1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 03 (Class XII, Semester 01)
Module Name/Title	Coordination Compounds: Part 2
Module Id	lech_10902
Pre-requisites	Werner's theory of coordination compounds, coordination entity, ligands, chelates, primary and secondary valency, nomenclature
Objectives	After going through this module, the learners will be able to: 1. Understand and identify the different types of isomerism shown by various coordination compounds, 2. Know that the bonds of coordination compounds have a directional property, 3. Understand that these compounds have magnetic properties and are generally coloured 4. Understand the nature of bonding in terms of valence bond theory and crystal field theory
Keywords	Structural Isomerism, Stereoisomerism, Geometrical and Optical Isomerism, Paramagmetic and Diamagnetic Compounds, Valence Bond Theory and Crystal Field Theory

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1. Introduction to Types of Isomerism and Bonding in Coordination Compounds

This module discusses in detail the types of isomerism noted in coordination compounds involving different ligands and different coordination numbers. A main feature of transition metal complexes is the presence of closely spaced d orbitals / energy levels of the central metal ions/atoms. The study of the ligands that distort or disturb these energy levels is the key to coordination chemistry. Two significant properties of coordination compounds are colour and magnetic behaviour. The theories that offer an explanation to the above behaviour are valence bond theory and crystal field theory, however the most accurate is ligand field theory which is studied at a higher level. Both the theories have their strengths and limitations.

2. 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 and chemical properties. Two principal types of isomerism are known among coordination compounds and each of these can be further subdivided into different types.

(a) Stereoisomerism

(i) Geometrical isomerism

(ii) Optical isomerism

(b) Structural isomerism

(i) Linkage isomerism

(ii) Coordination isomerism

(iii) Ionisation isomerism

(iv) Solvate isomerism

Stereoisomers have the same chemical formula and bonding sequence but they have different spatial arrangement of the ligands around the central atom. Structural isomers have different bonding sequence. A detailed account of these isomers is given below.

Stereoisomerism

i) 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 $[MX_2L_2]$ (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 as depicted in Fig.1a.

Fig 1a: Geometrical isomers (cis and trans) of $[Pt(NH_3)_2Cl_2]$
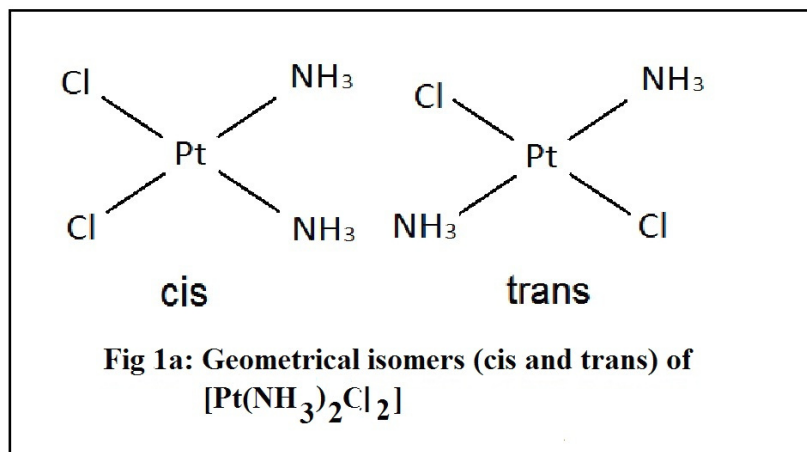
Other square planar complexes of the type MABXL (where A, B, X, L are unidentates) show three isomers-two *cis* and one *trans*. You may attempt to draw these structures. Such isomerism is not possible for tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented *cis* or *trans* to each other (Fig. 1b).

