# Coordination Chemistry

The branch of inorganic chemistry that deals with the study of coordination compounds is called coordination chemistry.

The name coordination compound comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another. Because these compounds are usually formed by donation of electron pairs of ligands to metals, the name is appropriate.

Although the history of bonding and interpretation of reactions of coordination compounds really begins with Alfred Werner (1866-1919), coordination compounds were known earlier. Many coordination compounds have been used as pigments since antiquity. Examples still use include Prussian blue $KFe[Fe(CN)_6]$ and aureolin $K_3[Co(NO_2)_6].6H_2O$, yellow.

## Complex ion

Complex ion is a positively or negatively charged species which contains a central metallic atom and a suitable number of ligands surrounding the central metallic atom. The central metallic atom may be in zero, positive or negative oxidation state. The ligands may be either neutral molecules or anions (generally) or combination of the neutral molecules and anions. Examples of complex ions are $[Co^{3+}(NH_3)_6]^{3+}$ ,$[Ni^0(CN)_4]^{4-}$ , $[Fe^{2+}(CN)_6]^{4-}$ , $[Co^-(CO)_4]^-$ , $[Co^{3+}(NH_3)_5Cl]^{2+}$.

## Neutral complex

A complex which has no charge on it is called neutral complex. It is a non electrolyte, dose not undergo ionization and hence dose not give any ions in aqueous solution. Examples of neutral complexes are $[Co^{3+}(NH_3)_3Cl_3]^0$ , $[Ni^0(CO)_4]^0$ , $[Pt^{2+}(NH_3)_2Cl_2]^0$ , $[Ni^{2+}(dmg)_2]^0$.

### Ligands or coordinating groups and central metallic atom

The neutral molecules or ions (usually anions) which are attached with the central ion in complex compounds are called ligands or co-ordinating groups. For example in the complex ion,$[Fe(CN)_6]^{3-}$ the six $CN^-$ ions which are attached with the central $Fe^{3+}$ ion act as ligands. In Lewis sense, in most of the complex compounds the ligands act as Lewis bases (electron pair donors) and the central metal ion acts as a Lewis acid (electron pair acceptor), i.e. in most of the complex compounds the ligands donate one or more electron pairs to the central metal ion.

| $M^{n+}$ | $+$ | $xL$ | $\longrightarrow$ | $[ML_x]^{n+}$ |
|---|---|---|---|---|
| Central metal ion(Lewis acid or electron pair acceptor) | | Ligand (Lewis base or electron pair donor) | | Complex compound |

In a ligand the atom which actually donates the electron pair to the central metal ion is called donor or coordinating atom. The ligands are attached with the central metal ion through their donor atom (or atoms).

The metallic atom with which the ligands are attached through coordinating bonds is called central metallic atom. This metallic atom may be in zero, positive or negative oxidation state.

## Coordination sphere and ionization sphere

While writing the structural formula of a given complex compound the central metal atom and the ligands attached with it are always written in a square bracket, [ ]. This square bracket is called coordination (or inner) sphere. The portion outside the coordination sphere is called ionization (or outer) sphere. Thus in $[Co(NH_3)_5Cl]Cl_2$, the square bracket which contains the central metal ion ($Co^{3+}$ ion) and the ligands (five $NH_3$ molecules and one $Cl^-$ ion) is coordination sphere and the portion that contains two $Cl^-$ ions is ionization sphere.

The species written in ionization sphere are ionizable and hence can be precipitated by means of a suitable precipitating agent while those given in the coordination sphere (i.e. metallic atom and ligands) are non ionizable and hence cannot be precipitated.

$$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

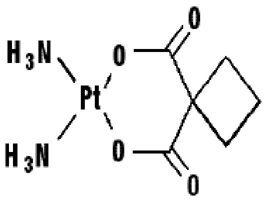
Two $Cl^-$ ions present in ionisation sphere can be precipitated as AgCl (white ppt) by adding $AgNO_3$ solution.

$$2Ag^+ + 2Cl^- \longrightarrow 2AgCl\downarrow$$

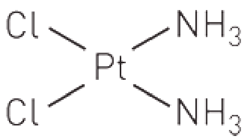
$Cl^-$ ion written in coordination sphere is not ionisable and can, therefore, not be precipated.

