**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 CrCl<sub>3</sub>, CoCl<sub>2</sub> or PdCl<sub>2</sub> have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt(III) 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 CoCl<sub>3</sub>.6NH<sub>6</sub> (Yellow) gave 3 mol AgCl 1 mol CoCl<sub>3</sub>.5NH<sub>6</sub> (Purple) gave 2 mol AgCl 1 mol CoCl<sub>3</sub>.4NH<sub>6</sub> (Green) gave 1 mol AgCl 1 mol CoCl<sub>3</sub>.4NH<sub>6</sub> (Violet) gave 1 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(III) Chloride-Ammonia Complexes Formula Colour Solution conductivity corresponds to [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>3Cl<sup>-</sup> [CoCl(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>2Cl<sup>-</sup> [CoCl2(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup>Cl<sup>-</sup> Yellow 1:3 electrolyte 1:2 electrolyte Purple 1:1 electrolyte Green [CoCl2(NH<sub>3</sub>)<sub>4</sub>] + Cl1:1 electrolyte Violet Note that the last two compounds in the above Table have identical empirical formula, CoCl<sub>3</sub>.4NH<sub>3</sub>, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds. The main postulates are: 1. In coordination compounds metals show two types of linkages (valences)-primary and secondary. 2. The primary valences are normally ionisable and are satisfied by negative ions. 3. 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. 4. 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,  $[Co(NH_3)_6]^{3+}$ ,  $[CoCl(NH_3)_5]^{2+}$  and  $[CoCl_2(NH_3)_4]^+$  are octahedral entities, while  $[Ni(CO)_4]$  and  $[PtCl_4]^{2-}$  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.MgCl<sub>2</sub>.6H<sub>2</sub>O, Mohr's salt, FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.6H<sub>2</sub>O, potash alum, KAl(SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as [Fe(CN)<sub>6</sub>]<sup>4-</sup> of K<sub>4</sub>[Fe(CN)<sub>6</sub>] do not dissociate into Fe<sup>2+</sup> and CN<sup>-</sup> 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, [CoCl3(NH3)3] is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules three chloride ions. Other examples are  $[Ni(CO)_4]$ ,  $[PtCl_2(NH_3)_2]$ ,  $[Fe(CN)_6]^{4-}$ ,  $[Co(NH_3)_6]^{3+}$ . 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 or ion. For example, the central atom/ion in the coordination entities:  $[NiCl_2(H_2O)_4]$ ,  $[CoCl(NH_3)_5]^{2+}$  and  $[Fe(CN)_6]^{3-}$  are  $Ni^{2+}$ ,  $Co^{3+}$  and  $Fe^{3+}$ , 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  $Cl_{1}$ , small molecules such as  $H_{2}O$  or  $NH_{3}$ , larger molecules such as  $H_{2}NCH_{2}CH_{2}NH_{2}$  or  $N(CH_{2}CH_{2}NH_{2})_{3}$ or even macromolecules, such as proteins. CH<sub>2</sub>COO When a ligand is bound to a metal ion through a single donor atom, as with Cl<sup>-</sup>, H<sub>2</sub>O or NH<sub>3</sub>, the ligand is said to be  $\sim$  CH<sub>2</sub>COO<sup>-</sup> unidentate. When a ligand can bind through two donor atoms as in H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>(ethane-1,2-diamine) or C<sub>2</sub>O<sub>4</sub><sup>2-</sup>(oxalate), CH<sub>2</sub>COO the ligand is said to be **didentate** and when several donor atoms are present in a single ligand as in N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion (EDTA<sup>4-</sup>) 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 - N === O said to be a **chelate ligand**. The number of such ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. nitrito-N nitrito-O Ligand which has two different donor atoms and either of the two ligetes in the complex is called **ambidentate** ligand. Examples of such ligands are the NO<sub>2</sub><sup>-</sup> and SCN<sup>-</sup> ions. NO<sub>2</sub><sup>-</sup> ion can coordinate either through nitrogen or  $M \leftarrow NCS$  $M \leftarrow SCN$ thiocyanato-S thiocyanato-N through oxygen to a central metal atom/ion.Similarly, SCN<sup>-</sup> 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,  $[PtCl_6]^{2-}$  and  $[Ni(NH_3)_4]^{2+}$ , the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions,  $[Fe(C_2O_4)_3]^{3-}$  and  $[Co(en)_3]^{3+}$ , the coordination number of both, Fe and Co, is 6 because  $C_2O_4^{2-}$  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  $K_4[Fe(CN)_6]$ , 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,  $[Co(NH_3)_6]^{3+}$  is octahedral,  $[Ni(CO)_4]$  is tetrahedral and  $[PtCl_4]^{2-}$  is square planar. Following figure shows the shapes of different coordination polyhedra. Octahedral Tetrahedral Square planar Trigonal Square bipyramidal pyramidal Shapes of different coordination polyhedra. M represents the central atom/ton and L, a unidentate ligand. 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(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g.,  $[Co(NH_3)_4Cl_2]^+$ , 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: (i) The central atom is listed first. (ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge. (iii) 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. (iv) 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. (v) There should be no space between the ligands and the metal within a coordination sphere. (vi) 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,  $[Co(CN)_6]^{3-}$ ,  $[Cr(H_2O)_6]^{3+}$ , etc. (vii) The charge of the cation(s) is balanced by the charge of the anion(s).

