CO-ORDINATION Compound

ADDITIONAL POINTS FOR SYNOPSIS

Molecular or addition compounds :

These compounds are formed when solution of two or more salts mixed in molecular proportions are allowed to crystalize.

Ex: $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow K_2SO_4.Al_2(SO_4)_324H_2O$

 $CoCl_3 + 6NH_3 \rightarrow [Co(NH_3)_6] Cl_3$

These compounds are of two types:

Double Salts :

These compounds are stable only in crystalline state but lose their identify in solution and break down into simpler ions.

Ex: KCI.MgCl₂.6H₂O
$$\xrightarrow{\text{In aq}}$$
 K⁺ + Cl⁻ + Mg⁺²

carnallite

Ex: $K_4[Fe(CN)_6]$

$$FeSO_4 (NH_4)_2 SO_4.6H_2O \xrightarrow{aqueous}{solution} Fe^{+2} + NH_4^{+} + SO_4^{-2} (Mohr's salt).$$

Complex compounds :

These are the compounds which retain their identities even when dissolved in water. They do not give all the ions in solution. They are known as complex compounds.

aqueous

$$\rightarrow$$
 4K⁺ + [Fe(CN)₆]⁴⁻ complex ion.

Mixed complexes : The complex which contains different ligands are called mixed complexes Examples [Co $(NH_3)_4$.NO₂.Cl]Cl

Complex Ion :

A complex ion may be defined as an electrically charged species formed by the combination of a simple cation or neutral atom surrounded by a group of ions or neutral molecules. Cationic complex : A complex ion which has a net positive charge.

 $[Co(NH_3)_6]^{+3}, [Ni(H_2O)_6]^{+2}$

Anionic complex : A complex ion which has a net negative charge

 $[\operatorname{Ag}(\operatorname{CN})_2]^-, [\operatorname{Fe}(\operatorname{CN})_6]^{-4}$

Neutral complex : A complex which has no net charge

 $[Ni(CO)_4], [Co(NH_3)_3Cl_3]$

Compounds containing very stable complex part i.e, the part of which does not dissociate in solution are also called perfect complexes or penetration complexes

Compounds carrying the complex part which has tendency to ionise reversibly in aqueous solution are called imperfect or normal complexes

Co-ordination number:

The total number of monovalent ligands or the total number of donor atoms Co-ordinated to the central metal ion or atom in a complex.

Example: $[Co(NH_3)_6]Cl_3$: $[Co(NH_3)_3Cl_3]$: coordination No.of Co is six

Co-ordination sphere:

The central atom or ion along with the co-ordinated ligands are enclosed in square brackets [], is collectively called co-ordination sphere. The charge on the co-ordination sphere is the algebraic sum of the charges carried on the central metal ion and the ligands attached to the central atom.

Ex: $[Co(NH_3)_5Cl]SO_4$. In this complex, five ammonia molecules and one chloride ion Co-ordinated to central cobalt ion. They are in the Co-ordination sphere. Ions or molecules in the Co-ordination sphere are not ionised in solution. For example in the above complex, chloride ion

 (\mathbb{Q}^{-}) is not ionsied in solution. Only sulphate ion (SO_4^{-2}) is free and can be tested.

Ligand:

Any ion or molecule having atleast one atom with a lone pair of electrons qualifies as a ligand. The atom having a lone pair acts like donor atom or donor site. The ligands are attached to central metal atom or ion through coordinate bonds. Ligand donates electron pair hence, a lewis base while the central metal ion lewis acid.

Ex. $[Co(NH_3)_5Cl]^{+3}$ Central ion = Co^{+3}

 $\label{eq:ligands} \mbox{Ligands} \mbox{ = } \mbox{NH}_3 \mbox{ molecules and } \mbox{Cl}^- \mbox{ ion}$

Types of ligands :

Depending upon the number of donor atoms or sites, ligands may be classified into various types. a) Unidentate or monodentate ligands:- Ligands which have only one donor atom.