Fig 1b: Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]$
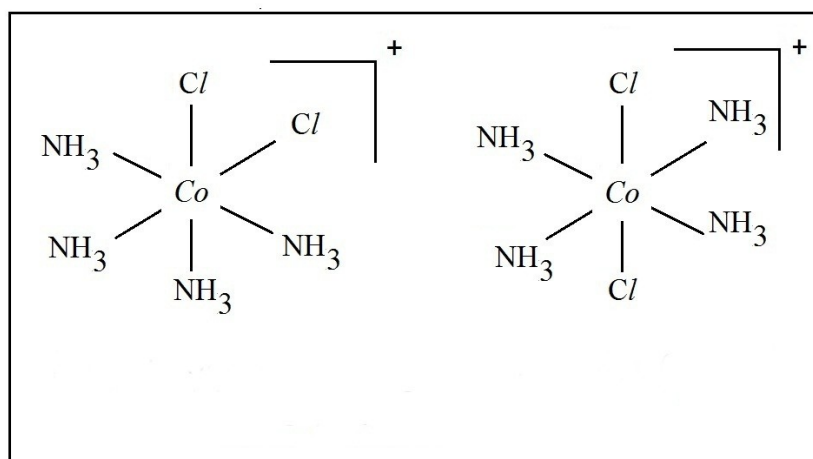
Geometric isomerism also arises in octahedral complexes when didentate ligands L − L [*e.g.*, $NH_2\ CH_2\ CH_2\ NH_2$ (en)] are present in complexes of formula $[MX_2(L-L)_2]$ (Fig. 1c).
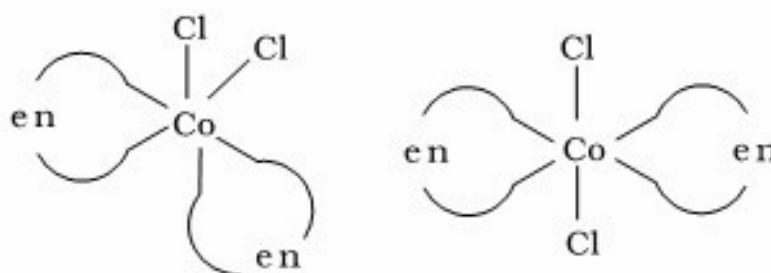
Fig 1c: Geometrical isomers (cis and trans) of [CoCl$_2$(en)$_2$]

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma$_3$b$_3$] like [Co(NH$_3$)$_3$(NO$_2$)$_3$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer (Fig.1d).

**Fig 1d: The facial (fac) and meridional (mer) isomers of [Co(NH$_3$)$_3$(NO$_2$)$_3$]**

Problem 1: Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Solution: Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.
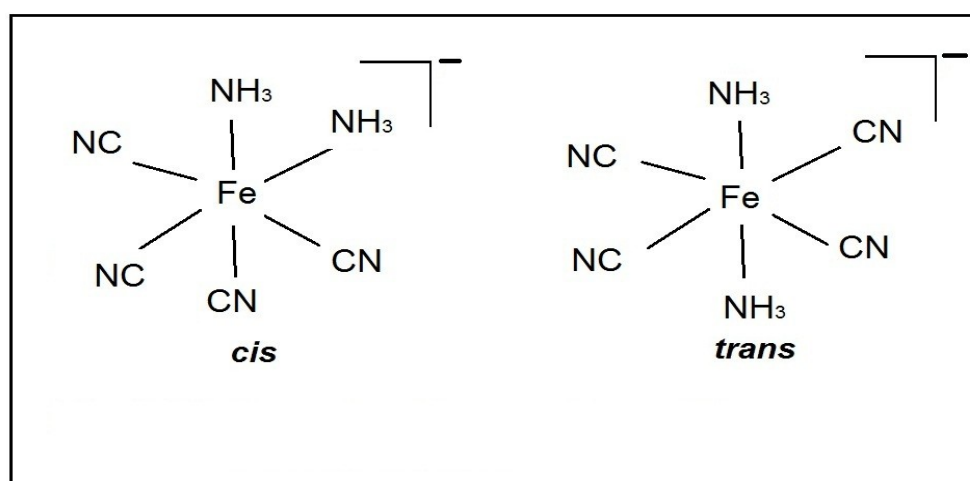
ii) Optical Isomerism

Optical isomers are mirror images that cannot be superimposed on one another. These are called *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 (Fig. 1e).

