

Coordination Compounds

[TOPIC 1] Introduction, Nomenclature and Isomerism of Coordination Compounds

For a metal compound made by the combination of two or more ions/molecules in which all the ions/molecules do not dissociate into its constituents in aqueous solution are known as **complex compounds**.

Coordination compounds are the compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds. e.g. $[\text{CoCl}_3(\text{NH}_3)_3]$ is a coordination compound in which cobalt is surrounded by three ammonia molecules and three chloride ions. The species within the square bracket are coordination entities.

If the coordinate species carries a positive or negative charge, it is called a **complex ion**. e.g. $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

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. Double salt such as Mohr's salt $\{\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}\}$ dissociates into simple ions completely when dissolved in water but complex compound such as $\text{K}_4[\text{Fe}(\text{CN})_6]$ does not dissociate into its ions (i.e. K^+ , Fe^{2+} and CN^- ions.)

1.1 Terminology Related to Coordination Compounds

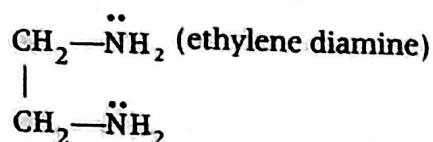
Ligand

The donor atoms, ions or molecules which donate a pair of electrons to the central metal atom or ion and form coordinate bonds are called ligands.

Denticity

The number of ligating (donor) atoms present in a ligand is called the denticity of ligand.

Ligands may be **unidentate** [containing only one donor atom], **didentate** or **bidentate** [containing two donor atoms like



or polydentate [more than two donor atoms], e.g. EDTA⁴⁻ (ethylene diamine tetra-acetate ion) a hexadentate ligand.

Ambidentate Ligand

Unidentate ligands containing more than one coordinating atoms are called ambidentate ligands. e.g. NO₂⁻ can link through N or O.

Central Metal Atom or Ion

In a coordination entity, the metal atom or ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it is called central metal atom or ions.

Coordination Number

The number of ligand donor atoms to which the metal is directly bonded is called coordination number. In case of bidentate ligands, the number of donor atoms will be double e.g. in [Cu(NH₃)₄]²⁺ and [Fe(C₂O₄)₃]⁴⁻, coordination numbers of Cu and Fe are 4 and 6 respectively.

Coordination Sphere and Counter Ions

The central atom/ion and the ligands attached to it are enclosed in the square brackets are collectively known as **coordination sphere**.

The ionisable groups written outside the brackets are called **counter ions**. For example in K₂[PtCl₆], [PtCl₆]²⁻ is the coordination sphere and K⁺ ions are the counter ions.

Coordination Polyhedron

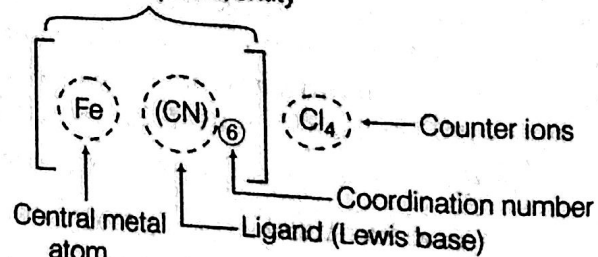
It is the spatial arrangement of the ligand atoms which are directly attached to the central atom ion. The most common coordination polyhedra are octahedral, square planar and tetrahedral.

Charge on the Complex Ion

The charge carried by a complex ion is the algebraic sum of the charges carried by the central metal ion and the total ligands attached to the central metal ion.

For example, in the complex ion, [Cu(NH₃)₄]²⁺, Cu²⁺ ion carries a charge of +2 and as NH₃ molecules are neutral, therefore, the net charge on the complex ion is +2.

Coordination sphere/entity



Depicting various terms used in coordination compounds

Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one type of donor groups are known as homoleptic, e.g. [Co(NH₃)₆]³⁺. Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic, e.g. [Co(NH₃)₄Cl₂]⁺.

1.2 Rules for Writing Formula of Mononuclear Coordination Compounds

- (i) Formula of complex cation (simple or complex) is written first.
- (ii) Coordination entity is enclosed in square brackets.
- (iii) In coordination sphere, central atom is written first, followed by ligands in alphabetical order of their names.
- (iv) In abbreviated ligands like en, ox, first letter of abbreviation is considered.
- (v) When ligands are polyatomic, their formulas are enclosed in parenthesis.
- (vi) There should be no space between the ligands and the metal within a coordination sphere.
- (vii) 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.
- (viii) The charge of the cation is balanced by the charge on the anion.

1.3 Rules for Naming of Mononuclear Coordination Compounds

- (i) Complex cation is named first followed by anion. (if present)
- (ii) The ligands are named in an alphabetical order before the name of the central atom/ion.
- (iii) Names of the anionic ligands end in *-o*. e.g. chloro, cyano etc. Neutral ligands have no special ending like NH_3 (ammine), H_2O (aqua) and positive ligands end in *-ium* like NO^+ (nitrosonium).
- (iv) Prefixes mono, di, tri etc. are used to indicate the number of individual ligands in coordination entity. When the names of the ligands includes a numerical prefix, then the terms, *bis*, *tris*, are used, the ligand to which they refer being placed in parenthesis.