Name	Formula	Donor Atom
Water	H ₂ O	9
Ammonia	NH ₃	CN
Pyridine	C ₅ H ₅ N	<u>ON</u>
Carbonyl	CO	0
Nitrosyl	NO	N
Halide	X ⁻	X
Hydroxide ion	OH-	0
Cyanide ion	CN ⁻	N or C
Nitrito	ONO-	0
Oxide ion	0 ⁻²	0
Thio Cyanate	SCN	S or N
Acetate	CH₃COO⁻	0
Peroxide ion	O ₂ ²⁻	0
Carbonate ion	CO3 ²⁻	0
Phosphine	PH₃	Р
Nitrosyl	NO NO	Ν
Sulphato	SO ₄ -2	0
Sulphido	S ²⁻	S
Thiosulphato	$S_2O_3^{2-}$	S
Nitrato	NO ₃	0
Amido	NH ₂ ⁻	N

b) Bidentate ligands:

These Ligands have two donor atoms and therefore, can coordinate to the central ion at two positions

CO-ORDINATION Comp.



Penta dentate ligands Ex: $CH_2 COO^{-1}$ $CH_{2} - \ddot{N} < CH_{2}COO$ $CH_{2}COO$ $CH_{2}COO$ H $CH_{2}COO^{-}$ Ethylene diammine triacetate Hexa dentate ligands $\begin{array}{c} \hline \text{OOCH}_2\text{C} \\ \hline \text{OOCH}_2\text{C} \end{array} N - \text{CH}_2 - \text{CH}_2 - \text{N} \\ \hline \text{CH}_2\text{COO} \\ \hline \text{CH}_2\text{COO} \end{array}$ Ethylene diammine tetra acetate Hexa dentate **EDTA** Polydentate ligands have flexidentate character not necessarily that all the donor atoms present in the polydentate ligands should form coordinate bonds with central metal atom or ion. d) π acid ligands : These are also known as π acceptor ligands. Many ligands like CO and NO etc. have lone pairs as well as π or π^* orbitals. These ligands form normal σ bond through the lone pair of electrons. The vacant π or π^{*} orbitals of the ligand are involved in the formation of π bond with the central atom by accepting lone pair of electrons. e) Bridging ligands: Some monodentate ligands can simultaneously coordinate with two or more metal atoms. Such ligands act as a bridge and is known as bridging ligand. f) Chelating ligands: Bidentate or polydentate ligands are attached by two or more donor atoms to the same central metal ion giving a ring structure to the complex ion. Such ligands are called chelating ligands and the resulting complex is called a chelate $\begin{bmatrix} CH_2 - NH_2 \\ CH_2 - NH_2 \end{bmatrix} \xrightarrow{Cu} \begin{bmatrix} NH_2 - CH_2 \\ NH_2 - CH_2 \end{bmatrix}$ Chelate complexes are more stable than ordinary complexes due to restricted movement of ligands. IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS: 1. In ionic complexes, the cation is named first and then the anion. Non-ionic complex are given a one word name. Eq: K_2 [Pt Cl₆] potassium hexachloroplatinate(IV) While naming the complex ion, the number and name of the ligands are given first followed by the 2. name of the central metal atom with its oxidation state written in Roman numerical in parantheses. $[Co (NH_3)_5 Cl] Cl_2 penta - amine chlorocobalt (III) chloride$ 3. Naming of Ligands. Prefixes: a. The number of each type of ligand is indicated by using the Greek prefixes like di. tri. tera. When the name of the ligand includes a numerical prefix such as dipyridyl, ethylene diammine etexterms bis-(for two molecules of the ligand) tris (three molecules) tetrakis (four) pentakis (five) etc. one and followed by the name of the ligand in brackets. Naming of negative ligand: When the name of the ligand end in –ide, it is converted into – 0 Ligand Name Fluoride (F^{-}) Fluoro Halide (X^{-}) Halo 45

Cyanide
$$(CN^-)$$
 Cyano
Hydroxide (OH^-) Hydroxo
Oxide (O^{-2}) Oxo
Amide (NH_2^-) Amido
If the name of the ligand ends in
 $-ate \rightarrow -ato$
 $-ite \rightarrow -ito$
Sulphate $(SO_4^{-2}) \rightarrow sulphato$
Oxalate $(C_2O_4^{-2}) \rightarrow Oxalato$
Nitrite $(\overline{O} - N =) \rightarrow Nitrito$
Sulphite $(SO_3^{-2}) \rightarrow Sulphito$
Neutral ligands are named as such -
NH₂CH₂CH₂NH₂ — Ethylene diammine
C₅ H₅N — Pyridine
H₂O — Aqua
CO — Carbonyl
NO — Nitrosyl
NH₃ — Ammine
Positive ligands get the ending -ium
NO⁺ \rightarrow Nitrosonium

 $NO_2^+ \rightarrow Nitronium$

 $\rm NH_2 \rm NH_3^+ \rightarrow \rm Hydrazinium$

4. Order of preference of ligands:

C.

d.

