A salt is formed by the neutralizaton of an acid by a base. There are diferent types of salts. They are:-

a) Simple salt

b) Molecular (or) additon compounds

a) Simple salt

A simple salt is formed by the neutralizaton of an acid by a base.

 $\mathsf{KOH} + \mathsf{HCI} \to \mathsf{KCI} + \mathsf{H_2O}$

Normally, a simple salt ionizes in water and produces ions in soluton. The soluton of the simple salt exhibits the propertes of its component ions.

b) Molecular (or) additoo compouods

i) Double salts

These are molecular compounds which are formed by the evaporaton of soluton containing two (or) more salts in stoichiometric proportons. Hence the molecular compounds which dissociate in soluton into its constituent ions are known as double salt. Double salts retain their propertes only in solid state. They are also called as latce compounds.

Example

K₂SO₄ . Al₂(SO₄)₃ . 24H₂O - Potash alum

FeSO₄ . (NH₄)₂ SO₄. 6H₂O - Mohr's salt

 K_2SO_4 . $AI_2(SO_4)_3$. $24H_2O \rightarrow 2K^+ + 2AI^{3+} + 4SO_4^{2-} + 24H_2O$

The double salts give the test of all their consttuent ions in soluton.

ii) Coordioatoo (or complex) compouods

Coordinaton compound is 'a compound formed from a Lewis acid and a Lewis base'. The molecular compounds, do not dissociate into its constituent ions in soluton are called coordinaton compounds.

Example

 $Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2$. 4KCN (or)

K₄[Fe(CN)₆] Ferrous cyanide

 $Fe(CN)_2$. 4KCN \rightarrow 4K⁺ +

[Fe(CN)6]⁴ Complex anion

In K₄[Fe (CN)₆] the individual components lose their identty.

The metal of the complex ion is not free in soluton unlike metal in double salt in soluton.

Nature of coordioatoo (or) complex compounds

i) An anionic complex compound contains a complex anion and simple caton.

 $\mathsf{K}_4 \ [\mathsf{Fe}(\mathsf{CN})_6] \to \qquad 4\mathsf{K}^+ \ + \qquad [\mathsf{Fe}\ (\mathsf{CN})_6\]^{4\text{-}}$

simple caton complex anion

ii) A catonic complex contains complex caton and simple anion

 $[\operatorname{Co}(\operatorname{NH}_3)_6] \operatorname{Cl}_3 \rightarrow \ [\operatorname{Co}(\operatorname{NH}_3)_6]^{3^+} + \operatorname{3Cl}^-$

Complex caton simple anion

iii) In the case of a complex compound, [Cr (NH3)6] [Co(CN)6], it

gives both complex caton and complex anion

 $[Cr(NH_3)_6] [Co(CN)_6] \rightarrow [Cr(NH_3)_6]^{3+} + [Co(CN)_6]^{3-}$

complex caton complex anion

TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) Lewis Acid All electron acceptors are Lewis acids.

(b) Lewis Base

All electron donors are Lewis base.

(c) Central metal ion

In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are atached. The acceptor metal caton is referred to as central metal caton. Hence, central metal caton in a complex serves as a lewis acid.

(d) Ligand (Latn word meaning to bind)

A ligand is an ion (or) a molecule capable of functoning as an electron donor. Therefore the neutral molecules or ions which are directly atached to the central metal ion are called as ligand (or) coordinaton groups. These coordinaton groups or ligands can donate a pair of electrons to the central metal ion (or) atom. Hence, in a complex compound ligands act as Lewis bases.

Examples: $[Ni(NH_3)_6]^{2+}$: Ligand = NH₃ molecule and Central metal ion = Ni²⁺ $[Co(NH_3)_5CI]^{2+}$: Ligands = NH₃ molecule and Cl⁻ ion

Types of ligaods

Ligands can be classifed on the basis of charge, number of donor site and bonding

(a) Oo the basis of charge

- (i) Negatve ligands : ligands which carry negatve charge e.g. CN^{-} , CI^{-} , Br^{-} , NH_2^{-} , NO_2^{-} etc
- (ii) Positve ligands : ligand which carry positve charge e.g. NO₂⁺, NO⁺, NH₃⁺ etc
- (iii) Neutral ligands: ligands which do not carry any charge e.g. H₂O, NH₃, PH₃, CO etc

