Class : 11

2023 – 24

COORDINATION COMPOUNDS

Werner's Theory of Coordination Compounds:

- Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds such as $CrCl_3$,$CoCl_2$ or $PdCl_2$ have primary valence of 3, 2 and 2 respectively.
- 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.

Table: Formulation of Cobalt(III) 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	$[CoCl(NH_3)4]^{+}Cl$	1: 1 electrolyte

- Werner in 1898, propounded his theory of coordination compounds. The main postulates are: In coordination compounds metals show two types of linkages (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.

Difference between a double salt and a 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 that double salts such as carnallite, KCl, $MgCl_2 \cdot 6H_2O$, Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, potereht alum, $KAl(SO_4)_2 \cdot 12H_2O$, etc. dissociate into simple ions completely wher dissolved in water. However, complex ions such as $[Fe(CN)_6)^4$ of $K_4[Fe(CN)_6]$ do not dissociate into Fe^{2+} and CN^-ions.

Definitions of Some Important Terms Pertaining to Coordination Compounds

- **Coordination entity :** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.
- **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 or ion.

Ligands:

- The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. When a ligand is bound to a metal ion through a single donor atom, ss with Cl,H_2O or NH_3, the ligand is said to be unidentate.
- When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_3$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be didentate and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate.

- 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 denticity of the ligand Ligand which has two different donor atoms is called ambidentate ligand Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion cll 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 donar atoms to which the metal is directly bonded.

- **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.
- **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.
- **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.

  Homoleptic and heteroleptic complexes: Complexes in which a metal is bound to only one kind of donor groups, e.g., $[Co(NH_3)_6]^{3+}$, 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:

The following rules are applied while writing the formulas:

The central atom is listed first.

- The ligands are then listed in alphabetical order.
- Polydentate ligands are also listed alphabetically.
- The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets.
- There should be no space 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, $[Co(CN)_6]^{3-}$,$[Cr(H_2O)_6]^{3+}$, etc.
- The charge of the cation(s) is balanced by the charge of the anion(s).

Naming of Mononuclear Coordination Compounds

The following rules are used when naming coordination compounds:

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

The ligands are named in an alphabetical order before the name of the central atom/ion.

Names of the anionic ligands end in -0 , those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO.

- Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity.
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

  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.

- The neutral complex molecule is named similar to that of the complex cation. The following examples illustrate the nomenclature for coordination compounds.
- (i) $|Cr(NH_3)_3(H_2O)_3|Cl_3$ is named as:
  triamminetriaquachromium(III) chloride
  (ii) $[Co(H_2NCH_2CH_2NH_2)_3]^2(SO_4)_3$ is named as:
  tris(ethane-1,2-diamine)cobalt(III) sulphate
  (iii) $\left[Ag(NH_3)_2\|Ag(CN)_2\right]$ 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.

Stereoisomerism

(i) Geometrical isomerism
(ii) Optical isomerism

Structural isomerism

(i) 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.

Geometric Isomerism : This type of isomerism arises in heterolytic complexes due to different possible geometric arrangements of the ligands.

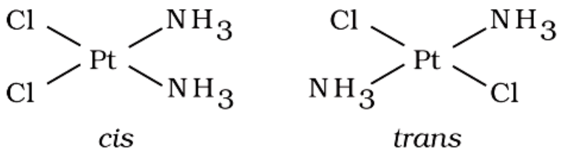


Fig.: Geometrical isomers (cis and trans) of $P([NH_3)_2Cl_2]$

In a square planar complex of formula $[MX_2\ L_2]$ (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.

Other square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers-two cis and one trans.