In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the *cis*-isomer shows optical activity (Fig. 1f). The transform is superimposable on its mirror image and is optically inactive.

Fig 1e: Optical isomers (d and l) of $[Co(en)_2]^{3+}$

Fig 1f :Optical isomers (d and l) of cis-$[Pt\ Cl_2\ (en)_2]^{2+}$
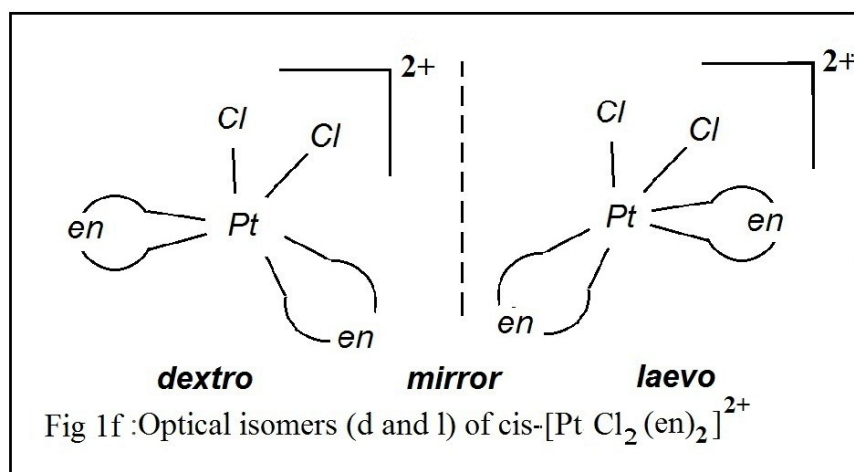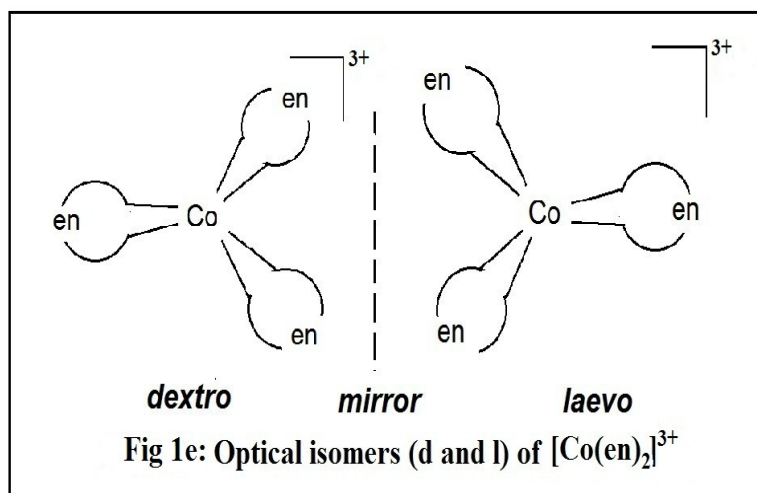
Problem 2: Draw the structures of geometrical isomers of $[Fe\ (NH_3)_2(CN)_4]^-$

Solution:

Problem 3: Out of the following two coordination entities which is chiral (optically active) ?

    a) Cis—$[CrCl_2(ox)_2]^{3-}$ b) trans—$[CrCl_2(ox)_2]^{3-}$

Solution: The two entities are represented as:

cis   trans

$$[CrCl_2(ox)_2]^{3-}$$
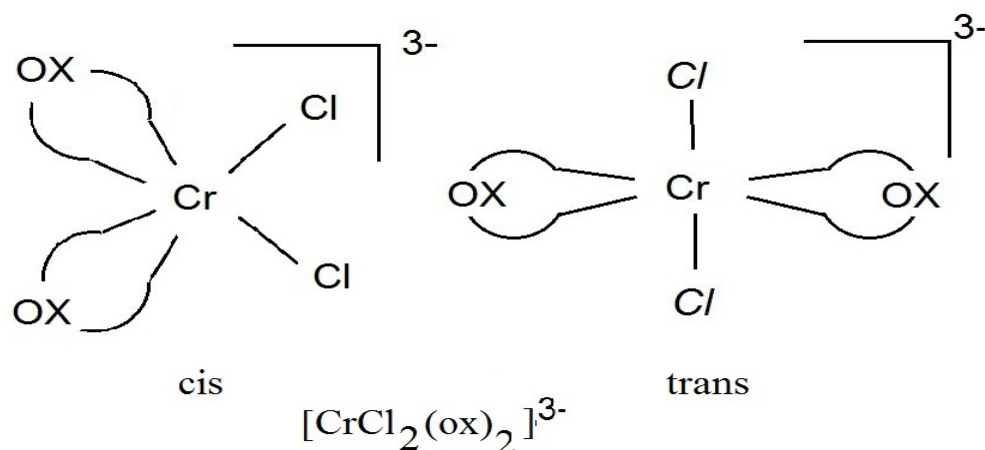
Out of the two cis isomer is chiral (optically active) as it will not be superimposable on its mirror image.

Structural isomerism

i)   Linkage Isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, SCN^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN. Jørgensen discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen (–NO_2).

ii)   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 $[Co(NH_3)_6]$ $[Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}.

iii)   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 ionization isomers $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

iv)   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 $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

**Problem 4:** Indicate the type of isomerism exhibited by the following complexes and draw the structures for these isomers:

   a) $K[Cr(H_2O)_2(C_2O_4)_2]$
   b) $[Pt(NH_3)(H_2O)Cl_2]$

Solution:

   a)   Both geometrical and optical isomers can exist for $K[Cr(H_2O)_2(C_2O_4)_2]$.

Geometrical: Trans isomer is optically inactive, while cis isomer is optically active.

trans - isomer

cis- isomer

Optical:

optically active cis isomer
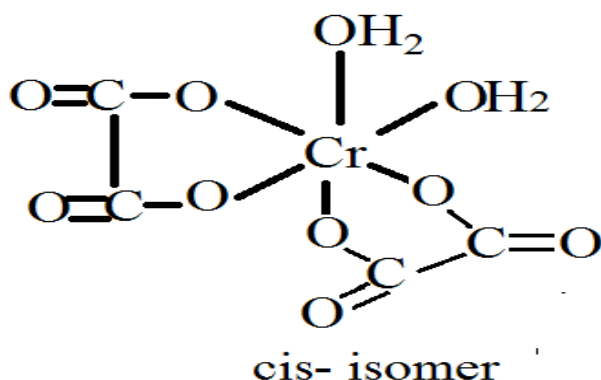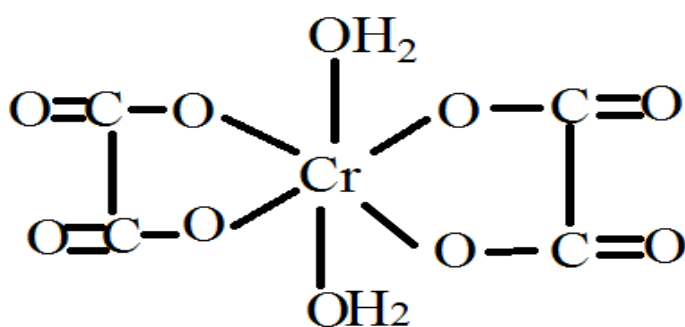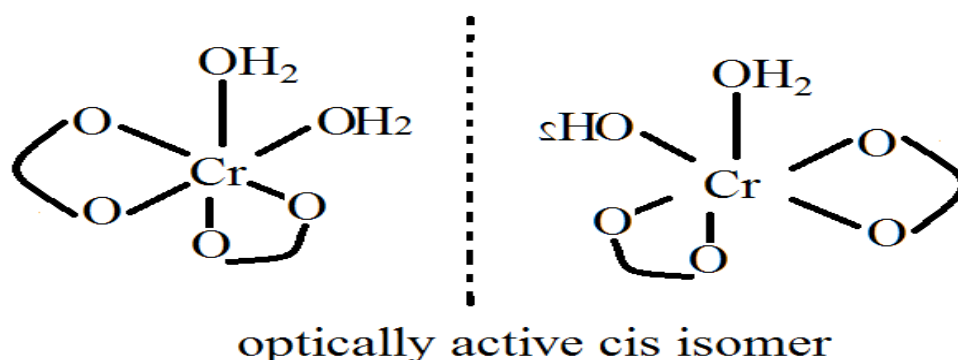
  b) [Pt(NH₃)(H₂O)Cl₂] : It has only geometric isomers, namely cis and trans isomers.
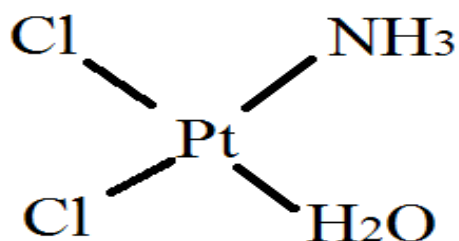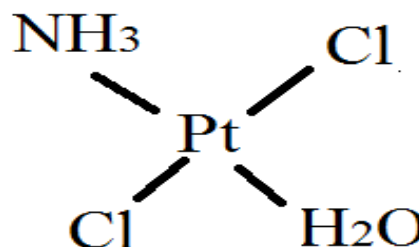
     cis- isomer   trans - isomer

