

Coordination Compounds

We know that transition metals form a large number of complex compounds in which the metal atoms are bound to a number of anions or neutral molecules by sharing of electrons. In modern terminology such compounds are called coordination compounds. The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. New concepts of chemical bonding and molecular structure have provided insights into the functioning of these compounds as vital components of biological systems. Chlorophyll, haemoglobin and vitamin B12 are coordination compounds of magnesium, iron and cobalt respectively. Variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

Werner's theory of Coordination Compounds: Alfred Werner (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques. Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds such as CrCl₃, CoCl₂ or PdCl₂ have primary valences of 3, 2 and 2 respectively. In a series of compounds of cobalt(II) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol CoCl₂.xNH₃ (Yellow) gave 3 mol AgCl
1 mol CoCl₂.xNH₃ (Purple) gave 2 mol AgCl
1 mol CoCl₂.xNH₃ (Green) gave 1 mol AgCl
1 mol CoCl₂.xNH₃ (Violet) gave 0 mol AgCl

These observations, together with the results of conductivity measurements in solution can be explained if (i) six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown in Table given below, where the atoms within the square brackets form a single entity which does not dissociate under the reaction conditions. Werner proposed the term secondary valence for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

Formulation of Cobalt(II) Chloride-Ammonia Complexes

Colour	Formula	Solution conductivity corresponds to
Yellow	[Co(NH ₃) ₆] ³⁺ 3Cl ⁻	1:3 electrolyte
Purple	[CoCl(NH ₃) ₅] ²⁺ 2Cl ⁻	1:2 electrolyte
Green	[CoCl ₂ (NH ₃) ₄] ⁺ Cl ⁻	1:1 electrolyte
Violet	[CoCl ₃ (NH ₃) ₃] ⁰	1:1 electrolyte

Note that the last two compounds in the above Table have identical empirical formula, CoCl₃.4NH₃, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds. The main postulates are:

- In a coordination compounds metals show two types of ligands (valences)-primary and secondary.
- The primary valences are normally ionisable and are satisfied by negative ions.
- The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers. In modern formulations, such spatial arrangements are called coordination polyhedra. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions.
- He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, [Co(NH₃)₆]³⁺, [CoCl(NH₃)₅]²⁺ and [CoCl₂(NH₃)₄]⁺ are octahedral entities, while [Ni(CO)₄] and [PtCl₄]²⁻ are tetrahedral and square planar, respectively.

Difference between Double Salt and Complex: Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, KCl.MgCl₂.6H₂O, Mohr's salt, FeSO₄.(NH₄)₂SO₄.6H₂O, potash alum, KAl(SO₄)₂.12H₂O, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as [Fe(CN)₆]⁴⁻ or K₄[Fe(CN)₆] do not dissociate into Fe²⁺ and CN⁻ ions.

Definitions of Some Important Terms Pertaining to Coordination Compounds:

(a) Coordination entity

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, [CoCl₂(NH₃)₄]⁺ is a coordination entity in which the cobalt ion is surrounded by four ammonia molecules and two chloride ions. Other examples are [Ni(CO)₄], [PtCl₂(NH₃)₂], [Fe(CN)₆]⁴⁻, [Co(NH₃)₆]³⁺.

(b) Central atom/ion

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom/ion. For example, the central atom/ion in the coordination entities: [NiCl₂(H₂O)₂], [CoCl₂(NH₃)₄]²⁺ and [Fe(CN)₆]³⁻ are Ni²⁺, Co³⁺ and Fe³⁺, respectively. These central atoms/ions are also referred to as Lewis acids.

(c) Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl⁻, small molecules such as H₂O or NH₃, larger molecules such as H₂NCH₂CH₂NH₂ or N(CH₂CH₂NH₂)₃ or even macromolecules, such as proteins.