- (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. But if the complex ion is an anion, the name of the metal ends with the suffix '*-ate*'.

Note The 2004 IUPAC draft recommends that anionic ligands will end with *-ido* so that chloro would become chlorido, etc.

1.4 Isomerism in Coordination Compounds

This arises due to different structural arrangements (structural isomerism) or spatial arrangements (stereoisomerism) of compounds having same formula.

Structural Isomerism

Ionisation Isomerism

When the complexes with same composition give different ions in solution. e.g. $[\text{Co}(\text{NH}_3)_5\text{Br}] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5 \text{SO}_4] \text{Br}$.

Solvate/ Hydrate Isomerism

When complex differ in the number of water (Solvent) molecules present as ligand, e.g. $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$

Linkage Isomerism

When complexes differ only in the point of attachment of the ambidentate ligand with central metal atom. e.g. $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$

Coordination Isomerism

When the interchange of ligands take place between cationic and anionic entities of different metal ions present in a complex. e.g. $[\text{Co}(\text{en})_3] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{en})_3] [\text{Co}(\text{CN})_6]$.

Stereoisomerism

Geometrical Isomerism

When similar groups are present in adjacent position, it is *cis*. When they are present in opposite position it is *trans*. It occurs in square planar compound of type $[MA_2B_2]$, $[MA_2BC]$, $[M(AB)_2]$

$[AB = \text{unsymmetrical ligand}]$ and octahedral complexes of type $[MA_4B_2]$, $[M(AA)_2B_2]$ or $[M(AA)_2BC]$ [$AA = \text{symmetrical bidentate ligand}$] and $[MA_3B_3]$ shows *fac* and *mer* geometrical isomers.

Optical Isomerism

This is shown by complexes whose mirror images are non-superimposable. Such complexes are called **optical isomers**. It is shown by octahedral complexes and exists in two forms *laevo* and *dextro*. The isomer which rotates the plane polarised light towards right is called *dextro* rotatory (*d*-) and the other rotates towards left is called *laevo* - rotatory (*l*-). It is shown by the complexes of the type $[M(AA)_3]$, $[M(AA)_2B_2]$ [only *cis*- form shows optical isomerism but not *trans* form], $[M(AA)_2AB]$ (only *cis* - form but not *trans* forms) and $M(AA)_2B_2$. [$AA = \text{bidentate ligand like en, ox}$]

NOTE Square planar complexes of the type $[MABCD]$ shows three geometrical isomers: two *cis* and one *trans*.

Tetrahedral complexes $[MA_4]$ or $[MA_3B]$ do not show geometrical isomerism because the relative positions of unidentate ligands attached with central atom are the same with respect to each other.

[TOPIC 2] Bonding and Stability in Coordination & Organometallic Compounds

2.1 Werner's Theory of Coordination Compounds

According to Werner's theory, metals consist of two types of valencies called **primary valency** and **secondary valency**. Primary valency is same as shown by the metal in its simple salts and it is equal to oxidation state.

Secondary valency is the valency satisfied towards ligands. Hence, it is equal to its coordination number. The ions or groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination number.

2.2 Valence Bond Theory

Its postulates are :

- (i) Metal-ligand bond is formed by the donation of electrons by ligand to metal.
- (ii) Metal atom/ion must have vacant orbitals of equal energies, equal to the number of ligands to be attached.
- (iii) Sometimes unpaired $(n - 1)d$ electrons pair up to create empty orbitals.
- (iv) Depending upon the type of hybridisation d^2sp^3 (or sp^3d^2), dsp^2 and sp^3 , the shapes of the complex are octahedral, square planar and tetrahedral respectively.
- (v) If no unpaired electron is present, then complex is **diamagnetic**. If unpaired electrons are present, complex is **paramagnetic**.

- (vi) If coordination number is 6, complex is octahedral with sp^3d^2 or d^2sp^3 -hybridisation.
- (vii) In strong field ligand, the d -electrons of central metal are pair up against Hund's rule. e.g; CO, NO, CN^- , NO_2^- , NH_3 , en (ethylene diamine). Some weak field ligands are H_2O , X^- , NO_3^- , ROH, etc.
- (viii) If complex formed involves inner $(n-1)d$ orbitals for hybridisation, it is called **inner orbital** or **low spin** or **spin paired complex**, e.g. $[Ni(CN)_4]^{2-}$. Whereas, if complex formed involves outer $(n)d$ orbitals for hybridisation, it is called **outer orbital**, **high spin** or **spin free complex**, e.g. $[Ni(H_2O)_6]^{2+}$.