Fig.: Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]$

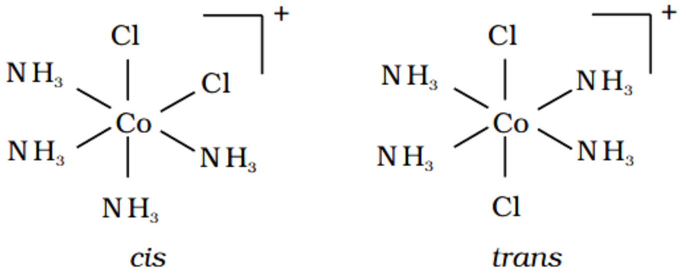


Fig.: Geometrical isomers (cis and trans) of $\left[CoCl_2(en)_2\right]$

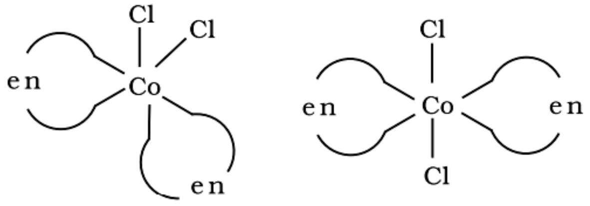
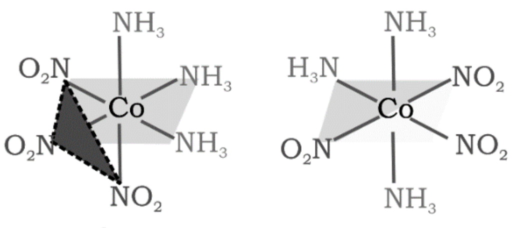


Fig.: The facial (fac) and meridional (mer) isomers of $[Co(NH_3)_3(NO_2)_3]$



fac– *mer–*

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.

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.

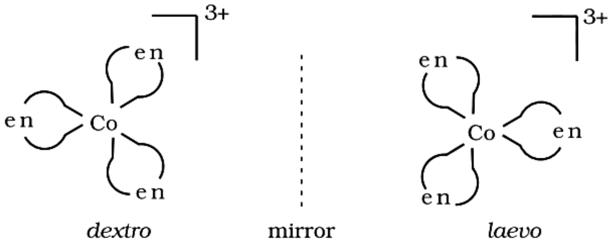


Fig.: Optical isomers (d and I) of $\left[Co(en)_3\right]^{3+}$

∴ In a coordination entity of the type $\left[PtCl_2(en)_2\right]^{2+}$, only the cis-isomer shows optical activity.

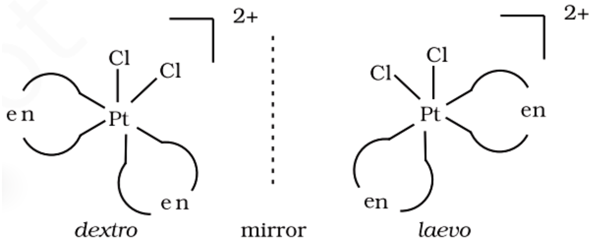


Fig.: Optical isomers (d and f) of cis- $\left[PtCl_2(en)_2\right]^{2+}$

- **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.
- **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 $[Co(NH_3)_6]\left[Cr(CN)_6\right]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^-ligands to Cr^{3+}.

- **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 $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

- **Solvate Isomerism :**
  This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl^2Cl_2 \cdot H_2O$ (grey-green).

Bonding in Coordination Compounds

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).

- **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.
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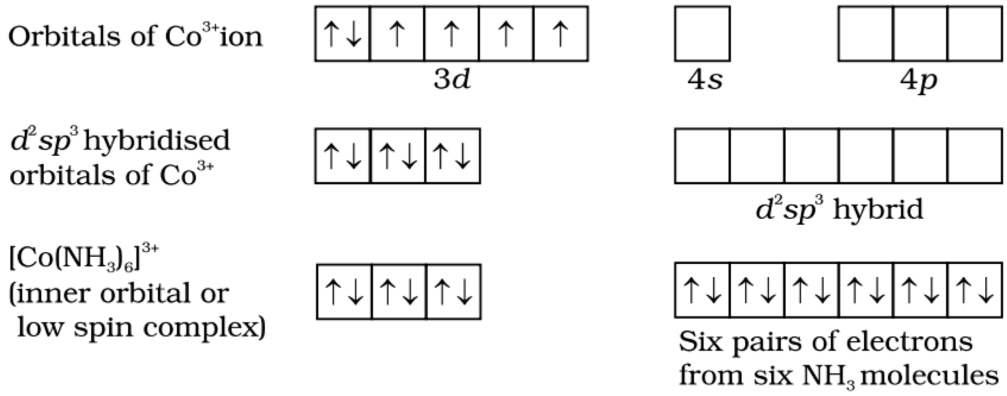
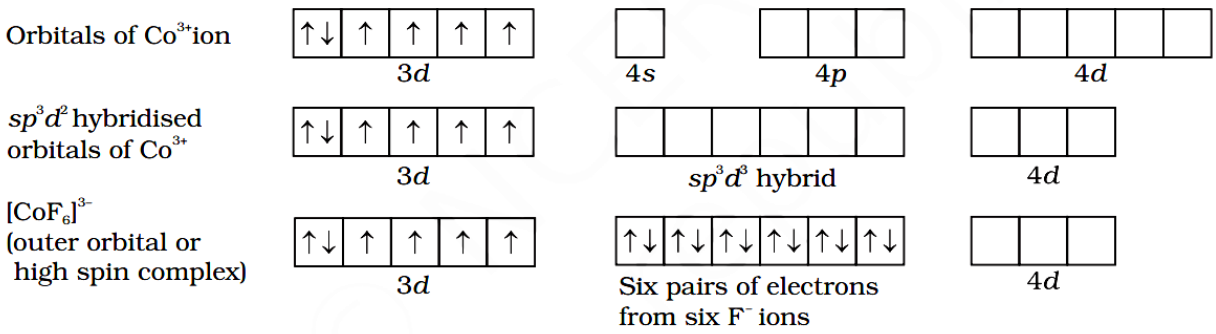
- **Table :** Number of Orbitals and Types of Hybridisation