(iii) Names of the anionic ligands end in -o, those of neutral and cationic ligands are the same except agua for H<sub>2</sub>O, ammine for NH<sub>3</sub>, carbonyl for CO and nitrosyl 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, bis, tris, tetrakis are used, the ligand to which they refer being placed in parentheses. For example, [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] is named as dichloridobis(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.  $[Cr(NH_3)_3(H_2O)_3]Cl_3$  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.  $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$  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.  $[Ag(NH_3)_2][Ag(CN)_2]$  is named as: diamminesilver(I) dicyanidoargentate(I)

ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer.

NH,

mer-

isomer [Cr(NH<sub>3</sub>)<sub>6</sub>][Co(CN)<sub>6</sub>], the NH<sub>3</sub> ligands are bound to Cr<sup>3+</sup> and the CN<sup>-</sup> ligands to Co<sup>3+</sup>.

(ii) Why the bonds in coordination compounds have directional properties?

treatment of the application of VBT and CFT to coordination compounds.

Number of Orbitals and Types of Hybridisations

(iii) Why coordination compounds have characteristic magnetic and optical properties?

then become the counter ion. An example is provided by the ionisation isomers [Co(NH<sub>3</sub>)<sub>5</sub>(SO<sub>4</sub>)]Br and [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub>.

allowed to overlap with ligand orbitals that can donate electron pairs for bonding. This is illustrated by the following examples.

Distribution of hybrid

orbitals in space

Tetrahedral

Square planar Trigonal bipyramidal

Octahedral

Octahedra1

sp<sup>3</sup>d<sup>3</sup> hybrid

Six pairs of electrons from six F<sup>-</sup> ions

(i) The cation is named first in both positively and negatively charged coordination entities.

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

**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

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A

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

Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula [MX<sub>2</sub>L<sub>4</sub>] in which the two

Another type of geometrical isomerism occurs in octahedral coordination entities of the type  $[Ma_3b_3]$  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

**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, I to the left). Optical isomerism is common in octahedral complexes involving didentate ligands

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

**Naming of Mononuclear Coordination Compounds:** 

coordination compounds. Each of which can be further subdivided

(i) Geometrical isomerism (ii) Optical isomerism

(i) Linkage isomerism (ii) Coordination isomerism(iii) Ionisation isomerism (iv) Solvate isomerism

detailed account of these isomers are given below.

Geometrical isomers (cis and

Geometrical isomers (cis and trans)

fac-

octahedron, we get the *meridional(mer)* isomer.

of [CoCl,(en),]

The factal (fac) and meridional (mer)

dextro

Coordinatio<u>n</u>

number

4 4

5

6

Orbitals of Co⁵⁺ion

sp³d² hybridised orbitals of Co³+

(outer orbital or high spin complex)

Orbitals of Ni2+ion

sp3 hybridised

dsp<sup>2</sup> hybridised orbitals of Ni<sup>2+</sup>

(low spin complex)

orbitals involved.

[Ni(CN)<sub>4</sub>]2-

Energy

Free metal ion

 $[CoF_{\epsilon}]^{3}$ 

tsomers of

[Co(NH3)3(NO2)3]

trans) of Pt [NH3)2Cl2

(a) Stereoisomerism

(b) Structural isomerism

naming coordination compounds:

ligands X may be oriented cis or trans to each other

Cl
NH<sub>3</sub>
NH<sub>3</sub>
NH<sub>3</sub>
Co
NH<sub>3</sub>
NH<sub>3</sub>
Cl
NH<sub>3</sub>
Cl
NH<sub>3</sub>
Cis
trans
Geometrical tsomers (cts and trans)
of [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>

This type of isomerism also arises when didentate ligands L-L [e.g., NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>(en)] are present in complexes of formula [MX<sub>2</sub>(L-L)<sub>2</sub>].

