

- The elements iron(Fe), Copper(Cu), Silver(Ag), gold(Au), Zinc(Zn), Mercury (Hg) tin(Sn) and lead (Pb) are generally termed as heavy metals. Metals having density more than 5 gm/cc are commonly known as **heavy metals**.
- Iron(Fe), Copper(Cu), Silver(Ag), gold(Au), Mercury (Hg) are heavy metals and also called (d-block elements). The elements in which the last electron enters the d-subshell of the penultimate energy level are called **d-block elements**. The d-block elements are called transition elements because they exhibit transitional behaviour between highly reactive ionic compounds forming s-block elements on one side and mainly the covalent compounds forming p-block elements on the other side. The transition elements contain the elements whose atoms or ions in their common oxidation state contains partially filled d-subshells. Coinage metal from group IB in elementary state and their ions in monovalent state and Zn, Cd, Hg from group IIB are non transitional due to completely filled d^{10} subshell.

Characteristics of transition metals

- They are hard and strong having high melting and boiling points.
- They are good conductor of heat and electricity.
- They are **malleable** and ductile.
- They form alloys with one another and with other metallic elements.
- They exhibit catalytic property for hydrogenation, oxidation, dehydration, etc.
- Most of the metals have great tendency to form complex compounds.
- They exhibit variable oxidation states.
- Their ions and compounds are coloured.
- Their general electronic configuration is $(n-1)d^{1-10} ns^{1-2}$.

Classification of transition metals

The transition metals are classified into four series as follows:

- First transition series or 3d series that consists the elements from Sc(21) to Zn(30). These elements lie in the 4th period of the periodic table.
- Second transition series or 4d series that consists the elements from Y(39) to Cd(48). These elements lie in the 5th period of periodic table.
- Third transition series or 5d series that consists the elements from La(57) and from Hf(72) to Hg(80). These elements lie in the 6th period of periodic table.
- Fourth transition series or 6d series that consists the elements from Ac(89) and beyond Ku(104). These elements lie in the 7th period of periodic table and is still incomplete.

Oxidation state of transition metals

- Most of the transition metals exhibit variable oxidation states i.e. they show variable valency in their compounds. A large number of oxidation states of transition metals are related to their electronic configuration. Oxidation states of the first transition series of elements are illustrated in the table given below

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+1, +2, +3, +4, +5, +6
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

- The outermost electronic configuration of the transition metals is $(n-1)d^{1-10} ns^{1-2}$. Since the energy levels of $(n-1)d$ and ns orbitals are quite close to each other, hence both the $(n-1)d$ and ns orbitals are available for bonding purposes. Therefore the number of oxidation states shown by these metals depend upon the number of d-electrons and s-electrons they have.
The outer electronic configuration of Sc is $3d^1 4s^2$. It exhibits an oxidation state of +2 in those compounds in which it uses both of its 4s-electrons. It can also exhibit a +3 oxidation state when it uses its two 4s-electrons as well as one d-electrons in chemical bonding

The study of common oxidation states gives the following conclusion:

- The variable oxidation state shown by the transition metals are due to outer ns and inner $(n-1)d$ electrons in bonding.
- The most common oxidation state shown by the metals of first transition series is +2, except Sc. This oxidation state arises from the loss of two $4s$ electrons. This means that after Sc, d -orbitals become more stable than the s -orbital.
- The highest oxidation states are observed in fluorides and oxides. The highest oxidation state shown by any transition metal is +8. It is shown by ruthenium(Ru) and osmium(Os).
- The transition metals in the +2 and +3 oxidation states mostly form ionic bonds. In compounds of the higher oxidation states, the bonds are essentially covalent. For example, in permanganate ion (MnO_4^-), all bonds formed between Mn and oxygen are covalent.
- Oxidation state increases on moving down the group. For example, Fe shows the common oxidation state of +2 and +3, but Ru and Os in the same group form compounds in the +4, +6 and +8 oxidation state.
- Transition metal also form compounds in low oxidation states such as 0 and +1. For example, Ni in $Ni(CO)_4$ has 0 oxidation state.