1. Bonding in Coordination Compounds:

Though Werner's theory could explain the structure of coordination compounds and various isomers known it could not answer basic questions like:

  i. Why only certain elements possess the remarkable property of forming coordination compounds?

  ii. Why the bonds in coordination compounds 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.

2.   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 hybridization to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on (Table 1). 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^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

Table 1: Number of orbitals and types of hybridisations

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, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in diagram.
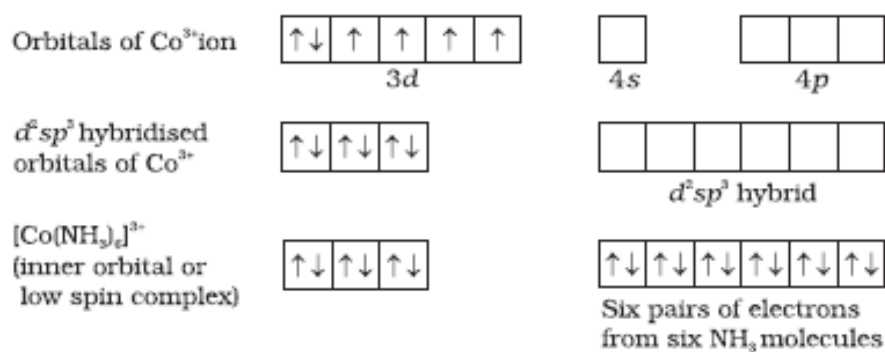

Diagram 1

Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complex. Ligands that cause pairing of d electrons are called strong ligands. The

paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital ($4d$) in hybridisation (sp^3d^2). It is thus called outer orbital or high spin or spin free complex and the ligand which does not cause pairing of d electrons is a weak ligand.
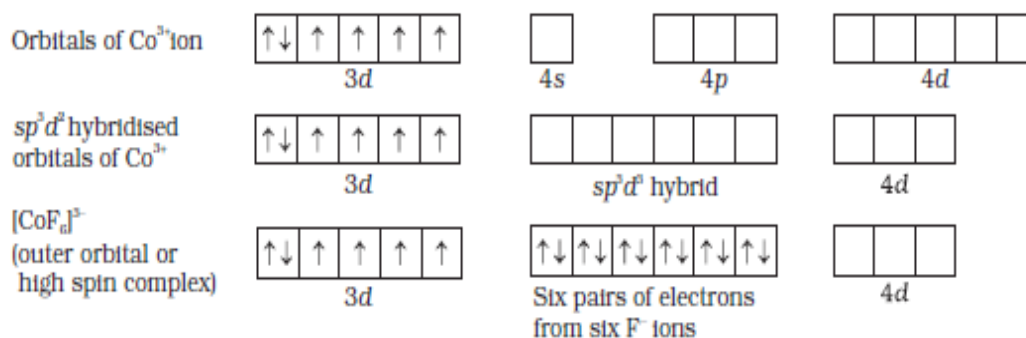