Ligands are arranged alphabetically whether they are negative, neutral or positive. Numerical prefixes showing the number of ligands are not considered in giving the orders. Naming of the central metal ion :

i. When the complex is a cation no suffix is added to its name. Its name is given as such along with its oxidation state in Roman numericals in paranthesis.

Ex : 1. $[Cu(NH_3)_4]SO_4$ -- Tetrammine copper (II) sulphate

2. $[Cu(NH_3)_4(NO_2)G(NO_3) - Tetrammine chloro nitro cobalt (III) nitrate$

ii. If the complex ion is anion, suffix –ate is added to the latin name of the central metal. The oxidation state of the central metal is put in paranthesis against its name.

Ex : 1. $K_3[Fe(C_2O_4)_3]$ -- Potassium trioxalato ferrate (III)

2. $Na_3[Co(NO_2)_6]$ --- Sodium hexa nitro cobaltate (III)

iii. Bridging groups in bidentate ligands : For ligands which act as bridge between two metal atoms, the Greek letter μ (mu) is written before their names.

$$(NH_3)_4Co$$
 NH_2 Co $(NH_3)_4$ $(NO_3)_4$ $(NO_3)_4$

In this case, the ligands are NH_2^- , NO_2^- and NH_3 the oxidation state of cobalt is +3 i.e. 4 x (o) + x -1 -1 + x + 4 x (0) + 4 x -1 = 0 x = + 3

Tetra ammine cobalt (III) - μ amido - μ - nitro tetra ammine cobalt (III) nitratePoint of attachment:

	When a ligand can coordinate through more than one atom, then the point of attachment of the ligand is indicated by putting the symbol of the atom through which coordination occurs after the name of the ligand.			
	Ex: $- NO_2^-$ [Through N] : N - Nitrito			
	- ONO [–] [Through O] : O - Nitrito			
	– SCN [–] [Through S]: Thiocyanato;			
	– NCS [–] [Through N]: Iso thiocyanato.			
	Ex: $\left[Co(NH_3)_3(NO_2)_3\right]$ - Triammine N - trinitrito cobalt (III)			
	$\left[Co(NH_3)_5(ONO)\right]SO_4$ Penta ammine nitrito cobalt (III) sulphate			
	ISIOMERISM IN COORDINATION COMPLEXES : Two or more compounds having the same molecular formula but different structural arrangements are called isomers and the phenomenon is called isometism.			
	Isomerism in coordination complexes			
	\checkmark			
	 I. Structural isomers 1. Ionisation isomerism 2. Hydrate isomerism 3. Co-ordination isomerism 4. Linkage isomerism 			
I. 1.	STRUCTURAL ISOMERS : Ionisation isomerism: The compounds with same molecular formula but yield different ions in aqueous solution are called ionisation isomers.			
	Ex: (1) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ mode of ionisation is,			
	$[Co(NH_3)_5Br]SO_4 \rightarrow [Co(NH_3)_5Br]^{+2} + SO_4^{-2}$ violet			
	$[Co(NH_3)_5SO_4]Br \rightarrow [Co(NH_3)_5SO_4]^{+1} + Br^{-1}$			
	(Red) [Pt(NH ₃) ₄ Cl ₂]Br and [Pt(NH ₃) ₄ Br ₂]Cl ₂			
2.	Hydrate isomerism: This isomerism arises due to difference in the number of water molecules attached to the metal ion as ligands in the coordination sphere. Ex: There are three isomers having the molecular formula CrCl ₃ .6H ₂ O. they are			
	(i) $[Cr(H_2O)_6]Cl_3$ - Violet			
	(ii) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ -Bluish-Green			
	(iii) $[Cr(H_2O)_4Cl_2]Cl.2H_2O \rightarrow Green$			
3	They differ in their physical and chemical properties			
υ.	This isomerism arises due to interchange of ligands with in the coordination sphere. Ex: (i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Co(CN)_6][Cr(NH_3)_6]$			
	$[Cu(NH_3)_4][Pt Cl_4] and [Cu(Cl_4)_4][Pt (NH_3)_4]$			
4.	Linkage isomerism:			
The compounds which have the same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers.				
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Ex: (1) In NO_2^- ion, the nitrogen atom as well as the oxygen atom can donate their lone pairs. This gives two isomers. They are