Note: Zinc, cadmium and mercury are considered as non-typical transition metals because they don't have variable oxidation states. Their oxidation state is only +2. In these metals, d -orbitals are completely filled

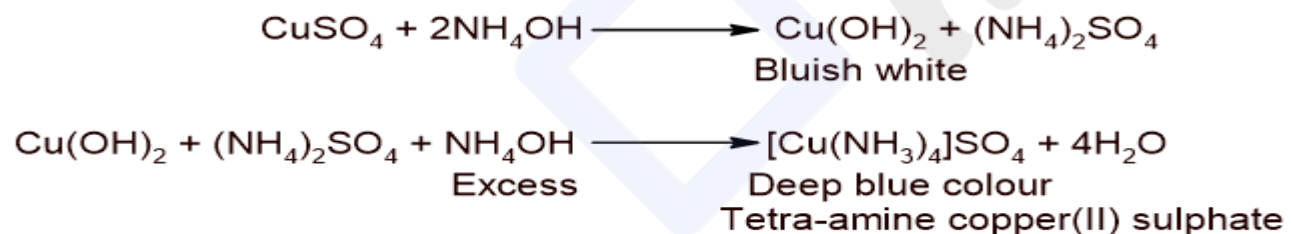
Metal complexes and complex ion

Transition metals are well known for complex compound formation. These metals and their ions show a strong tendency for complex formation. The tendency of transition metals to form complexes is due to two factors:

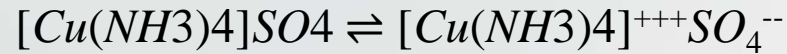
1. These ions are very small in size and therefore has high positive charge density which facilitates acceptance of lone pair of electrons from certain molecules(CO, NO, NH₃, H₂O, etc) or with ions (F⁻, Cl⁻, CN⁻, etc) called ligands.
2. They have vacant orbitals and these orbitals accept lone pairs of electrons donated by ligands to form coordinate covalent bonds.

The greater the charge on metal ions, the stronger the power of attraction for lone pair of electrons.

Those compounds which retain their identities even when dissolved in water or any other solvent and their properties are completely different from those of the constituents are called coordination or complex compounds. For example, when ammonium hydroxide solution is added to blue copper sulphate solution, a light coloured precipitate of copper hydroxide appears in the beginning but on adding an excess of ammonia, the precipitate at once dissolves to give a deep blue colour.



Tetra-amine copper(II) sulphate is a complex compound and it ionizes in solution as:



Complex ion

The Cu^{++} ion almost disappears from the solution and ammonia enters into an intimate association with Cu^{++} ion yielding a new ion of composition $[Cu(NH_3)_4]^{++}$. Such an ion is called a complex ion. The complex compounds formed by the association of one or more molecules of ammonia with metal cations are called ammines. These were amongst the earliest complex compound discovered. A large number of complex compounds of different types are now known.

- A compound in which a metal atom or ion is coordinated to two or more anions or neutral molecules and retain its identity in solid as well as the solution is called complex or coordinate compound. In these compounds, the number of species surrounding the central metal atom is beyond its electrovalency or covalency. For example, in $[Cu(NH_3)_4]SO_4$, the electrovalency of copper is two but it is surrounded by four NH_3 molecules
- A coordinate compound generally contains one or more complex ions. For example:
 $[Cu(NH_3)_4]SO_4$ contains $[Cu(NH_3)_4]^{+}$ complex ion
 $K_4[Fe(CN)_6]$ contains $[Fe(CN)_6]^{4-}$ complex ion
 $[Ag(NH_3)_2]Cl$ contains $[Ag(NH_3)_2]^{+}$ complex ion
 $[Pt(NH_3)_4][PtCl_4]$ contains $[Pt(NH_3)_4]^{+2}$ and $[PtCl_4]^{-2}$ complex ions.