(b) Oo the basis of oumber of dooor sites

- Mooodeotate or uoideotate ligaods: Ligands which coordinate to central atom or ion through one donor atom and form only one coordinate bond are called monodentate/ unidentate ligands
 E.g. H₂O, NH₃[,] OH⁻, CN⁻, O²⁻ etc
- (ii) **Bideotate ligaods** : ligands which coordinate to central metal atom or ion through two donor atoms and form coordinate bonds are called bidentate ligands eg,

соо⁻ | соо⁻ , йн₂ – сн₂ – йн₂

(iii) **Plolydeotate ligaods**: Ligands which coordinate to central metal atom or ion through more than two donor atoms are called polydentate ligands and the resulting complets is called polydentate ligands e.g. EDTA is hexadentatae ligand

(c) Oo the basis of boodiog

(i) Chelatog ligaods: A bidentate or polydentate ligand which forms two or more coordinate bond with central metal atom or ion in such a way that a fve or six membered ring is formed is called chelatng ligand and the resulting complex is called metal chelate. This property is called chelaton e.g.

$$\begin{array}{c|c} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array} \begin{array}{c|c} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array} \begin{array}{c|c} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array} \begin{array}{c|c} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array} \begin{array}{c|c} CH_2 - CH_2 \\ | \\ NH_2 - CH_2 \end{array}$$
Chelating ligand Chelate

(ii) **Ambideotate ligaods**: Monodentate ligand containing more than one coordinatng atoms are called ambidentate ligands

e.g NO_2^- can coordinate with metal atom or ion through either N or O atom

$$M \longleftarrow 0^{-} - N = 0 \qquad M \longleftarrow N$$

Nitrito Nitro 0

(e) Coordinaton number

The total number of coordinate bonds through which the central metal ion is atached with ligand is known as coordinaton number Example For example in

 $K_4[Fe(CN)_6]$ the coordinaton number of Fe(II) is 6 and in $[Cu(NH_3)_4]SO_4$ the coordinaton number of Cu(II) is 4.

(f) Coordinaton sphere

The central metal ion and the ligands that are directly atached to it, are enclosed in a square bracket, called coordinaton sphere or frst sphere of atracton

(g) Oxidaton number or Oxidaton state of central metal atom/ ion It is the number that represent an electric charge with an atom or ion actually has or appears to have when combined with other atom

e.g. $[Cu(NH_3)_4]^{2+}$ NH₄ is neutral, monodentate ligand. Let oxidaton state of the metal ion be x then

x + 4(0) = +2 x = 2. Oxidaton number of Cu is +2

Rules for writng formula of coordinaton compounds

- (i) Formula of the caton whether simple or complex must be writen frst followed by anion
- (ii) The coordinaton sphere the sequence of symbols is :
 First metal name followed by anionic ligand then neutral ligand fnally catonic ligand. Ligands of same type are arranged alphabetcally
- (iii) Polyatomic ligands are enclosed in parentheses
 e.g In Na[PrBrCl(NO⁺²)₂NH₃(NO)] sequence in coordinaton sphere is metal atom, alphabetcal sequence of anionic ligand Br⁻, Cl⁻, NO₂⁻, followed by neutral ligand NH₃ and then catonic ligand NO⁺

IUPAC nomenclature of coordinaton compounds

The rules are outlioed below

1. In naming the entre complex, the name of the caton is given frst and the anion second (just as for sodium chloride), no mater whether the caton or the anion is the complex species.

2. In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).

3. Ligand names generally end with 'O' if the ligand is negatve ('chloro' for Cl⁻, 'cyano' for CN-, 'hydrido' for H-) and unmodifed if the ligand is neutral

('methylamine' for MeNH₂). Special ligand names are 'aqua' for water, 'ammine' for ammonia, 'carbonyl' for CO, nitrosyl' for NO.

4. A Greek prefx (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omited for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, liketriphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefxes bis, tris, tetrakis instead.

For example, [Ni(PPh₃)₂Cl₂] is named dichlorobis(triphenylphosphine) nickel(II). 5. A Roman numeral or a zero in parentheses is used to indicate the oxidaton state of the central metal atom.