 $[Co(NH_3)_5 NO_2]Cl_2 \rightarrow Nitrogen is the donor$

(Yellow)

 $[Co(NH_3)_5(ONO)]Cl_2 \rightarrow Oxygen is the donor (Red)$

(2)
$$[Cr(H_2O)_{\xi}SCN]Cl_{\chi}$$
 and $[Cr(H_2O)_{\xi}NCS]Cl_{\chi}$

II. STEREO ISOMERS :

I. Geometrical isomerism:

Geometrical isomerism is due to identical ligands occupying different positions either adjacent to one another – cis form or opposite to one another – trans form. This is called cis – trans isomerism.

a. Geometrical isomerism in complexes of coordination Number 4:

The complexes having co ordination number 4 adopt tetrahedral or square planar geometry. The geometrical isomerism is not possible in tetrahedral complexes. This is because in tetrahedral geometry all the four positions are adjacent to one another in these complexes.

complexes with co ordination number 2 and 3 do not show geometrical isomerism. Square planar complexes of the type MA_2X_2 , MA_2YY , $MABX_2$, MABXY can exist as geometrical isomers but not MA_4 , MA_3B , Here A and B are neutral ligands such as

 H_2O , NH_3 , CO, NO where as X and Y are anionic ligands such as Cl^- , NO_2^- , CN^- etc. Ex: $[Pt(NH_3), Cl_2]$ exist in cis and transforms.

М

trans-form

b. The square planar complexes containing unsymmetrical bidentate ligands such as $[M(AB)_2]$ also show geometrical isomerism for example $[Pt(gly)_2]$ where gly =

 $H_2NCH_2COO^-$ (glycinato) exists in cis and trans forms.



Geometrical isomerism in complexes of co-ordination number 6: These complexes adopt octahedral geometry

The octahedral complexes of the type MA_4X_2 , MA_2X_4 , MA_3X_3 , MA_4XY can exhibit geometrical isomerism.

Octahedral complexes of the type MABCDEF exist in 15 different geometrical isomeric forms.

Ex: (1) An octahedral complex $\left[Co(NH_3)_4 Cl_2 \right]^+$ can exist as cis - and trans – isomers.

Octahedral complexes of the type $M (AA)_2 X_2$ and $M(AA)_2 XY$ can also exist as cis and trans isomers. Where A represents a symmetrical bidentate ligand such as ethylene diammine (en),oxalate ion (ox). For example an octahedral complex $[Co(en)_2 Cl_2]^+$ exist as two isomers.

Octahedral Complexes :



Octahedral Co-ord. No.= 6

Square Planar Co-ord, No.=4 Tetrahedral Co-ord. No.= 4

Example:

Formula	Representation	mode of	total no	1°	2 °
		ionisation	of ions	valency	valency
Pt.Cl ₄ .6NH ₃	$[Pt (NH_3)_6]Cl_4$	$[Pt(NH_3)_6]^{+4} + 4Cl^{-1}$	1+4	4	6
$K_4[Fe(CN)_6]$	$K_4[Fe(CN)_6]$	$4K^{+}+[Fe(CN)_{6}]^{-4}$	4+1	2	6
Ni(CO) ₄	$[Ni(CO)_4]$	Does not ionise	0	0	4
$K_2 \text{pt} \text{Cl}_6$	$K_2 [p_t Cl_6]$	$2K^{+} + [Pt Cl_6]^{-2}$	2+4	4	6
CoCl ₃ .5NH ₃	$[Co(NH_3)_5 Cl]Cl_2$	$[Co(NH_3)_5Cl]^{+2}+2Cl^{-1}$	1+2	3	6
CoCl ₃ .3NH ₃	$[\text{Co}(\text{NH}_3)_3 \text{ Cl}_3]$	Does not ionise	0	3	6

Valance Bond theory:

Valence bond theory is helpful in deciding the nature of bonding, geometry, magnetic properties etc. It was proposed by Pauling.

The modern theories which explain the formation of complex compounds are valance –bond theory, crystal field theory and ligand field theory.

The simplest theory to explain bonding in complex compounds is the valence bond theory and its developed by Linus Pauling. The salient features of the theory are as follows.

- 1. The central metal loses a requisite number of electrons to form the ion. The number of electrons lost is the valency of the resulting cation.
- 2. The cation makes available a number of orbitals equal to its coordination number, for the formation of covalent bonds with the ligands.
- 3. The cation orbitals hybridize to form a new set of equivalent hybrid orbitals with definite directional characters.
- 4. The nonbonding metal electrons occupy the inner d orbitals and do not participate in the hybridization.
- 5. Each ligand contains a lone pair of electrons. A covalent bond is formed by the overlap of a vacant hybrid orbital of metal and a filled orbital of the ligand.