When a ligand is bound to a metal ion through a single donor atom, as with Cl⁻, H₂O or NH₃, the ligand is said to be **unidentate**. When a ligand can bind through two donor atoms as in H₂NCH₂CH₂NH₂ (ethane-1,2-diamine) or C₂O₄²⁻ (oxalate), the ligand is said to be **bidentate** and when several donor atoms are present in a single ligand as in N(CH₂CH₂NH₂)₃, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion (EDTA⁴⁻) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

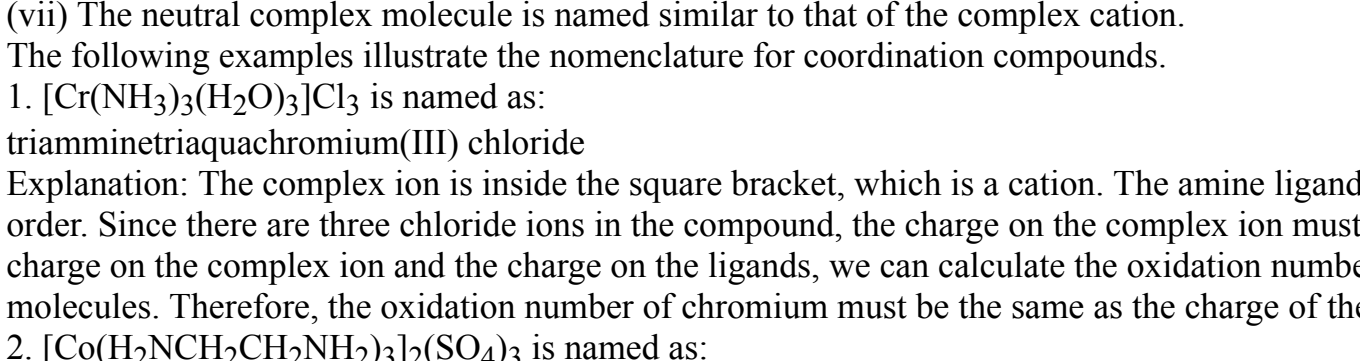
When a di- or polydentate ligand uses its two or more donor atoms simultaneously to bind a single metal ion, it is said to be a **chelate ligand**. The number of such ligating groups is called the **denticy** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Ligand which has two different donor atoms and either of the two ligates in the complex is called **ambidentate** ligand. Examples of such ligands are the NO₂⁻ and SCN⁻ ions. NO₂⁻ ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN⁻ ion can coordinate through the sulphur or nitrogen atom.

Coordination Number: The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the central metal is directly bonded. For example, in the complex ions, [PtCl₄]²⁻ and [Ni(NH₃)₆]²⁺, the coordination number of Pt and Ni are 6 and 4 respectively.

Similarly, in the complex ions, [Fe(C₂O₄)₃]³⁻ and [Co(en)]³⁺, the coordination number of both, Fe and Co, is 6 because of C₂O₄²⁻ and en (ethane-1,2-diamine) are didentate ligands. It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

Coordination sphere: The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the coordination sphere. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex K₄[Fe(CN)₆], the coordination sphere is [Fe(CN)₆]⁴⁻ and the counter ion is K⁺.

Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example, [Co(NH₃)₆]³⁺ is octahedral, [Ni(CO)₄] is tetrahedral and [PtCl₄]²⁻ is square planar. Following figure shows the shapes of different coordination polyhedra.



Oxidation number of central atom: The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in [Cu(CN)₄]³⁻ is +1 and it is written as Cu(I).

Homoleptic and heteroleptic complexes: Complexes in which a metal is bound to only one kind of donor groups, e.g., [Co(NH₃)₆]³⁺, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g., [Co(NH₃)₅Cl]²⁺, are known as heteroleptic.

Nomenclature of Coordination Compounds: Nomenclature is important in Coordination Chemistry because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers. The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

Formulas of Mononuclear Coordination Entities: The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom. The following rules are applied while writing the formulas:

- The central atom is listed first.
- If the ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
- Why the bonds between the ligands and the metal within a coordination sphere.
- When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, [Co(CN)₆]³⁻, [Cr(H₂O)₆]³⁺, etc.
- The charge of the cation(s) is balanced by the charge of the anion(s).