An electrically charged ion which consists of a central metal atom or ion surrounded by a group of ions or neutral molecules is called a complex ion. For example, $[\text{Ni}(\text{NH}_3)_6]^{++}$ is a complex ion in which the central Ni^{++} ion is surrounded by six NH_3 molecules. Some examples of complex ions are: $[\text{Co}(\text{NH}_3)_6]^{+++}$, $[\text{Cu}(\text{NH}_3)_4]^{++}$, $[\text{Ag}(\text{CN})_2]^-$, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^-$, etc

The complex ion carrying a positive charge is called cationic complex and the one with a negative charge is called anionic complex and the complex with no charge is called neutral complex

The metal atom or ion to which two or more anions or neutral molecules are attached is called a central metal atom or ion. For example, in the complex ion $[\text{Co}(\text{NH}_3)_6]^{+++}$, Co^{+++} is the central metal ion and in the complex compound $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, Pt^{++} is the central metal ion

The molecular or ionic species which gets attached directly to the central metal atom or ion during the formation of the complex is called a ligand. The ligands are attached to the central atom or ion through a co-ordinate bond. For example, in $[\text{Cu}(\text{NH}_3)_4]^{++}$, NH_3 is the ligand

Shape of complex ions

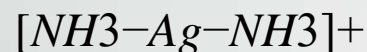
Complex ions have a definite geometrical shape. It is due to that the bond between central metal and ligand is directional in nature. The shape of the complex ion depends upon:

- Numer of ligands (coordination number)
- Types of hybridization

1. 2-coordinated complex ion

The complex ion in which central metal ion is forming two coordinate covalent bonds or attached to two ligands is called 2-coordinated complex ion. Formula: ML_2

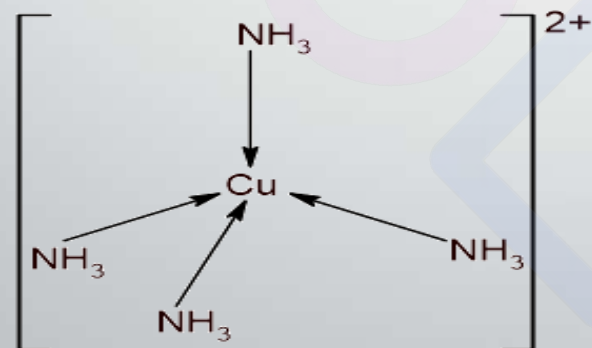
Structure : Linear shape $\rightarrow [Ag(NH_3)_2]$



2. 4-coordinated complex ion

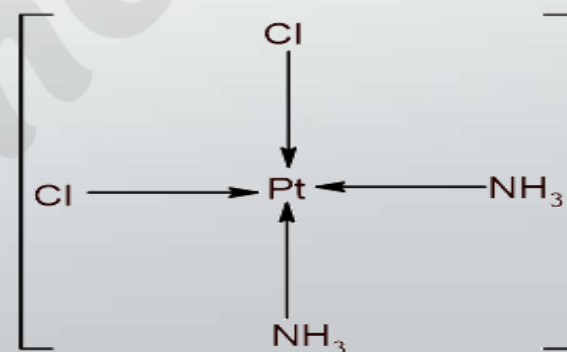
The complex ion in which central metal ion is forming four coordinate covalent bonds or attached to four ligands is called 4-coordinated complex ion. Formula: ML_4

i. Tetrahedral



Tetra amine copper (II) ion

ii. Square planar



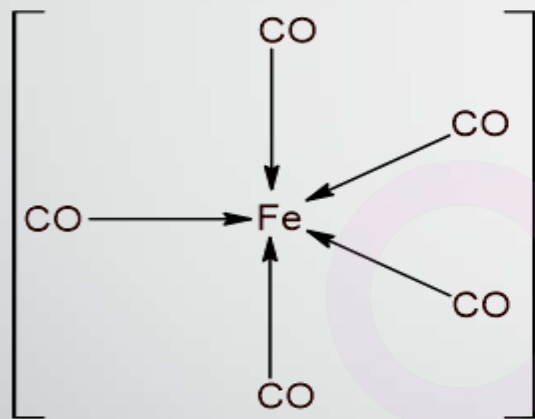
Dichloro diamine platinum (II)

3. 5-coordinated complex ion

The complex ion in which central metal ion is forming five coordinate covalent bonds or attached to five ligands is called 5 coordinated complex ion. Formula: ML_5

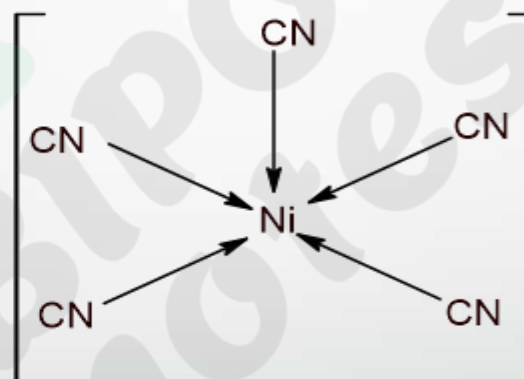
Structure:

Trigonal bipyramidal



$Fe(CO)_5$
Iron pentacarbonyl

Square pyramidal

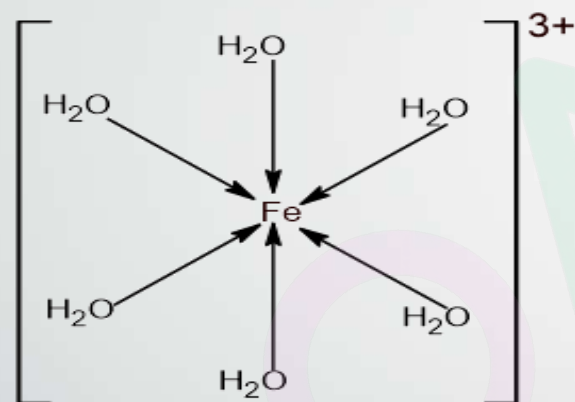


$[Ni(CN)_5]^{--}$
Nickel pentacyanide

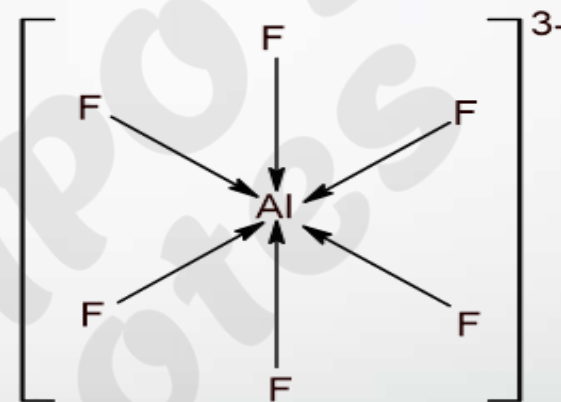
4. 6 coordinated complex ion

The complex ion in which central metal ion is forming six coordinate covalent bonds or attached to six ligands is called 6 coordinated complex ion. Formula: ML_6

Structure: They have octahedral shape (four ligands are on one plane, one is above the plane and one is below the plane). eg



$[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$
Hexa aqua iron(III) ion



$[\text{AlF}_6]^{---}$
Hexa fluoro aluminate

Co-ordination number

The total number of ligands attached directly to the central metal atom or ion in a complex is called co-ordination number. For example, co-ordination number of Ag^+ in $[\text{Ag}(\text{CN})_2]^-$ is 2, co-ordination number of Ni^{++} in $[\text{Ni}(\text{NH}_3)_6]^{++}$ is 6, co-ordination number of Fe^{++} in $[\text{Fe}(\text{CN})_6]^{--}$ is 6 and co-ordination number of Cu^{++} in $[\text{Cu}(\text{NH}_3)_4]^{++}$ is 4.

Colour of transition metal complexes

Most of the compounds of transition metal are coloured in the solid or in the solution state. The color of the substance arises from the property of the substance to absorb light of certain wavelengths in the region of visible light ($\lambda=3800\text{-}7600 \text{ \AA}$). The transition metal complexes are coloured due to the presence of unpaired electrons in their d-orbitals. In an isolated atom or ion of complex, all the five d-electrons are of the same energy, which is said to be degenerate. These d-orbitals don't have the same energy under the influence of combining anions or electron-rich molecules called ligands. The d-orbitals split into two sets of orbitals having slightly different energies

