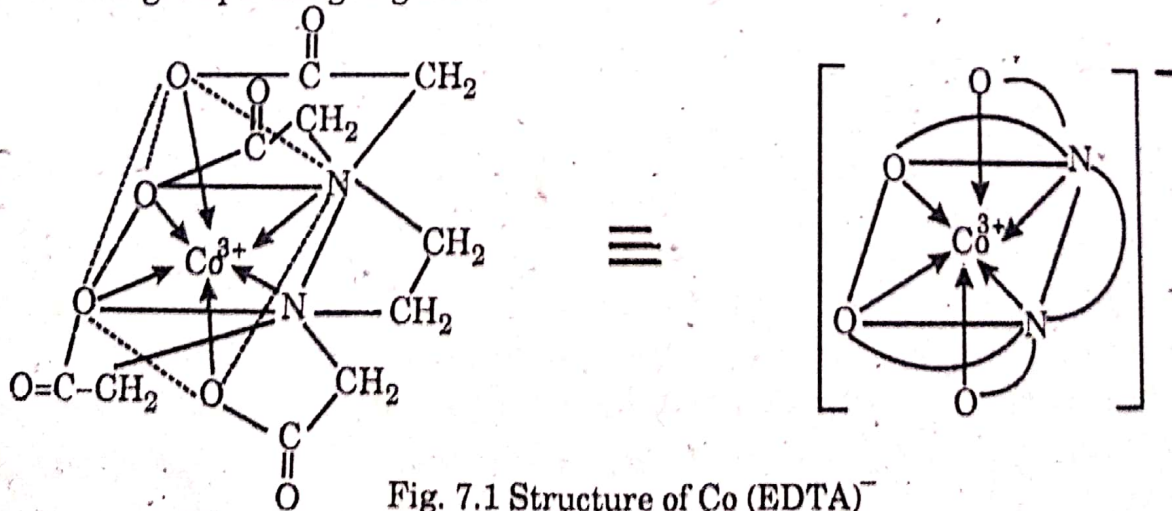


Fig. 7.1 Structure of $\text{Co}(\text{EDTA})^-$