## Application of the formation of metal complexes

1- Used as anti-cancer compounds (carboplatin and cisplatin).
2- Formation of chelates in analytical chemistry. Examples are:
    a- Gravimetric estimation and identification of $Ni^{2+}$ ions by dimethyl glyoxime.
    b- Separation of $Co^{2+}$ ion from $Ni^{2+}$ ion by α - nitroso β - naphthol solution.
    c- Estimation of $Mg^{2+}$ ion and $Ca^{2+}$ ion by EDTA.
3- Formation of chelates in softening water and estimation of hardness of water.
4- Formation of chelates in removing poisonous metals from the body.
5- Separation of ions by solvent extraction method.
6- Role of metal chelates in living system (hemoglobin, chlorophyll in plants).



Carboplatin



Cis-Platin

## General Characteristics of Transition Metals (d- Block Elements)

The position of d- block elements

*d-block elements lie between s-and p- block elements

**d-block elements are present in 4th period ($_{21}$Sc to $_{30}$Zn = 10 elements), 5th period ($_{39}$Y to $_{48}$Cd = 10 elements), 6th period ($_{57}$La, $_{72}$Hf to $_{80}$Hg =10 elements) and 7th (incomplete) period which contains 8 elements $_{89}$Ac, $_{104}$Ku to $_{110}$Uun.

***d-block elements are present in (3 – 12 groups).

## Electronic Configuration

d-block elements are defined as those elements whose outer shells are incomplete (partially-filled).

| 1st or 3d series (4th period) | | 2nd or 4d series (5th period) | |
|---|---|---|---|
| Scandium | $_{21}$Sc [$_{18}$Ar] $3d^1 4s^2$ | Yttrium | $_{39}$Y [$_{36}$Kr] $4d^1 5s^2$ |
| Titanium | $_{22}$Ti [$_{18}$Ar] $3d^2 4s^2$ | Zirconium | $_{40}$Zr [$_{36}$Kr] $4d^2 5s^2$ |
| Vanadium | $_{23}$V [$_{18}$Ar] $3d^3 4s^2$ | Niobium | $_{41}$Nb [$_{36}$Kr] $4d^4 5s^1$ * |
| Chromium | $_{24}$Cr [$_{18}$Ar] $3d^5 4s^1$ * | Molybdenum | $_{42}$Mo [$_{36}$Kr] $4d^5 5s^1$ * |
| Manganese | $_{25}$Mn [$_{18}$Ar] $3d^5 4s^2$ | Technetium | $_{43}$Tc [$_{36}$Kr] $4d^6 5s^1$ * |
| Iron | $_{26}$Fe [$_{18}$Ar] $3d^6 4s^2$ | Ruthenium | $_{44}$Ru [$_{36}$Kr] $4d^7 5s^1$ * |
| Cobalt | $_{27}$Co [$_{18}$Ar] $3d^7 4s^2$ | Rhodium | $_{45}$Rh [$_{36}$Kr] $4d^8 5s^1$ * |
| Nickel | $_{28}$Ni [$_{18}$Ar] $3d^8 4s^2$ | Palladium | $_{46}$Pd [$_{36}$Kr] $4d^{10} 5s^0$ * |
| Copper | $_{29}$Cu [$_{18}$Ar] $3d^{10} 4s^1$ * | Silver | $_{47}$Ag [$_{36}$Kr] $4d^{10} 5s^1$ * |
| Zinc | $_{30}$Zn [$_{18}$Ar] $3d^{10} 4s^2$ | Cadmium | $_{48}$Cd [$_{36}$Kr] $4d^{10} 5s^2$ |

3rd or 5d series

(6th period)