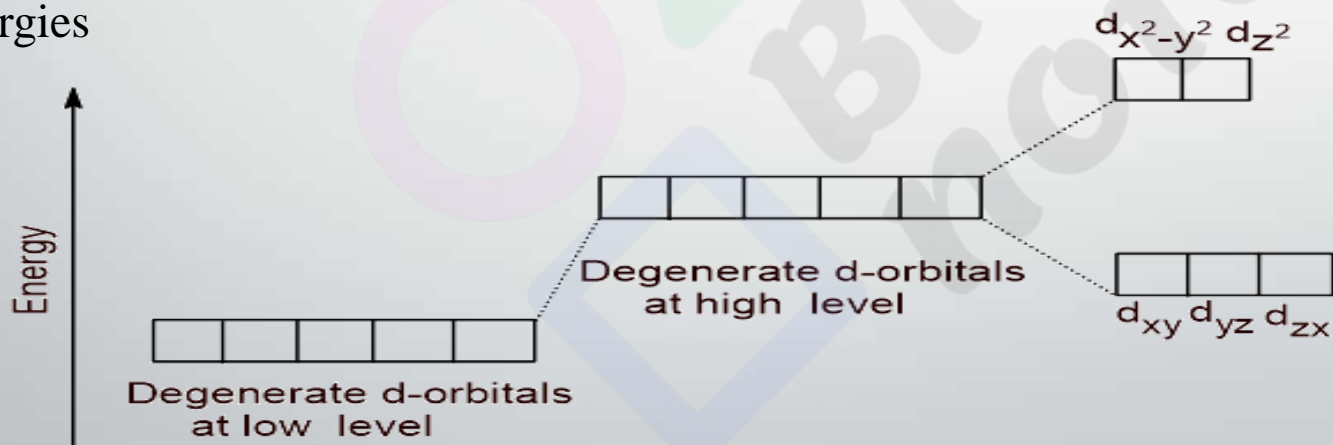


Fig: Representation of crystal field splitting of d-orbitals in an octahedral complex

- In the transition elements which have partly filled d-orbitals, the transition of electrons takes place from one of the lower d-orbitals to some higher d-orbital within the same subshell. The energy required for this transition falls in the visible region. So, when white light falls on these complexes, they absorb a particular colour from the radiation for the promotion of electrons and the remaining colours are emitted. The colour of the complexes is due to this emitted radiation. For example, the d^1 complex, $[\text{Ti}(\text{H}_2\text{O})_6]^{+++}$. This ion exists in an aqueous solution of Ti^{+++} and gives rise to purple colour. The single d-electron in the complex will occupy the lowest energy orbital available to it, i.e. one of the three degenerate t_{2g} orbitals. The purple colour is the result of absorption of light and promotion of the t_{2g} electron to the e_g level. The transition can be represented as $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$.
- The transition metals in elemental form or in the ionic form have one or more unpaired electrons. When light falls on the sample, the electrons from the lower energy level get promoted to a higher energy level due to the absorption of light of a characteristic wavelength or colour. This wavelength of the absorbed light depends upon the energy difference of the two levels. Rest of the light gets transmitted. The transmitted light has a colour complementary to the absorbed colour. Therefore, the compounds or solution appears to be of the complementary colour. For example, $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$ ion absorb red radiation and appear blue-green (blue-green is a complementary colour to red).

The relationship between the colours of the absorbed and the transmitted light is given in the table below

Absorbed light	Transmitted light
IR	White
Red	Blue-green
Orange	Blue
Yellow	Indigo
Yellow-green	Violet
Green	Purple
Blue-green	Red
Blue	Orange
Indigo	Yellow
Violet	Yellow-green
UV	White

- However, if radiations of the wavelength except one are absorbed, then the colour of the substance will be the colour of the transmitted radiation. For example, if a substance absorbs all colours except green, then it would appear green to the light.

The colour of transition metal ions arises from the excitation of electrons from the d-orbitals of lower energy to the d-orbitals of higher energy. Light radiations corresponding to such small amounts of energy that are required for the d-d transition are available in the visible region. It is for this reason that transition metal ions have the property to absorb certain radiations from the visible regions and exhibit complementary colours. The transition metal ions which have completely filled d-orbitals are colourless as there are no vacant d-orbitals to permit the promotion of the electron. Therefore, $\text{Zn}^{++}(\text{3d}^{10})$, $\text{Cd}^{++}(\text{4d}^{10})$ and $\text{Hg}^{++}(\text{5d}^{10})$ ions are colourless. The transition metal ions which have completely empty d-orbitals are also colourless. Thus, Sc^{+++} and Ti^{++++} ions are colourless unless a coloured anion is present in the compound

Colours and the outer electronic configurations of some important ions of the first transition series metals are given below:

Ion	Outer electronic configuration	Number of unpaired electrons	Colour of the ion
Sc ⁺⁺⁺	3d ⁰	0	Colourless
Ti ⁺⁺⁺	3d ¹	1	Purple
Ti ⁺⁺⁺⁺	3d ⁰	0	Colourless
V ⁺⁺⁺	3d ²	2	Green
Cr ⁺⁺⁺	3d ³	3	Violet
Mn ⁺⁺	3d ⁵	5	Light pink
Mn ⁺⁺⁺	3d ⁴	4	Violet
Fe ⁺⁺	3d ⁶	4	Green
Fe ⁺⁺⁺	3d ⁵	5	Yellow
Co ⁺⁺	3d ⁷	3	Pink
Ni ⁺⁺	3d ⁸	2	Green
Cu ⁺⁺	3d ⁹	1	Blue
Cu ⁺	3d ¹⁰	0	Colourless
Zn ⁺⁺	3d ¹⁰	0	Colourless

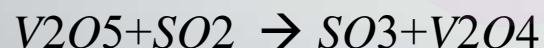
The ions of s and p block elements are colourless because of the excitation of electrons from the lower s or p orbitals to the higher s, p or d orbitals can only be carried out by the absorption of a very high amount of energy which is associated only with the radiation in the ultra-violet region. There is, therefore no absorption of light from the visible region.

Catalytic properties

Most of the transition metals and their compounds have good catalytic properties. Nickel(Ni), Platinum(Pt), Palladium(Pd), Iron(Fe), Copper(Cu), vanadium pentoxide(V_2O_5), etc. are important catalysts. Some important catalysts used are:

- Finely divided iron (Fe) in the manufacture of ammonia by Haber's process.
- Vanadium pentoxide (V_2O_5) or Platinum (Pt) in the oxidation of SO_2 to SO_3 in contact process.
- Nickel (Ni) powder in the hydrogenation of unsaturated organic compounds.
- Ferrous sulphate and hydrogen peroxide (Fenton's reagent) are used for the oxidation of alcohol to aldehyde.
- Copper (Cu) is used for the dehydrogenation of alcohols.

According to the modern theory of catalysis, a catalytic substance is capable of forming an unstable intermediate compound that readily decomposes yielding the product and regenerating the catalyst. The transition metals on account of their variable valency are able to form unstable intermediate compounds very readily. For example, during the conversion of SO_2 to SO_3 , V_2O_5 adsorbs SO_2 molecules on its surface and gives oxygen to it to form SO_3 and V_2O_4 . V_2O_4 reacts with oxygen to form V_2O_5 .



In some cases, transition metals provide a suitable surface for the reaction to take place. The reactants are adsorbed on the surface of the catalyst where the reaction occurs.

d-orbitals in complex ions of octahedral complex (crystal field theory)

The Crystal field theory (CFT) is the model for the bonding interaction between transition metals and ligands. It was proposed by Hans Bethe in 1929. When the ligands approach the central metal ion, the degeneracy of the electronic orbital state usually d-orbitals is broken due to the static electric field produced by the surrounding charge distribution. Because electrons repel each other, the d-electrons closer to the ligands will have higher energy than those further away, resulting in the d-orbitals splitting. In most cases, the d-orbitals are degenerate, but sometimes they can split with the e_g and t_{2g} subsets having different energy. The $d_{x^2-y^2}$ and d_{z^2} all point directly along the x,y and z axes. They form an e_g set. On the other hand, the lobes of the d_{xy} , d_{xz} and d_{yz} all line up in the quadrants, with no electron density on the axes. These three orbitals form the t_{2g} set. CFT is the bonding model that explains many important properties of transition metal complexes, including their colours, magnetism, structure, stability and reactivity. The central assumption of CFT is that metal-ligand interactions are purely electrostatic. According to this theory, in a free isolated gaseous ion, the five d orbitals are degenerate (have equal energy) but in the solution or compound state, the energy of the d-orbitals is changed which cause the splitting into different energy d-orbitals. This is called crystal field splitting. Octahedral complexes have six ligands symmetrically arranged around a central atom defining the vertices of an octahedron. Octahedral molecular geometry describes the shape of compounds wherein six atoms or groups of atoms or ligands are symmetrically arranged around a central atom. The octahedron has eight faces, hence the prefix octa is given. For a free ion, such as gaseous Ni^{2+} or Mo, the d-orbitals are degenerate.