Limitations of Valence Bond Theory

- (i) It does not distinguish between weak and strong ligands.
- (ii) It could not give any satisfactory explanation for the colour of the complexes.
- (iii) It does not give an exact explanation of thermodynamic or kinetic stabilities of coordination compounds.
- (iv) It does not give quantitative interpretations of magnetic moment data.
- (v) It fails to explain relative energies of different shapes.
- (vi) It fails to predict tetrahedral and square planar structures of some 4-coordinate complexes.
- (vii) It is based on the number or assumptions.

2.3 Crystal Field Theory (CFT)

It is more appropriate theory than VBT. According to CFT, under the influence of ligand field, degeneracy of the d -orbital is destroyed and it splits into two or more energy levels. The extent of splitting depends upon the strength of

ligand. A strong ligand causes greater splitting while a weak ligand causes smaller splitting.

The difference of energy between the two sets of d -orbital (in octahedral complexes) is called **Crystal Field Splitting Energy (CFSE)** or Δ_o . In case of octahedral complexes, e_g set [$d_{x^2-y^2}, d_{z^2}$] is of higher energy while in case of tetrahedral complexes t_{2g} set (d_{xy}, d_{yz}, d_{zx}) has higher energy.

Factors Affecting the Magnitude of CFSE

Nature of Ligands

The ligands with smaller size, large negative charge, with good σ donor and π acceptor properties will give large field splitting.

The increasing order of the values Δ_o is given below
 $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

This series is called **spectrochemical series**. In case of d^4 ions, two possible pattern of electron distribution arise.

These are explained below.

- (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 weak field ligands and they form high spin complexes.
- (ii) If $\Delta_o > P$, the fourth electron enters t_{2g} orbital giving the configuration $t_{2g}^4 e_g^0$. Ligands for which $\Delta_o > P$, are strong field ligands and they form low spin complexes.

NOTE Tetrahedral complexes are rarely formed in low spin.

Oxidation State of M-Ion

Higher is the oxidation state of M -ion higher is the CFSE.

Geometry of the Complex

Splitting is different for tetrahedral and octahedral complexes.

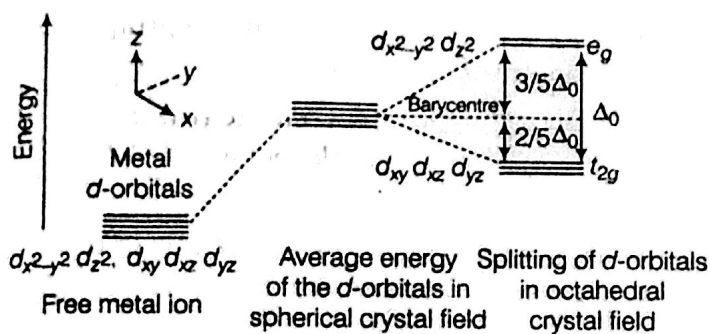


Fig. 9.1 d-orbital splitting in an octahedral crystal field

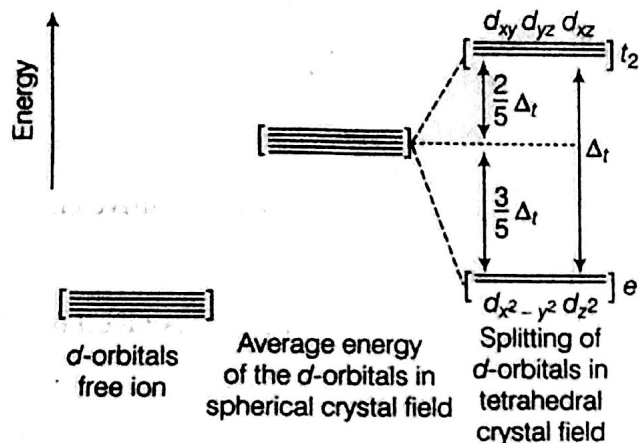


Fig. 9.2 d-orbital splitting in a tetrahedral crystal field

Colour in Coordination Compounds

When light of certain frequency falls on the complex, it absorbs light from visible range for transition of electrons from lower d -energy level to higher d -energy level. Colour of the compound is the complementary colour of the absorbed light. This is called $d-d$ transition of electron.

2.4 Bonding in Metal Carbonyls

Compounds which have at least one metal-carbon bond are called **organometallic compounds**. The metal-carbon bond in metal carbonyls possesses both σ and π character. The $M-C$ σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The $M-C$ π -bond is formed by the donation of a pair of electron 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. In these the oxidation state of metal is zero.

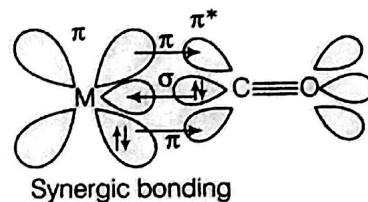


Fig. 9.3 Example of synergic bonding interactions in a carbonyl compounds

2.5 Uses of Coordination Compounds

Coordination compounds provide critical insights into the functioning and structure of vital components of biological system. Coordination compounds also find extensive applications in metallurgical processes, analytical and medicinal chemistry.