6. If the complex ion is negatve, the name of the metal ends in 'ate' for example, ferrate, cuprate, nickelate, cobaltate etc.

7. If more than one ligand is present in the species, then the ligands are named in alphabetcal order regardless of the number of each.

For example, NH₃ (ammine) would be considered as 'a' ligand and come before CI-(chloro). **Some additooal ootes**

i) Some metals in anions have special names

B Borate ,Au Aurate, Ag Argentate, Fe Ferrate, Pb Plumbate, Sn Stannate, Cu Cuprate, Ni Nickelate

ii) Use of brackets or enclosing marks. Square brackets are used to enclose a complex ion or neutral coordinaton species.

Examples

[Co(en)₃]Cl₃ tris(ethylenediamine)cobalt(III) chloride

$\begin{bmatrix} Co(NH_3)_3(NO_2)_3 \end{bmatrix} \ triamminetrinitrocobalt~(III) \\ K_2[CoCl_4] \ potassiumtetrachlorocobaltate(II) \\ note that it is not necessary to enclose the halogens in brackets.$

Name of Negatie ligaods

Ligand	Name	Ligand	Name
H	Hydrido	HS	Mercapto
O2-	Охо	NH2 ⁻	Amido
O2 ²⁻	Peroxo	NH ²⁻	Imido
O ₂ H ⁻	Perhydroxo	NO₃⁻	Nitrato
OH	Hydroxo	ONO ⁻	Nitrito
F-	Fluoro	NO ₂ ⁻	Nitro
Cl	Chloro	N-3	Nitride
Br⁻	Bromo	P ₃₋	Phosphido
 -	lodo	N₃⁻	Azido
CO3	Carbonato	CNO ⁻	Cyanato
C ₂ O ₄ -	Oxalate	NCO	Cyanato
CH ₃ CO ₂ ⁻	Acetate	SCN⁻	Thiocyanato
SO4 ²⁻	Sulphato	HCO₃⁻	Hydrogencarbonato
SO3 ²⁻	Sulphito	S4O6 ²⁻	Tetrathionato
S2-	Sulphido	HSO₃⁻	Hydrogensulphito
NH2CH2CO2 ⁻	glycinato	C₅H₅⁻	Cyclopentadienyl
(⁻ OCCH ₂) ₂ NCH ₂ CH ₂ CH ₂ N	Ethylenediammine	S ₂ O ₃ ²⁻	Thiosulpahato
(CH2CO2 ⁻)2	tetraacetato		
	(EDTA)		

Name of neutral ligands

Ligand	Name	Ligand	Name
C₅H₅N	pyridine	NH2(CH2)2NH2	ethlenediammine
(ру)		(en)	
NH₃	Ammine	CH ₃ NH ₂	Methylamine
H₂O	Aqua/aquo	CO	Carbonyl
C ₆ H ₆	Benzene	NO	Nitrosyl
N2	Dinitrogen	CS	Thiocarbonyl
O2	Dioxygen	NS	Thionitrosyl
Ph₃P	Triphenylphosphine	CH ₃ COCH ₃	Acetone

