Co-ordination Compounds

Co-ordination compounds are compounds in which the metal atoms are bound to a number of anions or neutral molecules.

Alfred Werner theory of coordination compounds:

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.

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$(NH_3)_6]^{3+}$, and [Co$Cl_2(NH_3)_4]^+$ are octahedral entities, while [Ni$(CO)_4$] and [Pt$Cl_4$4]$^{2-}$ are tetrahedral and square planar, respectively.

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 fact that double salts dissociate into simple ions completely when dissolved in water. However, complex ions such as do not dissociate .

Important definitions

- **Co-ordination entity** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example [Co(NH_3)$_6$]$^{3+}$is a coordination entity in which the cobalt ion is surrounded by six ammonia molecules.

- **Cental 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.For example [Co(NH_3)$_6$]$^{3+}$.These central atoms/ions are also referred to as **Lewis acids**.

- **Ligands** The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

When a ligand can bind through two donor atoms as in H_2NCH_2CH_2NH_2 (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**.

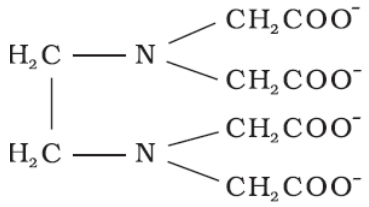


Fig 1. Ethylenediaminetetraacetate ion (EDTA4–)

 # EDTA is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

Ligand which can ligate through 2 different atoms is called ambidentate ligand.

- **Co-ordination number** The number of donor atoms to which a metal ion in a complex is bound is called the co-ordination number of the metal ion. In $[PtCl_6]^{2-}$ the co-ordination number of Pt is 6.

 # While calculating co-ordination number only sigma bonds are considered (no pie bonds are considered)

- **Oxidation number** The charge the metal ion would carry if all the ligands are removed along with the electron pair that are shared with the central atom is called its oxidation number.

- **Homoleptic and hetroleptic groups** Complexes in which the metal is bound to only one kind of donor atoms is called homoleptic, where as when it is bound to different donor atoms it is called as a hetroleptic complex.

NOMENCLATURE OF CO-ORDINATION COMPOUNDS.(According to rules by International Union of Pure and Applied Chemistry).

- **Formulae of Mononuclear Co-ordination entities.**

1. Central atom is listed first
2. The ligands are listed next. The charge on the list doesn't affect its place in the list.
3. Polydentate ligands are also listed alphabetically. In case of an abbreviated ligand the first letter of the abbreviation is used for its placement alphabetically.
4. 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.
5. There should be no space between the ligands and the metal within a coordination sphere.
6. 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.
7. The charge of the cation(s) is balanced by the charge of the anion(s).

- **Naming of Mononuclear co-ordination compounds**

The names of coordination compounds are derived by following the principles of additive nomenclature. The following rules are used when naming coordination compounds:

1. The cation is named first in both positively and negatively charged coordination entities.
2. The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).
3. Names of the anionic ligands end in –o, 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. These are placed within enclosing marks ( ).
4. 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.
5. Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
6. 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.
7. The neutral complex molecule is named similar to that of the complex cation.

ISOMERISM IN CO-ORDINATION 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.
There are two types of isomerism in co-ordination compounds.

1. **Stereo isomerism**

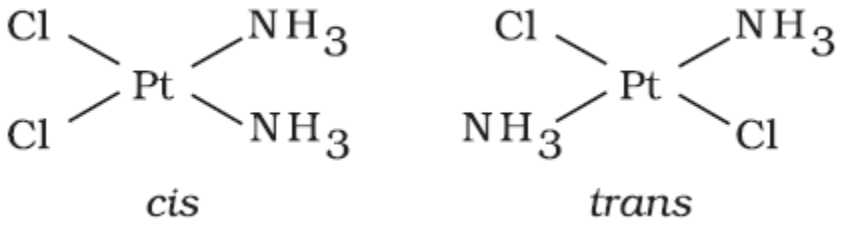
a) Geometrical isomerism
b) Optical isomerism

2. **Structural isomerism**

a) Linkage isomerism
b) Co-ordination isomerism
c) Ionisation isomerism
d) Solvate isomerism

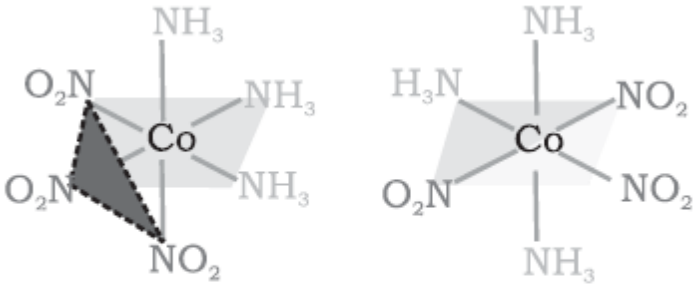
Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds.