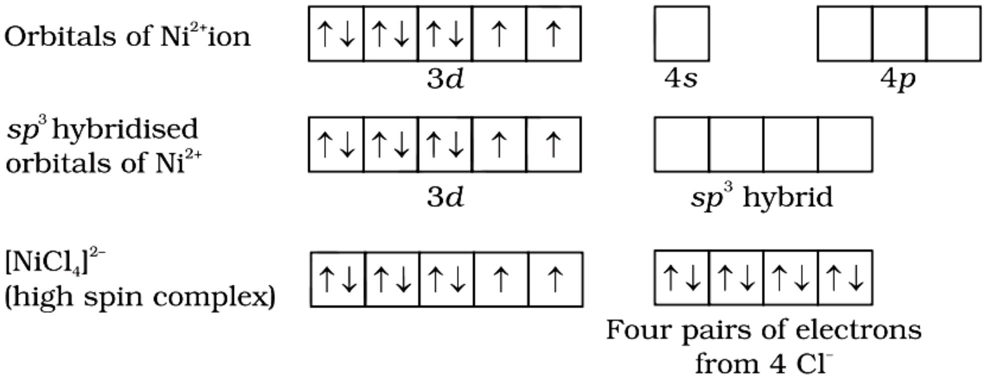
Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^3	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral



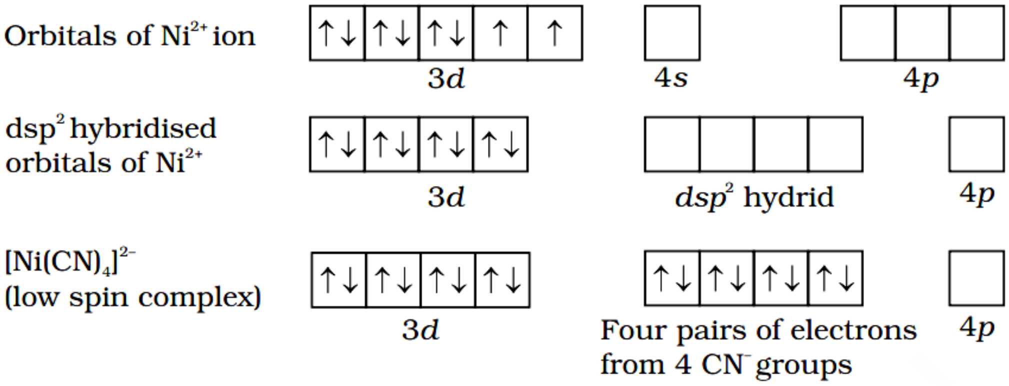
In the formation of this complex, since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complex. The paramagnetic octahedral complex, $[CoF_6)^2$ uses outer orbital ($4d$) in hybridisation (sp^3d^2). It is thus called outer orbital or high spin or spin free complex Thus:



In tetrahedral complexes one s and three p orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally.



- $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.
- In the square planar 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 $3d^8$.



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.