Optical isomers (d and i) of [Co(en)<sub>3</sub>]<sup>3+</sup>.

In a coordination entity of the type [PtCl<sub>2</sub>(en)<sub>2</sub>]<sup>2+</sup>, only the cis-isomer shows optical activity.

Optical isomers (d and i) of cis-iptCl<sub>2</sub>(en)<sub>3</sub>|<sup>2+</sup> dextro mirror laevo

Linkage Isomerism: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS<sup>-</sup>, 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<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)]Cl<sub>2</sub>, 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<sub>2</sub>).

mirror

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<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> (violet) and its solvate isomer [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>.H<sub>2</sub>O (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?

Many approaches have been put forth to explain the nature of bonding in coordination compounds viz. Valence Bond Theory (VBT),

**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

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

4d

4d

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 diagram. Each  $Cl^2$  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

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

**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.

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

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

dipolar molecules like NH<sub>3</sub> and H<sub>2</sub>O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d

subscript o is for octahedral). Thus, the energy of the two eg orbitals will increase by  $(3/5)\Delta o$  and that of the three  $t_{2g}$  will decrease by  $(2/5)\Delta o$ .

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

(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, eg 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  $\Delta$ 0 (the

The crystal field splitting, Do, 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

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

Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta o$  and the pairing energy, P (P represents the energy

Colour in Coordination Compounds: One of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the

Colour of coordination

entity

Yellow Orange

Pale Yellow

The colour in the coordination compounds can be readily explained in terms of the crystal field theory. Consider, for example, the complex  $[Ti(H_2O)_6]^{3+}$ ,

which is violet in colour. This is an octahedral complex where the single electron ( $Ti^{3+}$  is a  $3d^1$  system) in the metal d orbital is in the  $t_{2g}$  level in the ground state of the complex. The next higher state available for the electron is the empty  $e_g$  level. If light corresponding to the energy of blue-green region is absorbed

 $(t_{2g}^{\phantom{1}}e_{g}^{\phantom{0}0} \rightarrow t_{2g}^{\phantom{2}0}e_{g}^{\phantom{2}0})$ . Consequently, the complex appears violet in colour . The crystal field theory attributes the colour of the coordination compounds to d-d

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from [Ti(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> on heating renders it colourless. Similarly, anhydrous CuSO<sub>4</sub> is white, but CuSO<sub>4</sub>.5H<sub>2</sub>O is blue in colour. The influence of the ligand on

didentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratios en:Ni, 1:1, 2:1, 3:1, the following series of reactions and their associated

the colour of a complex may be illustrated by considering the  $[Ni(H_2O)_6]^{2+}$  complex, which forms when nickel(II) chloride is dissolved in water. If the

Limitations of CRystal Field Theory: The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of

The metal-carbon bond in metal carbonyls possess both s and p character. The M–C s bond is formed by the donation of lone pair of electrons on the carbonyl

**Importance and applications of Coordination Compounds:** The coordination compounds are of great importance. These compounds are widely present in

• Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of

• Hardness of water is estimated by simple titration with Na<sub>2</sub>EDTA. The Ca<sup>2+</sup> and Mg<sup>2+</sup> ions form stable complexes with EDTA. The selective estimation of

• Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity  $[Au(CN)_2]^-$  in aqueous solution. Gold can be separated in metallic form from this solution by

• Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure

the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems,

ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and

instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), a-nitroso-b-naphthol, cupron, etc.

carbon into a vacant orbital of the metal. The M–C p bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding p\* orbital of carbon monoxide. The metal to ligand bonding creates a **synergic effect** which strengthens the bond between CO and the metal.

complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is

Violet

Red

Blue

Violet

absorbed by the complex, it appears red. Following table gives the relationship of the different wavelength absorbed and the colour observed.

(i) If  $\Delta o < P$ , the fourth electron enters one of the  $e_q$  orbitals giving the configuration  $t_{2q}^{3}e_q^{1}$ .

Ligands for which  $\Delta o$  < P are known as **weak field ligands** and form high spin complexes.