Naming of Mononuclear Coordination Compounds:

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:

- The cation is named first in both positively and negatively charged coordination entities.
 - If the ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).
 - (iii) Names of the anionic ligands end in -o, those of neutral and cationic ligands are the same except aqua for H₂O, ammine for NH₃, carbonyl for CO and nitrile for NO. While writing the formula of coordination entity, these are enclosed in brackets ().
 - (iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bi, tris, tetrakis are used, the ligand to which they refer being placed in parentheses. For example, [NiCl₂(PPh₃)₂] is named as dichlorobis(triphenylphosphine)nickel(II).
 - (v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
 - (vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example, Co in a complex anion, [Co(SCN)₄]²⁻ is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe.
 - (vii) The neutral complex molecule is named similar to that of the complex cation.
- The following examples illustrate the nomenclature for coordination compounds.

1. [Cr(NH₃)₃(H₂O)₃]Cl₃ is named as: triamminetriaquachromium(III) chloride

Explanation: The complex ion is inside the square bracket, which is a cation. The amine ligands are named before the aqua ligands according to alphabetical order. Since there are three chloride ions in the compound, the charge on the complex ion must be +3 (since the compound is electrically neutral). From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

2. [Cr(ethane-1,2-diamine)Co(H₂O)₄]SO₄ is named as: tris(ethane-1,2-diamine)cobalt(III) sulphate

Explanation: The sulphate is the counter anion in this molecule. Since it takes 3 sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further, ethane-1,2-diamine is a neutral molecule, so the oxidation number of cobalt in the complex ion must be +3. Remember that you never have to indicate the number of cations and anions in the name of an ionic compound.

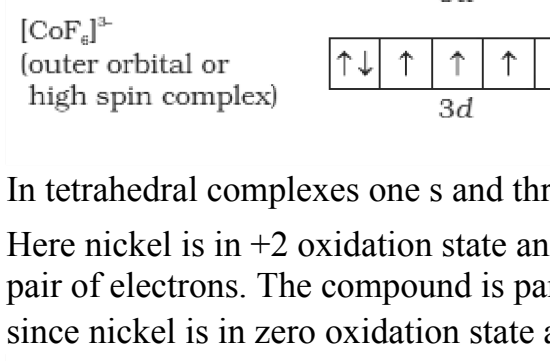
3. [Ag(NH₃)₂][Ag(CN)₂] is named as: diamminesilver(I) dicyanidoargentate(I)

Isomerism in Coordination Compounds: Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided

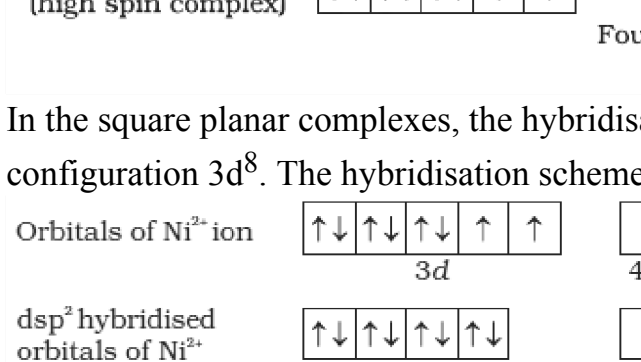
- (a) **Stereoisomerism**
 - Geometrical isomerism (ii) Optical isomerism
- (b) **Structural isomerism**
 - Linkage isomerism (ii) Coordination isomerism (iii) Ionisation isomerism (iv) Solvate isomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A detailed account of these isomers are given below.

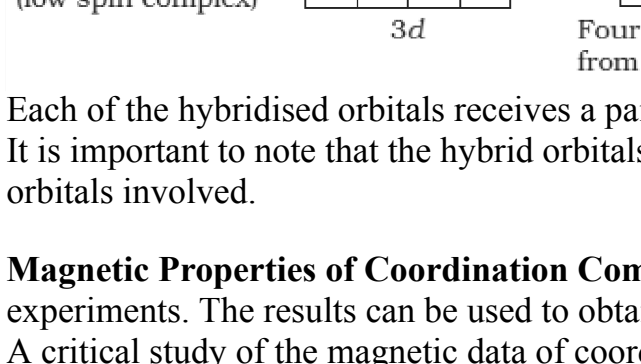
Geometric Isomerism: This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula [MX₂L₂] (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans* isomer.