Lanthanum $_{57}La$ $[_{54}Xe]\ 4f^0\ 5d^1\ 6s^2$

Hafnium $_{72}Hf$ $[_{54}Xe]\ 4f^{14}\ 5d^2\ 6s^2$

Tantalum $_{73}Ta$ $[_{54}Xe]\ 4f^{14}\ 5d^3\ 6s^2$

Tungsten $_{74}W$ $[_{54}Xe]\ 4f^{14}\ 5d^4\ 6s^2$

Rhenium $_{75}Re$ $[_{54}Xe]\ 4f^{14}\ 5d^5\ 6s^2$

Osmium $_{76}Os$ $[_{54}Xe]\ 4f^{14}\ 5d^6\ 6s^2$

Iridium $_{77}Ir$ $[_{54}Xe]\ 4f^{14}\ 5d^7\ 6s^2$

Platinum $_{78}Pb$ $[_{54}Xe]\ 4f^{14}\ 5d^9\ 6s^1$ *

Gold $_{79}Au$ $[_{54}Xe]\ 4f^{14}\ 5d^{10}\ 6s^1$ *

Mercury $_{80}Hg$ $[_{54}Xe]\ 4f^{14}\ 5d^{10}\ 6s^2$

# Physico-chemical Properties

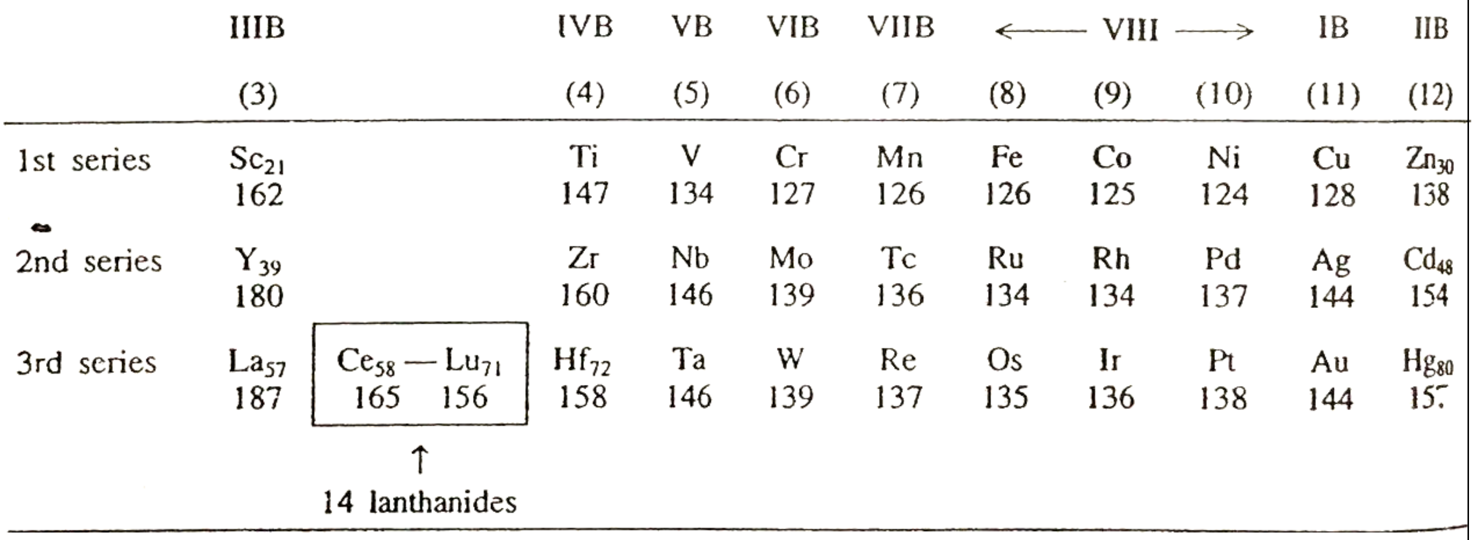
The transition elements show several properties. Some of these properties and their trends of variation are discussed below:

## 1- Atomic radii

The atomic radii of d-block elements are given in (Table 1). The following trends may be observed:

### *Variation of atomic radii in a given series (period)

For the elements from Sc to Mn the atomic radii decrease. This decrease is because of the gradual increase in nuclear charge with the increase in atomic number. The increased nuclear charge makes the atom to shrink in size and hence the size of the atom decreases. However, since the electrons added to 3d orbitals screen the 4s electron(s), the attraction between the nucleus and the 4s electron(s) decreases, i.e. due to the screening effect caused by 3d electrons the magnitude of nuclear charge decreases and consequently the atomic radii for the elements from Fe to Cu remain almost unchanged. Towards the end of each series, there is an increase in electron-electron repulsion between the electrons being added to 3d orbitals. This increase in repulsion becomes greater than that of the attraction between the nucleus and the 4s electron(s). Because of the greater magnitude of electron-electron repulsion, the electron cloud of Zn expands and hence its size also becomes greater than of Cu.



|  | IIIB<br>(3) |  | IVB<br>(4) | VB<br>(5) | VIB<br>(6) | VIIB<br>(7) | ← VIII<br>(8) | <br>(9) | → <br>(10) | IB<br>(11) | IIB<br>(12) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1st series | Sc$_{21}$<br>162 |  | Ti<br>147 | V<br>134 | Cr<br>127 | Mn<br>126 | Fe<br>126 | Co<br>125 | Ni<br>124 | Cu<br>128 | Zn$_{30}$<br>138 |
| 2nd series | Y$_{39}$<br>180 |  | Zr<br>160 | Nb<br>146 | Mo<br>139 | Tc<br>136 | Ru<br>134 | Rh<br>134 | Pd<br>137 | Ag<br>144 | Cd$_{48}$<br>154 |
| 3rd series | La$_{57}$<br>187 | Ce$_{58}$ — Lu$_{71}$<br>165 156<br>↑<br>14 lanthanides | Hf$_{72}$<br>158 | Ta<br>146 | W<br>139 | Re<br>137 | Os<br>135 | Ir<br>136 | Pt<br>138 | Au<br>144 | Hg$_{80}$<br>157 |

## **Variation of atomic radii in a given group

The covalent radii of the atoms of the elements of group 3 (Sc, Y and La) increase (as expected) from top to bottom as the atomic number increases. When we compare these values for the elements of other groups of transition elements, it is found that these values for the elements of 2$^{nd}$ transition series are higher (as expected) than those for the elements of 1$^{st}$ transition series, but these values for the elements of 3$^{rd}$ transition series are almost equal to those for the elements of 2$^{nd}$ transition series. The similarity in the covalent radii for the elements of 2$^{nd}$ and 3$^{rd}$ series is due to *lanthanide contraction* which takes place among lanthanides ($_{58}$Ce to $_{71}$Lu = 14 elements). These 14 lanthanides are present between $_{57}$La (group 3) and $_{72}$Hf (group 4) in 3$^{rd}$ transition series.

Due to the similarity in the covalent radii of the elements of 2$^{nd}$ and 3$^{rd}$ transition series, these elements show close similarity in their properties while the elements of 1$^{st}$ and 2$^{nd}$ transition series do not exhibit so close similarity.

## 2-Metallic character and related properties

All the transition metals show metallic character, (all these elements are metals). Since the transition elements have low values for their ionization energies, ns electrons can easily be lost by them to form $M^+$ or $M^{2+}$ cations and thus these elements show metallic character.

The metallic character of the transition elements is evident from the following properties of these elements:

***Electrical and thermal conductivity**. These elements are good conductors of electricity and heat because of the existence of metallic bonding (presence of free mobile electrons) among the atoms of these elements. Cu, Ag and Au show exceptionally high thermal and electrical conductivity.