Geometrical Isomers



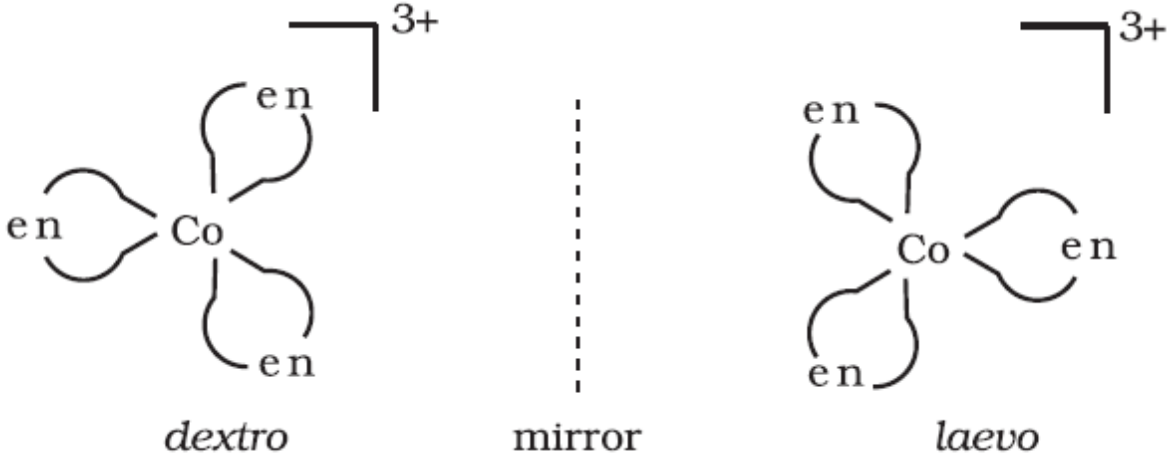
Arises in heteroleptic complexes due to different possible spatial arrangements.
It is not possible for Tetrahedral complexes , but possible for octahedral complexes due to its geometry.

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma_3b_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.



fac– *mer–*

Optical Isomers



dextro mirror *laevo*

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

Linkage Isomers

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.

Co-ordination Isomers

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Ionisation Isomers

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.

Solvate Isomers

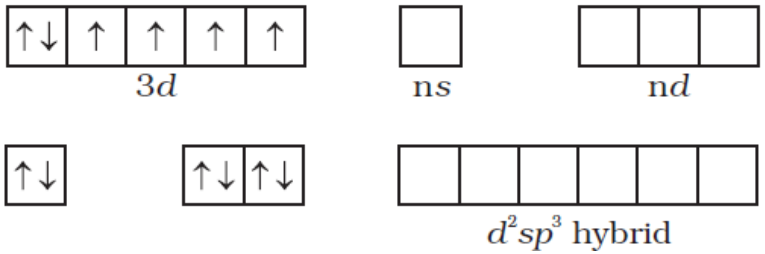
This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

BONDING IN CO-ORDINATION 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).

- **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.

CO-ORDINATION 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	Octagedral



Orbitals of Co^{3+} ion

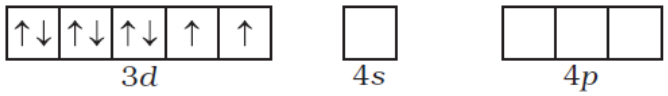
d^2sp^3 hybridised orbitals of Co^{3+} ion



$[Co(NH_3)_6]^{3+}$ inner orbital or low spin complex

In the above complex the Co ion is in its +3 oxidisation state and has the configuration $3d^6$. Six pairs of electrons, one from each NH3 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 (3*d*) is used in hybridisation, the complex, $[Co(NH3)_6]^{3+}$ is called an **inner orbital or low spin or spin paired complex**.

In tetrahedral complexes one s and three p orbitals are hybridised to form four equivalent orbitals oriented **tetrahedrally**, eg : $[NiCl_4]^{2-}$.



Orbitals of Ni 2+



sp3 hybridised orbitals of Ni 2+



[NiCl4]2- complex

Four pair of electrons from 4 Cl^-.

 # Here Ni is in +2 oxidisation state and the ion has the electronic configuration 3d8.Each Cl- donates a pair of electrons .
This complex is **paramagnetic** since it has two unpaired electrons.

- **Limitation of Valence Bond Theory**

1. It involves a number of assumptions.
2. It does not give quantitative interpretation of magnetic data.
3. It does not explain the colour exhibited by coordination compounds.

5. It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
6. It does not distinguish between weak and strong ligands.

- **CRYSTAL FIELD THEORY**

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand.

Ligands are treated as point charges in case of anions or 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) 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.

a) Crystal field splitting in octahedral coordination entities

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, the degeneracy of the *d* orbitals is removed due to **ligand electron-metal electron repulsions** in the octahedral complex to yield three orbitals of lower energy, $\mathbf{t_{2g}}$ set and two orbitals of higher energy, $\mathbf{e_g}$ set. This splitting of the Degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting .**

 # Spectrochemical series

It is an experimentally determined series based on the absorption of light by complexes with different ligands.The ligands are arranged in increasing order of their field strength.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 <$ en $< CN^- <$ CO

b) Crystal field splitting in octahedral 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 $\Delta_t = (4/9)\ \Delta_o$(t for tetrahedral and o for octahedral). Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

 # Bonding in metal carbonyls(Reason for stability)

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 trigonalbipyramid**al while **hexacarbonyl chromium(0) is octahedral**. **Decacarbonyldimanganese(0)** is made up of two **square pyramidal** $Mn(CO)_5$ units joined by a Mn – Mn bond. **Octacarbonyldicobalt(0)** has a Co – Co bond bridged by two CO groups.

The metal-carbon bond in metal carbonyls possess both *s* and *p* 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 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.