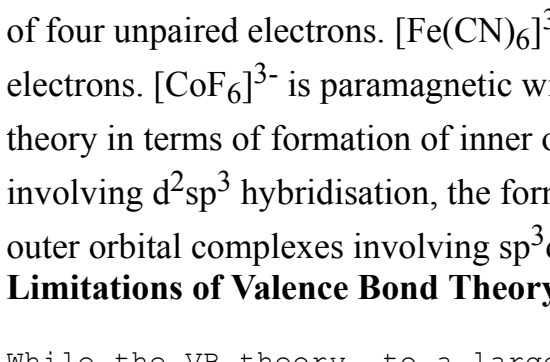
Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula [MX₂L₄] in which the two ligands X may be oriented *cis* or *trans* to each other



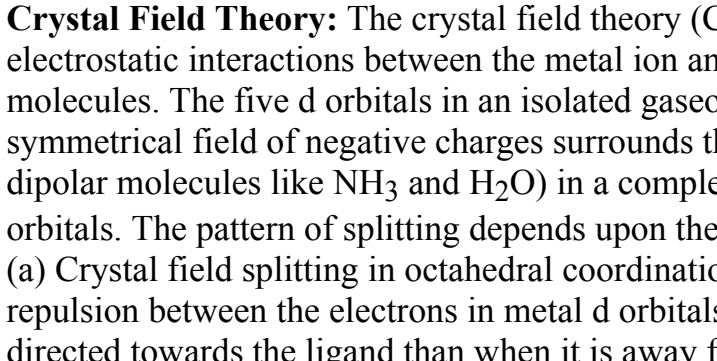
This type of isomerism also arises when didentate ligands L-L' [e.g., NH₂CH₂CH₂NH₂(en)] are present in complexes of formula [MX₂(L-L')₂].



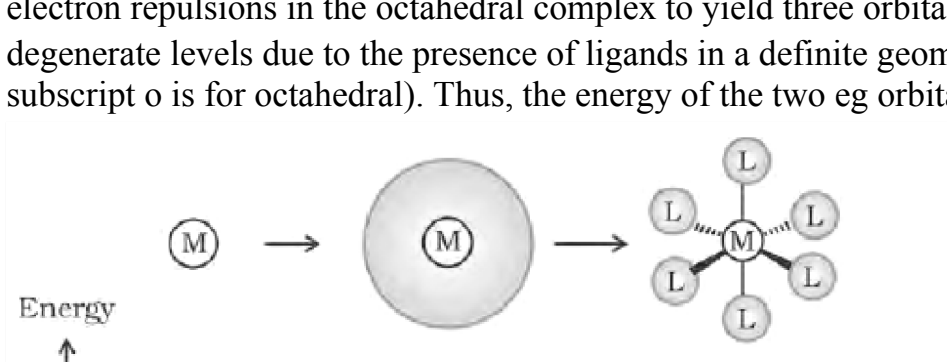
Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma₃b₃] like [Co(NH₃)₃(NO₂)₃]. If three donor atoms of the same ligands occupy adjacent positions, they form the *facial* (fac) isomer. When the positions are around the meridian of the octahedron, we get the *meridional* (mer) isomer.



Optical Isomerism: Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called *dextro* (d) and *laevo* (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving didentate ligands



In a coordination entity of the type [PtCl₂(en)₂]²⁺, only the *cis*-isomer shows optical activity.



Linkage Isomerism: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS⁻, which may bind through the nitrogen to give M-NCS or through sulphur to give M-SCN. Jorgensen discovered such behaviour in the complex [Co(NH₃)₅(NO₂)]Cl₂, which was obtained as the red form, in which the nitric ligand is bound through oxygen (-ONO), and as the yellow form, in which the nitrile ligand is bound through nitrogen (-NO₂).

Coordination Isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by [Co(NH₃)₆][Cr(CN)₆], in which the NH₃ ligands are bound to Co³⁺ and the CN⁻ ligands to Cr³⁺.

Ionisation Isomerism: This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers [Co(NH₃)₅(SO₄)]Br and [Co(NH₃)₅Br]SO₄.

Solvate Isomerism: This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex [Cr(H₂O)₆]Cl₃ (violet) and its solvate isomer [Cr(H₂O)₅Cl]Cl₂.H₂O (grey-green).