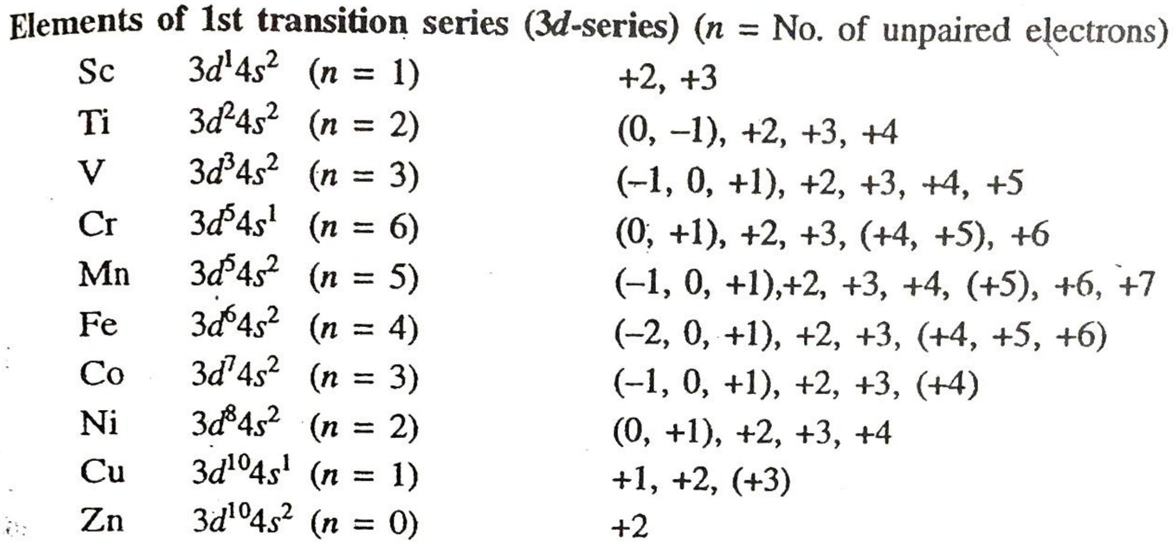
****Hardness**. These elements are hard (cannot be cut with a knife) and brittle. Their hardness due to the presence of strong metallic bonding among the atoms of these elements.

*****Crystal structure**. These elements have simple hexagonal close-packed (hcp), cubic close-packed (ccp) or body-centered cubic (bcc) lattices which are characteristic of metals

## 3-Variable oxidation states

With the exception of a few elements, most of the d-block elements show more than one oxidation state (variable or several oxidation states). The following two reasons have been given to explain why d-block elements show several oxidation states:

- (n-1)d and ns orbitals in the atoms of d-block elements have almost the same energies and hence electrons can be removed from (n-1)d orbitals as easily as they can be removed from ns orbital.
- After removing ns electron(s) the remainder is called core or kernel (penultimate shell). In case of most of d-block elements, the core is unstable and hence can lose one or more electrons, resulting in the formation of cations having different oxidation states (the removal of one or more electrons from the unstable core gives several oxidation states to transition metals.



**Elements of 1st transition series (3*d*-series)** ($n$ = No. of unpaired electrons)

| | | |
|---|---|---|
| Sc | $3d^1 4s^2$ ($n = 1$) | +2, +3 |
| Ti | $3d^2 4s^2$ ($n = 2$) | (0, –1), +2, +3, +4 |
| V | $3d^3 4s^2$ ($n = 3$) | (–1, 0, +1), +2, +3, +4, +5 |
| Cr | $3d^5 4s^1$ ($n = 6$) | (0, +1), +2, +3, (+4, +5), +6 |
| Mn | $3d^5 4s^2$ ($n = 5$) | (–1, 0, +1),+2, +3, +4, (+5), +6, +7 |
| Fe | $3d^6 4s^2$ ($n = 4$) | (–2, 0, +1), +2, +3, (+4, +5, +6) |
| Co | $3d^7 4s^2$ ($n = 3$) | (–1, 0, +1), +2, +3, (+4) |
| Ni | $3d^8 4s^2$ ($n = 2$) | (0, +1), +2, +3, +4 |
| Cu | $3d^{10} 4s^1$ ($n = 1$) | +1, +2, (+3) |
| Zn | $3d^{10} 4s^2$ ($n = 0$) | +2 |