Name of Positve ligands

Ligand	Name
NO ⁺	Nitosonium
NO2 ⁺	Nitronium
NH2NH3 ⁺	hydrazinium

Bidentate ligands					
Name of the Formula	Ch	arg Ab	br. Donor	site	UPAC name of ligand
species CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-	е				
Glycinate idn 🖉 🦯	-1	gly	2, One	e N and or	ne Glycinato
$CH_3 - C = NO$			O ator	n	
CH ₃ - C =N	1	do		N and ana	O Dimethyl alyevimete
	- 1	an	ig ∠,one	n and one	
	1	۸.) atom	Apotulopotopoto
	- 1	AC	ac iwo c	Jatom	Acelylacelonalo
Oxalate ionੱਸਿ₂ੁਸ₂ੋਸ₂ਾਸ₂ਾਸ₂	-2	Ox	c Two C) atoms	Oxalato
Ethylene	Zei	o En	Two N	l atoms	Ethvlenediamine
diamine(en)					,
Multdentate ligands					
Name of the Charg	le Abbri	Don	or site		IUPAC name of
species					ligand
Diethylene Zero	Dien	<u>3, th</u>	ree N atom	IS	Diethylene triamine
triamine		(tride	entate)		5
Triethyylene Zero	Trien	 4, F(our N atom	s	Triethylene amine
tetramine		(Tet	radentate)		,
Ethylenediamin -3	EDTA	.\ ³⁻ , Tł	nree O atorr	ns and two	Ethylenediamine
e triacetate ion		N at	oms		triacetate
		(pen	tadenate)		
Ethylenediamin -4	EDTA	⁴⁻ 6, tw	o N and fou	Ir O atoms	Ethylenediamine
e tetra-acetate		(He)	adentate		tetraacetato
ion		·			
Few examples to elabo	rate abo	ve rules	s		
<u>[PtCl₂(C₂H₅N)(NH₃)]</u>			Ammin	edichloro ((pyridine)platnum(II)
[Fe(CO)₅]			Pentaca	arbonyliroi	n(0)
<u> [PtCl₂ (NH₃)₄] [PtCl₄]</u>				nminedich	loroplatnum (IV)
			tetrachl	oroplatate	()
[Cr(NH₃)₄][CuCl₄]				nmine chr	omium(0)
			tetrachl	orocupera	te(IV)
Na[PtBrCl(NO ₂)(NH ₃)]			Sodium	ammineb	oromochloronitro
[Pt(py)₄][PtCl₄]				ridineplatr	num(II)
			Tertrac	hloroplatna	ate(II)
[CoCl(ONO)(en)₂] ⁺			Chlorob	is(ethylenc	diamine)nitritocobalt (III)
			ion		
[{(C₀H₅)₃P}Rh]Cl			Tris(trip	henylphos	phine)rodium(I)chloride
[Fe(H ₂ O) ₄ (C ₂ O ₄)] ₂ SO ₄			Tetraac	uooxalato	iron(III)sulphate

K₄[Fe(CN)6]	Potassium hexacyanoferrate(II)		
K₃[Fe(CN)₅NO]	Potassium pentacyanonitrosylferrate(II)		
Na[Ag(CN) ₂]	Sodim dicyanoargentate (I)		
[Fe(CO) ₅]	Pentacarbonyliron(0) Ferric		
Fe₄[Fe(CN)6]₃	hexacyanoferrate(II)		
[Fe(C ₅ H ₅) ₂]	Bis(cyclopentadienyl)iron(II) Sodium		
Na ₂ [Ni(NC) ₄]	tetraisocyanonickelate(II) Potassium		
[K₂[HgCl₄]	tetrachloromercurate(II) Tris (oxalato)		
[Cr(Ox) ₃] ³⁻	chromate (III) ion Choronitrito tetraamine		
[CoCl(NO ₂)(NH ₃) ₄]Cl	cobat(III) chloride Tris(ethylene		
[Co(en) ₃]Cl ₃	diammine) cobalt(III) chloride Sodium		
Na ₃ [AIF ₆]	hexafuoro aluminate(III)		
K[Cr(NH ₃) ₂ (CO ₃) ₂]	Potassium dicarbonate diammine		
	chromate(III)		
Na ₃ [Cr(en) ₂ (C ₂ O ₄) ₃]	Sodium tri oxalate bis (ethylene diammine)		
	chromate(III)		
[Co(NH ₃) ₅ (NCS)]Cl ₂	Pentaammineisocyannatocobalt(III)Chloride		
[Cr(H ₂ O) ₄ Cl ₂] ₂ SO ₄	Tetraaquodichlorochromium(III) sulphate		
[Ni(DMG)2]	Bis(dimethylglyoximato)nickel(II)		
K ₂ Hgl ₄	Potassium tetraiodomercurate(IV)		

8) naming of the bridging ligands of the bridged polynuclear complexes Complexes having two or more atoms are called polynuclear complexes. In these complexes, the bridge group is indicated by separating it from the rest of the complex by hyphen and adding the prefx μ -before the name of each different bridging group. Two or more bridging groups of the same type are indicated by di- μ , tri- μ etc. When a bridging ligand is atached to more than two metal atoms or ion, this is indicated by subscript to μ

Is named as Bis(ethylenediammine)cobalt(III)-μ-amido-μhydroxo-bis(ethylenediamine)cobalt(III)sulphate Or μ-amido-teyrakis (ethylenediammine)-μ-hydroxo-dicobat(III)sulphate

Werner's coordinaton theory Postulates of Weroer's theory

- 1) Every metal atom has two types of valencies
- i) Primary valency or ionisable valency
- ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidaton state of the metal ion. The primary valency of the metal ion is always satsfed by negatve ions.