Diagram 2

In tetrahedral complexes one s and three p orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for $[NiCl_4]^{2-}$. Here nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in the diagram 3. 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.

Diagram 3

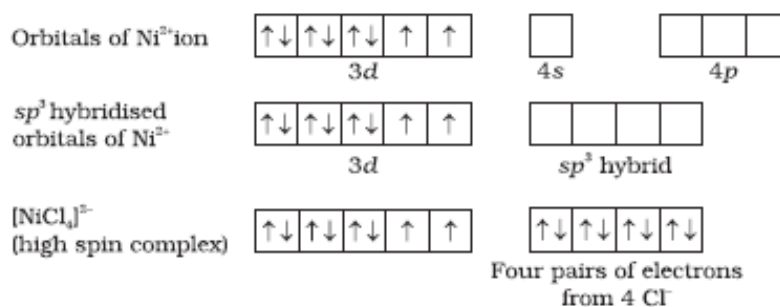In the square planar complexes, the hybridisation involved is dsp^2. An example is $[Ni(CN)_4]^{2-}$ Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram 4.
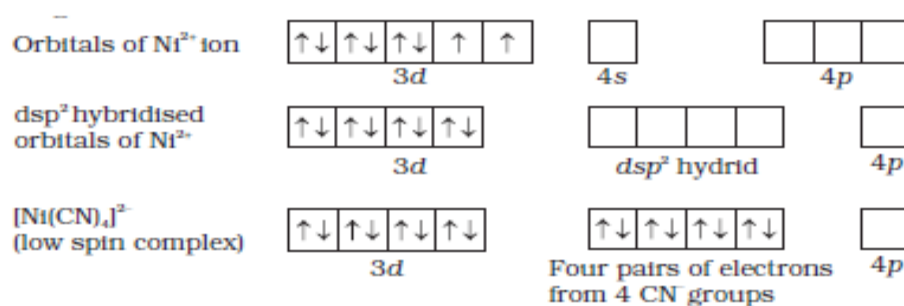
Diagram 4

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 hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

3. 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 structures adopted by metal complexes. The magnetic moment is proportional to the number of unpaired electrons.

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 Ti^{3+} (d^1); V^{3+} (d^2); Cr^{3+} (d^3); 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 d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6 (Fe^{2+}, Co^{3+}) 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 agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ions. However, with species containing d^4 and d^5 ions there are complications. $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ 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 $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the

other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

Problem 5: The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?

Solution: Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the d orbitals.

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:

i.   It involves a number of assumptions.

ii. It does not give quantitative interpretation of magnetic data.

iii. It does not explain the colour exhibited by coordination compounds.

iv. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

v.   It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.

vi. It does not distinguish between weak and strong ligands.