## Oxidation states shown by d-block elements of 1st transition series

In connection with the oxidation states exhibited by the d-block elements of 1st transition series the following points may be noted:

1- **+1 and +2 oxidation states.** The oxidation states shown in bracket are unstable oxidation states. These are low oxidation states. The remaining oxidation states are stable. Out of these stable oxidation states, +1 is the lowest oxidation states for Cu while for other elements the lowest oxidation state is +2. Cr and Cu both show +2 oxidation state when one 4s and one 3d electrons are lost while the remaining elements exhibit this oxidation state (+2) when both ns electrons are involved in bonding.

2- **Stabilization of unstable (low) oxidation states.** It may be seen that the low oxidation states like -1, 0, +1 are unstable. These states are stabilized by forming complexes with π-acid ligands like CO, CNR (isocyanide), $CN^-$ and $C_6H_6$. Examples $[Cr^{+1}(C_6H_6)_2]^+$, $Na^+[Co^{-1}(CO)_4]$, $[Ni^0(CNR)_4]^0$.

3- **High oxidation state.** The highest (maximum) oxidation state for the first five elements (Sc to Mn) is equal to the sum of the electrons in 4s and 3d orbitals, On the other hand, the highest oxidation state for the remaining five elements (Fe to Zn) is not equal to the sum of the electrons in 4s and 3d orbitals.

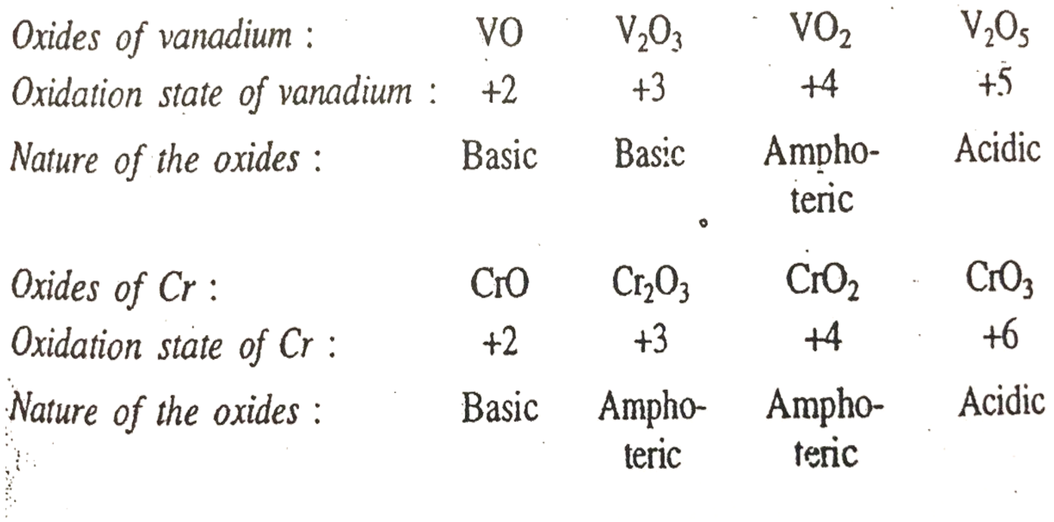
The high oxidation states of many transition metals like V(V), Cr(VI), Mn(IV), Mn(VII), Fe(III), Fe(VI), Co(III), Cu(III), Ag(II), Ag(III) etc. are oxidizing (unstable). These unstable oxidation states which are high oxidation states get stabilized by forming complexes with small highly electronegative ligands like $O^{2-}$ , $F^-$ , $Cl^-$ , per iodate $(IO_6)^{5-}$, tellurate $(TeO_6)^{6-}$.

4- **Ionic/ covalent character of compounds of a given transition metal in various oxidation states.** With the increase in the oxidation state of a given transition metal, the covalent character of its compounds increases. Thus the compounds of a given transition metal in lower oxidation states are ionic while those of the same metal in high oxidation states are covalent. Example $VCl_2$ is ionic,$VCl_3$ is less ionic while $VCl_4$ is covalent.