Co-ordination Number	Hybridisation	Geometry bond angle	Example
2	sp	linear, 180°	$\left[Ag(NH_3)_2\right]^+$
4	sp ³	tetrahedral, 109°.28'	Ni (CO) ₄
4	dsp ²	Square planar, 90°	$[Ni (CN)_4]^{-2}$
5 6	dsp ³ / sp ³ d d ² sp ³ / sp ³ d ²	120°, 90° trigonal bipyramid octahedral, 90°	$[\text{Ti } (\text{CN})_5]^{-3}$ $[\text{Fe } (\text{CN})_6]^{-4}$ $[\text{Cr } (\text{NH})]^{+3}$
	$sp^{3}d^{2} / d^{3}sp^{3}$	octahedral, 90°	$[Cr(H_2O)_6]^{+3}$

Some common examples are

Crystal Field Theory: (CFT)

The main points of the theory are:

The ligands are assumed to be point charges.

The metal cation is surrounded by the ligands with the lone pairs of electrons.

The attraction between metal cation and ligands are purely ionic.

The valence electrons of metal are repelled by the negatively charged ligands. So that they occupy those d- orbitals which have their lobes away from the direction of ligands. The effect of ligands is particularly marked on d-electrons and it depends on number of *electrons, their arrangement and also on nature of ligands*. The energy difference between two sets of d-orbitals is determined by Δ and is called Crystal Field Splitting Energy. The decreasing order of the field strength among some ligands are

 $CO > CN^{-} > NO_{2}^{-} > O^{-} \text{ phenanthroline > dipyridil > ethylenediammine > NH_{3} = pyridine > EDTA > H_{2}O > C_{2}O_{4}^{-2} > ethylalcohol > OH^{-} > F^{-} > NO_{3}^{-} > Cl^{-} > S^{-2} > Br^{-} > l^{-} (weak field ligand)$

In octahedral field the d-subshell split into two sets of orbitals e_g , with higher energy and t_{2g} with lower energy. In tetrahedral complexes t_{2g} set of orbitals have higher energy than e_g set of orbitals. Strong Ligands:

 CO, CN^-, NO_2^- , en, NH_3 , These ligands are forced to pair up the unpaired electrons. Hence they form inner orbital complexes.

Weak Ligands:

 $I^-, Br^-, C\ell^-, F^-, H_2O$. These ligands do not distrub the electronic cionfiguration of the metal. Hence they from outer orbital complexes.

i. Inner orbital complex :

If the complex is formed by the use of inner d-obritals for hybridisation $[d^2sp^3]$, it is called inner orbital complex. In the formation of inner complex, the electrons of the metal are forced to pair up and hence the complex will be either diamagnetic or will have lesser number of unpaired electrons. Such a complex is also called low spin complex (or) hyper ligated complex.

Oxidation state = $x + 4(-1) = -2 \implies x = +2$

Ex: $[Ni (CN)_4]^{-2}$ Hybridisation is dsp²

Shape is square planar Diamagnetic in nature

It is low spin complex.

Under the influence of CN^- , the unpaired electrons get paired.

Inner complexes are formed by strong ligands such as NH_3 , CN^- etc.



If the complex is formed by the use of outer d-orbitals for hybridisation (sp^3d^2) it is called an outer orbital complex. The outer orbital complex will have large number of unpaired electrons. Such a complex is also called high spin complex (or) Hypo ligated complex it is always paramagnetic.

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Many complex enzymes containing metal ions are used as catalysts in biochemical reactions. Complex compounds are used in electroplating industry.

The formation of soluble complexes is used in the extraction of some metals like Ag and Au The platinum complex , $[PtCl_2 (NH_3)_2]$ known as cisplatin is used in chemotherapic treatment of cancers.

Micronutrients for plants like Zn, Fe, Mg etc. are supplied in the form soluble chelate complexes.

ORGANOMETALLIC COMPOUNDS :

Organometallic compounds are defined as "compounds containing atleast one metal-carbon bonds".

Classification of organometallic compounds:

They can be broadly classified into two categories:

a. Sigma bonded compounds:

In these compounds the metal atom is linked to carbon atom by a sigma bond. These are formed mostly by metalloids.