- $[\mathrm{Mn(CN)_6}]^{3-}$ has magnetic moment of two unpaired electrons while $[\mathrm{MnCl_6}]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[\mathrm{Fe(CN)_6}]^{3-}$ has magnetic moment of a single unpaired electron while $[\mathrm{FeF_6}]^{3-}$ has a paramagnetic moment of five unpaired electrons.
- $[\mathrm{CoF_6}]^{3-}$ is paramagnetic with four unpaired electrons while $[\mathrm{Co(C_2O_4)_3}]^{3-}$ is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. $[\mathrm{Mn(CN)_6}]^{3-}$,$[\mathrm{Fe(CN)_6}]^{3-}$ and $[\mathrm{Co(C_2O_4)_3}]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation.

Limitations of Valence Bond Theory

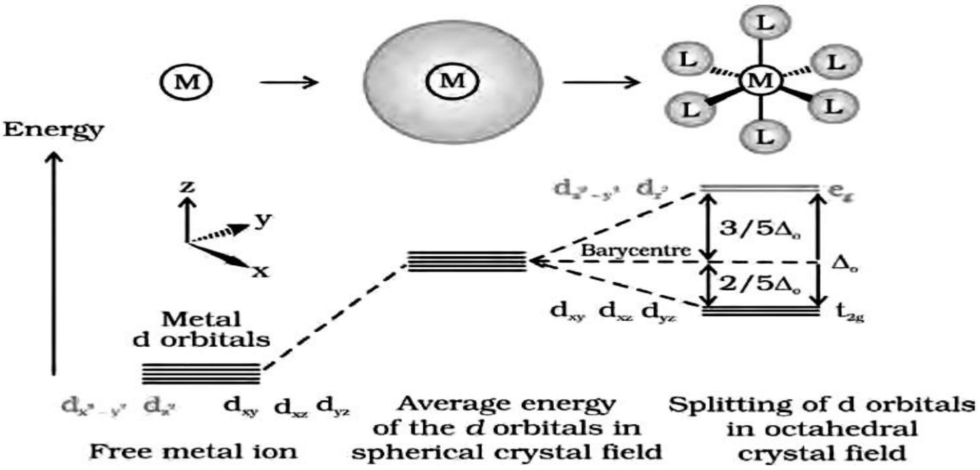
- It involves a number of assumptions.
- It does not give quantitative interpretation of magnetic data.
- It does not explain the colour exhibited by coordination compounds.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- It does 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.
- 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 in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals.

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.
- The $d_{x^2-y^2}$ and d_2 orbitals which point towards the axes atong the direction of the ligand will experience more repulsion and will be raised in energy; and the d_x, d_{yz} and d_x orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.
- The degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yicld three orbitals of lower energy, t_{2g} set and two orbitals of highef, energy, e_g set. This splitting of the degenerate levels due to the presence of ligand f in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0.



- The energy of the two e_g orbitals will increase by (3/5) Δ_0 and that df the three t_{2g} will decrease by (2/5)Δ_0.
- The crystal field splitting, Δ_0, 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 whercas 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:

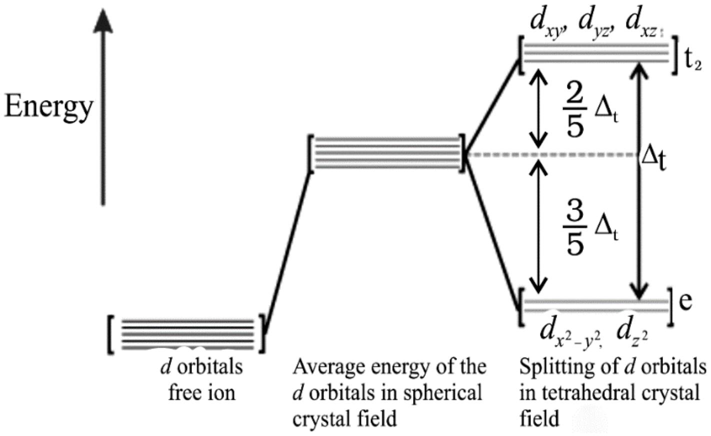
$$I^-<Br^-<SCN<Cl<S^{2-}<F^-<OH^-<C_2O_4^{2-}<H_2O<NCS^-<EDTA^+$$
$$<NH_3<en<CN-<CO$$

- Such a series is termed as spectrochemical series.
- Depends on the relative magnitude of the crystal field splitting, A, and the pairing energy, p (p represents the energy required for electron pairirs in a single orbital).
- Ligands for which $\Delta_0<p$ are known as weak field ligands and form high spin complexes.
- If $\Delta_0>p$, ligands which produce this effect are known as simols' field ligands and form low spin complexes.