4.   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 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 NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It 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 $d_{x^2-y^2}$ and d_{z^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 (the subscript o is for octahedral) (Fig.2). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_o$ and that of the three t_{2g} will decrease by $(2/5)\Delta_o$.
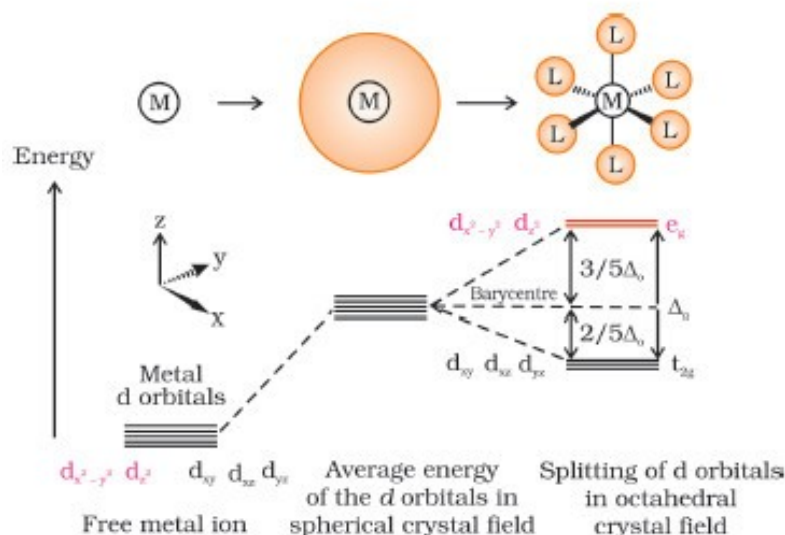

Fig 2: d orbital splitting in an octahedral crystal field

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 case, 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:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$
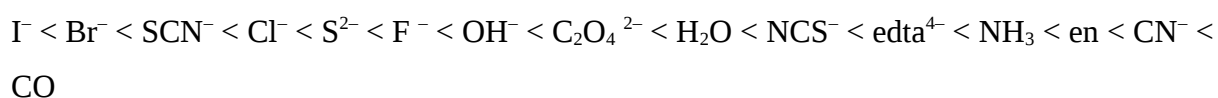
Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

 Let us assign electrons in the d orbitals of metal ion in octahedral coordination entities. Obviously, the single d electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3

coordination entities, the d electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 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. Which of these possibilities occurs, 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 $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$ Ligands for which $\Delta_o < P$ are known as *weak field ligands* and form high spin complexes.

(ii) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as *strong field ligands* and form low spin complexes.

Calculations show that d^4 to d^7 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 (Fig. 3) 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 $\Delta_t = (4/9) \Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.
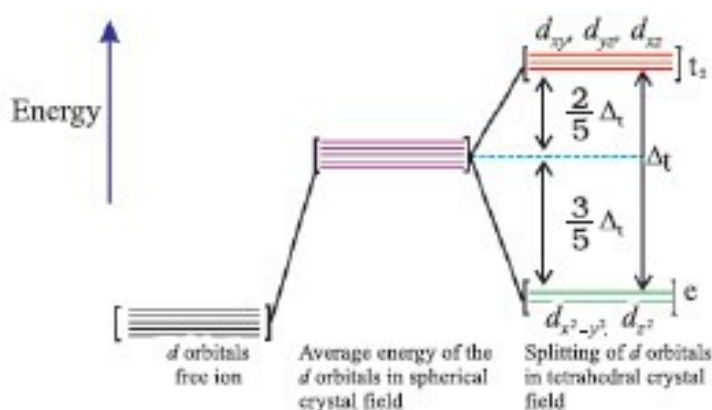

Fig 3: d orbitals splitting in a tetrahedral crystal field

Limitations of Crystal Field Theory

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent. However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the

greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series. Further, it does not take into account the covalent character of bonding between the ligand and the central atom. These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory which are beyond the scope of the present study

5. Summary

Coordination compounds show stereoisomerism as well as structural isomerism. The isomerism chart is summarised as below and examples of each type have been discussed.

(a) Stereoisomerism

(i) Geometrical isomerism (ii) Optical isomerism

(b) Structural isomerism

(i) Linkage isomerism

(ii) Coordination isomerism

(iii) Ionisation isomerism

(iv) Solvate isomerism

The two theories of bonding are Valence Bond Theory (VBT) and Crystal Field Theory (CFT). VBT explains with reasonable success, the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and has nothing to say about the optical properties of these compounds. CFT is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of d orbital energies of the central metal atom/ion. The splitting of the d orbitals provides different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimations of orbital separation energies, magnetic moments and spectral and stability parameters. However, the assumption that ligands constitute point charges creates many theoretical difficulties.