Bonding in Coordination Compounds:

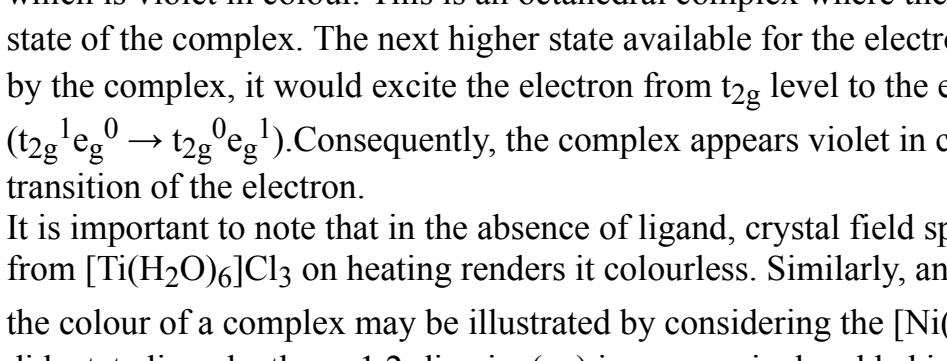
Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions like:

- (i) Why only certain elements possess the remarkable property of forming coordination compounds?
 - (ii) Why the bonds between the ligands and the metal within a coordination entity have directional properties?
 - (iii) Why coordination compounds have characteristic magnetic and optical properties?
- Many approaches have been put forth to explain the nature of bonding in coordination compounds viz., Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT). We shall focus our attention on elementary treatment of the application of VBT and CFT to coordination compounds.

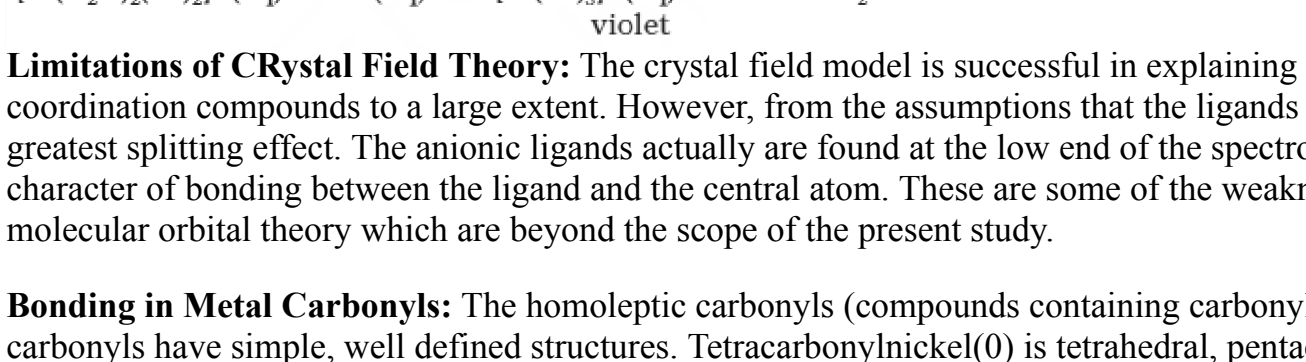
Valence Bond Theory: According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. This is illustrated by the following examples.

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp ³	Tetrahedral
4	dsp ²	Square planar
5	sp ³ d	Trigonal bipyramidal
6	sp ³ d ²	Octahedral

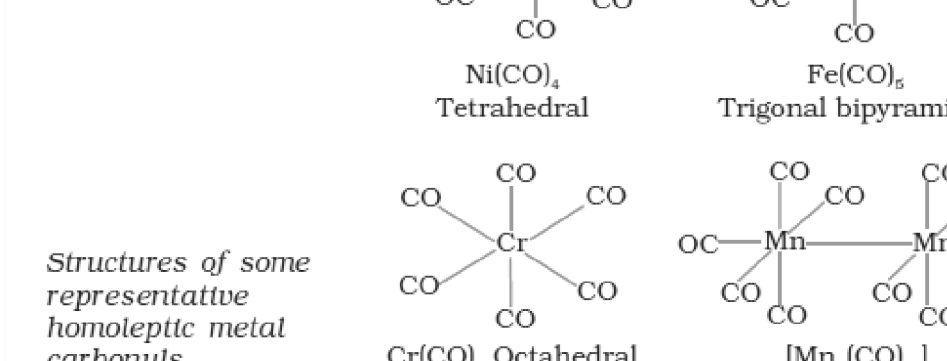
It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory. In the diamagnetic octahedral complex, [Co(NH₃)₆]³⁺, the cobalt ion is in +3 oxidation state and has the electronic configuration 3d⁶. The hybridisation scheme is as shown in diagram.