It does not make exact predictions regarding the tetrahedral and square planar structures of

orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

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

Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT). We shall focus our attention on elementary

**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<sub>3</sub> ligands are bound to  $Co^{3+}$  and the  $CN^{-}$  ligands to  $Cr^{3+}$ . In its coordination

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

called outer orbital or high spin or spin free complex. Thus:

since nickel is in zero oxidation state and contains no unpaired electron.

Type of

 $sp^3$ 

 $dsp^2$ 

 $sp^3d$ 

 $sp^3d^2$ 

 $d^2sp^3$ 

4p

dsp² hydrid

Four pairs of electrons from 4 CN groups

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 $_2$ O $_4$ ) $_3$ ] $^{3-}$  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 $_2$ O $_4$ ) $_3$ ] $^{3-}$  are inner orbital complexes involving  $d^2$ sp $^3$  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 $^3$ d $^2$  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:

(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.

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

Average energy

of the d orbitals in

spherical crystal field

d orbital splitting in an octahedral crystal field

arranged in a series in the order of increasing field strength as given below:

Splitting of d orbitals

in octahedral

crystal field

 $I^{-} < Br^{-} < SCN^{-} < Cl^{-} < S^{2-} < F^{-} < OH^{-} < C_{2}O_{4}^{2-} < H_{2}O < NCS^{-} < EDTA^{4-} < NH_{3} < en < CN^{-} < CO$ 

(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 eg level.

required for electron pairing in a single orbital). The two options are:

(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 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. The 'g' subscript is used for the octahedral and square planar complexes which have centre of symmetry. Since tetrahedral complexes lack symmetry, 'g' subscript is not used with energy levels.

Energy

Energy

Average energy of the d orbitals in spherical

d orbital splitting in a tetrahedral crystal

Wavelength of light

absorbed (nm)

535

500

475

310

600

498

by the complex, it would excite the electron from  $t_{2g}$  level to the  $\boldsymbol{e}_g$  level

+ en (aq) =  $[Ni(H_2O)_4(en)]^{2+}(aq)$  +  $2H_2O$ pale blue

blue/purple

+ 2H2O

 $[Mn_2(CO)_{10}]$ 

 $[Ni(H_2O)_4(en)]^{2+}(aq) + en (aq) = [Ni(H_2O)_2(en)_2]^{2+}(aq) + 2H_2O$ 

 $[Ni(H_2O)_2(en)_2]^{2+}(aq) + en (aq) = [Ni(en)_3]^{2+}(aq)$ 

Splitting of d orbitals in tetrahedral crystal

Table 9.3: Relationship between the Wavelength of Light absorbed and the

Colour of light

absorbed

Colour observed in some Coordination Entities

Yellow

Blue

Red

Blue Green

Ultraviolet

Blue Green

d orbitals

Coordinaton

entity

 $[Co(NH_3)_5(H_2O)]^{3+}$ 

transition of the electron.

colour changes occur:

Structures of some representative homoleptic metal

Synergic bonding

complex.

the addition of zinc.

Example of synergic bonding interactions in a carbonyl

industry and medicine. These are described below:

carbonyls.

 $[Ni(H_2O)_6]^{2+}$  (aq)

[CoCl(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>

[Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>

[Co(CN)<sub>6</sub>]<sup>3-</sup>

[Cu(H2O)4]2+

 $[T1(H_2O)_6]^{3+}$ 

possible patterns of electron distribution arise:

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. **Bonding in Metal Carbonyls:** The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral, pentacarbonyliron(0) is trigonalbipyramidal while hexacarbonyl chromium(0) is octahedral.

Decacarbonyldimanganese(0) is made up of two square pyramidal Mn(CO)<sub>5</sub> units joined by a Mn – Mn bond. Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups.

Tetrahedral

Trigonal bipyramidal

OCCO

Trigonal bipyramidal

Cr(CO), Octahedral

Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B12, cyanocobalamine, the anti– pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, [(Ph<sub>3</sub>P)<sub>3</sub>RhCl], a Wilkinson catalyst, is used for the hydrogenation of alkenes.
Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, [Ag(CN)<sub>2</sub>]<sup>-</sup> and [Au(CN)<sub>2</sub>]<sup>-</sup> than from a solution of simple metal ions.
In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, [Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>3</sup>-.
There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: cis–platin and related compounds.

nickel is converted to  $[Ni(CO)_4]$ , which is decomposed to yield pure nickel.

these ions can be done due to difference in the stability constants of calcium and magnesium complexes.