As the oxidation state of the transition metal increases, the charge density on the metal also increases. This results in the increase of the polarization of the anion charge cloud by the metal and hence covalent character increases (Fajan's Rules).

5- **Acidic/basic character of the compounds of a given transition metal in various oxidation states.** The increase in the covalent character also increases the acidic character of the compound. Thus the compounds of a given transition metal becomes more and more acidic as the oxidation state of the transition metal increases.

The variation of acidic, basic and amphoteric character of the oxides as shown below indicates that the oxides of a given transition metal in lower oxidation states are basic, those of the same in intermediate oxidation states are amphoteric while those of the metal in higher oxidation states are acidic.



| *Oxides of vanadium :* | VO | $V_2O_3$ | $VO_2$ | $V_2O_5$ |
|---|---|---|---|---|
| *Oxidation state of vanadium :* | +2 | +3 | +4 | +5 |
| *Nature of the oxides :* | Basic | Basic | Amphoteric | Acidic |

| *Oxides of Cr :* | CrO | $Cr_2O_3$ | $CrO_2$ | $CrO_3$ |
|---|---|---|---|---|
| *Oxidation state of Cr :* | +2 | +3 | +4 | +6 |
| *Nature of the oxides :* | Basic | Amphoteric | Amphoteric | Acidic |

## 4- Color of transition metal complex

The transition metal complex ions and complex compounds whose central atom contains partially-filled d-orbitals are usually colored in the solid form or in solution form.

When white light which is composed of many different colors falls on a colored complex ion or complex compound of a transition metal, the ion or the compound absorbs some portion of the white light and the remaining portion of the incident light is transmitted or reflected by the complex compound or ion.

* The transition metal complex ions whose central atom contains empty ($d^0$ configuration) or completely-filled d-orbitals ($d^{10}$ configuration) are colorless. This is because of the fact that since the d-orbitals of the central metal ion donot contain any electron (empty d-orbitals) or are completely-filled (contain all the electrons in the paired state), d-d electron transition is not possible and hence no light of any color or wavelength is absorbed by such ions in the visible region. Thus the transition metal ions containing empty d-orbitals ($Sc^{3+}$ and $Ti^{4+}$ ions) or completely-filled d-orbital ($Cu^+$ , $Ag^+$, $Zn^{2+}$, $Cd^{2+}$ , $Hg^{2+}$ etc.) are colorless.

## 5- Magnetic properties of transition metal ions and their complexes

When the transition metal ions or their complexes are placed in a magnetic field, they show different behavior. On the basis of this behavior these substances have been classified as paramagnetic substances, diamagnetic substances, ferromagnetic substances, antimagnetic substances and ferrimagnetic substances.

The transition metal complexes whose central atom/ion contains one or more unpaired electrons are paramagnetic while those whose central atom/ion has no unpaired electrons (all electrons are paired) behave as diamagnetic substances. The paramagnetic character increases with the increase in the number of unpaired electrons.

## 6- Tendency of transition metals to form complex compounds

The transition metal atoms or the cations derived from them have an ability to form complex compounds with certain molecules (CO, NO, $NH_3$ etc.) or ions ( $F^-$ , $Cl^-$, $CN^-$ etc.) these molecules or ions are called ligands. These ligands contain one or more lone pair of electrons which they can easily donate to the transition metal or cation and thus complete the vacant orbitals of those atoms or cations through the formation of L →M coordinate bonds.

The tendency of transition metal atom or cation to form the complex compounds is due to its following properties:

1- Due to the small size of the transition metal atoms or their cations and high effective nuclear charge, they have a high positive charge density on them. This high positive charge density makes the atoms or cations to attract (accept) the lone pairs from the ligands.

2- The transition metal cations or atoms have vacant d-orbitals [(n-1) d orbitals] in which they can accommodate the lone pairs of electrons donated by the ligands and thus can form L → M coordinate bonds.