Here nickel is in +2 oxidation state and the p ion has the electronic configuration 3d⁸. The hybridisation scheme is as shown in diagram. Each Cl⁻ ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, [Ni(CO)₄] has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.



In the square planar complex, the hybridisation involved is dsp². An example is [Ni(CN)₄]²⁻. Here nickel is in +2 oxidation state and has the electronic configuration 3d⁸. The hybridisation scheme is as shown in diagram.



Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron. It is important to note that the hybridised orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

Magnetic Properties of Coordination Compounds: The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the number of unpaired electrons and hence structures adopted by metal complexes. A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with upto three electrons in the d orbitals, like Ti³⁺ (d¹), V³⁺ (d²), Cr³⁺ (d³), two vacant d orbitals are available for octahedral hybridisation with 4s and 4p orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3d electrons are present, the required pair of 3d orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for d⁴ (Cr²⁺, Mn²⁺), d⁵ (Mn²⁺, Fe³⁺), d⁶ (Fe²⁺, Co³⁺) cases, a vacant pair of d orbitals results only by pairing of 3d electrons which leaves two, one and zero unpaired electrons, respectively.

The magnetic data of complexes with more than three spin pairings, especially with coordination compounds containing d⁴ ions. However, with species containing d⁴ and d⁵ ions there are complications. [Mn(CN)₆]³⁻ has magnetic moment of two unpaired electrons while [MnCl₆]³⁻ has a paramagnetic moment of four unpaired electrons. [Fe(CN)₆]³⁻ has magnetic moment of a single unpaired electron while [FeCl₆]³⁻ has a paramagnetic moment of five unpaired electrons. [CoF₆]³⁻ is paramagnetic with four unpaired electrons while [Co(C₂O₄)₃]³⁻ is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. [Mn(CN)₆]³⁻, [Fe(CN)₆]³⁻ and [Co(C₂O₄)₃]³⁻ are inner orbital complexes involving d²sp³ hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, [MnCl₆]³⁻, [FeCl₆]³⁻ and [CoF₆]³⁻ are outer orbital complexes involving sp³d² hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

Limitations of Valence Bond Theory:

- While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:
 - It does not give quantitative interpretation of magnetic data.
 - It does not explain the colour exhibited by coordination compounds.
 - It does not make quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
 - It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
 - It does not distinguish between weak and strong ligands.

Crystal Field Theory: The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH₃ and H₂O) in a complex, it becomes asymmetric and the degeneracy of the orbitals is lifted. The results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

(a) Crystal field splitting in octahedral coordination entities (In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand. Thus, the d_{xy}² and d_{yz}² orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o (Δ_o the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by (3/5)Δ_o and that of the three t_{2g} will decrease by (2/5)Δ_o.



The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below.

I⁻ < Br⁻ < SCN⁻ < Cl⁻ < S²⁻ < F⁻ < OH⁻ < C₂O₄²⁻ < H₂O < N₃⁻ < EDTA⁴⁻ < NH₃ < en < CN⁻ < CO

Such a series is termed as **spectrochemical series**. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the d orbitals of metal ion in octahedral coordination entities. Obviously, the single d orbital occupies one of the lower energy t_{2g} orbitals. In d² and d³ coordination entities, the d electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d⁴ ions, two possible patterns of electron distribution arise:

- (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or
 - (ii) it could avoid paying the price of the pairing energy by occupying the e_g level.
- These two cases possess adjacent positions, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

- (i) If Δ_o < P, the fourth electron enters one of the e_g orbitals giving the configuration t_{2g}³e_g¹.
 - (ii) If Δ_o > P, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration t_{2g}⁴e_g⁰.
- In both cases, the configuration of the complex is known as **strong field ligands** and form low spin complexes.

Calculations show that d⁴ to d⁷ coordination entities are more stable for strong field as compared to weak field cases.

(b) Crystal field splitting in tetrahedral coordination entities: In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that Δ<