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 $A_t=(4/9)\Delta_0$.
- Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, bow spin configurations are rarely observed.

  Fig.: d orbital splitting in a tetrahedral crystal field



Colour in Coordination Compounds :

- The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red.
- 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 $3d'$ 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 by the complex, it would excite the clectron from t_{2g} level to the e_g level $\left(t_{2g}{}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1\right)$. Consequently, the complex appears violet in colour:
- 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 $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4,5H_2O$ is blue in colour.

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 ligand 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.

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 (o) is octahedral.

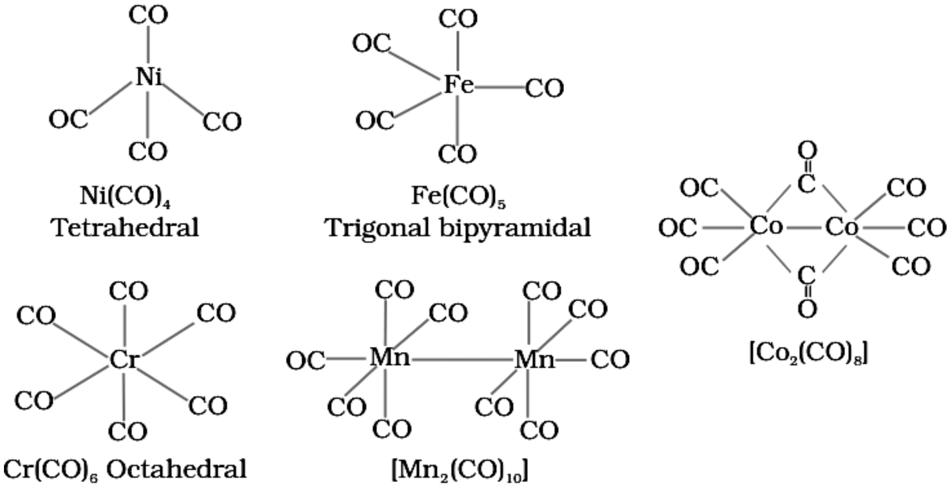


Fig: Structures of some representative homoleptic metal carbonyls

- The metal-carbon bond in metal carbonyls possess both s and p charactet. The M-C s bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The $\mathrm{M}-\mathrm{C}\pi$ bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

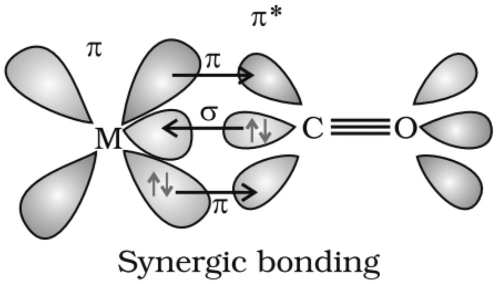


Fig.: Example of synergic bonding interactions in a carbonyl complex

Stability of Coordination Compounds

- The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant (stability or formation) for the association. Quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$\mathrm{M}+4\ \mathrm{L} \rightleftharpoons \mathrm{ML}_4$$

then the largher the stability constant, the higher the proportion of ML_4 that exist in solution.

$$
\begin{aligned}
M+L &\rightleftharpoons ML K_1=[ML]/[M][L]\\
ML+L &\rightleftharpoons ML_2\ K_2=[ML_2]/[ML][L]\\
ML_2+L &\rightleftharpoons ML_3 K_3=[ML_3]/[ML_2][L]\\
ML(n\text{-}1)+L &\rightleftharpoons ML_n K_4=[ML_n]/\left[ML_{(n-1)}\right][L]
\end{aligned}
$$

where $K_1, K_2, \ldots . K_n$, etc., are stepwise stability constants. The overall stability constant (β) of the formation of species ML_n from m and L can be given as:

$$M+nL \rightleftharpoons ML_n\ \beta=[ML_a/[M][L]^n$$

The stepwise and overall stability constant are therefore related as follows:

$$\beta_n=K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots\ldots K_n$$

The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of the formation constant.

Importance and Applications of Coordination Compounds

- The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:
- Coordination compounds find use in many qualitative and quantitative chemical analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α-nitroso- β-maphthol, cupron, etc.
- Hardness of water is estimated by simple titration with Na_2 EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.
- 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 B_{12}, cyanocobalamine, the anti -perniciuous anamia factor, is a coordination compound of cobalt.

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