3) Secondary valency corresponds to the coordinaton number of the metal ion or atom. The secondary valencies may be satsfed by either negatve ions or neutral molecules.

4) The molecules or ion that satsfy secondary valencies are called ligands.

5) The ligands which satsfy secondary valencies must project in defnite directons in space. So the secondary valencies are directonal in nature where as the primary valencies are non-directonal in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordinaton compounds.

Weroer's represeotatoo

Werner represented the frst member of the series $[Co(NH_3)_6]Cl_3$ as follows. In this representaton, the primary valency (doted lines) are satsfed by the three chloride ions. The six secondary valencies (solid lines) are satsfed by the six ammonia molecules.



Defects of Weroer's theory

Werner's theory describes the structures of many coordinaton compounds successfully. However, it does not explain the magnetc and spectral propertes.

Valence bond theory (VB Theory)

Valence bond theory, primarily the work of Linus Pauling regarded bonding as characterized by the overlap of atomic or hybrid orbitals of individual atoms. The postulates of valence bond theory:

1) The central metal atom/ion makes available a number of vacant orbitals equal to its coordinaton number.

These vacant orbitals form covalent bonds with the ligand orbitals.

3) A covalent bond is formed by the overlap of a vacant metal orbital and flled ligand orbitals. This complete overlap leads to the formaton of a metal ligand, σ (sigma) bond.

4) A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called 'hybridisaton'. A hybridised orbital has a beter directonal characteristics than an unhybridised one.

The following table gives the coordinaton number, orbital hybridisaton and spatal geometry of the more important geometrics

Coordinaton number	Types of hybridizaton	Geometry
2	sp	linear
4	sp ³	tetrahedral
4	dsp ²	square planar
6	d ² sp ³	octahedral
6	sp ³ d ²	octahedral

Magnetc moment

A species having at least one unpaired electron, is said to be paramagnetc. It is atracted by an external feld. The paramagnetc moment is given by the following spin-<u>only formula</u>.

 $\mu_{s} = \sqrt{n} (n+2) BM$

 μ_s = spin-only magnetc moment

n = number of unpaired electrons

BM = Bohr magneton, the unit which expresses the magnetc moment.

When the species does not contain any unpaired electron, it is diamagnetc.

Applicatons of valence bond theory

(i) If the ligand is very weak like F^- , H_2 , CI^- etc. It does not force the pairing of 3d electrons

and hence outer orbital octahedral complexes are formed by sp³d² hybridizaton.

(ii)But if the ligand is strong like CN^{-} , $(COO)_2^{2^-}$, ethylenediammine (en) etc, it forces the paring of 3d electrons and hence inner orbital octahedral complexes are formed by d^2sp^3 hybridizaton

(1) Atom or ion of d-block element contain 1,2 or 3 electrons in d-



Ti³⁺, V³⁺, Cr³⁺

Since two 3d orbitals are available for d^2sp^3 hybridizaton. Hence, these systems may accept six lone pairs from six ligands and they form octahedral complexes [Ti(H₂O)₆]³⁺, [V(H₂O)₆]³⁺, [Cr(H₂O)₆]³⁺

Since due to complexaton the unpaired electrons in (n-1) d- orbitals are not disturbed, the magnetc moment of free metal ions remains intact in octahedral complexes

More possibility

In additon to d²sp³ hybridisaton metal ions may undergo sp³ or dsp² hybridizaton forming tetrahedral or square planar complexes respectively Since in sp³ or dsp², the d-electrons are not disturbed, the magnetic moment of free metal ion remains intact n tetrahedral or square planar complex

(2) Atom or ion of d-block element contain 4,5 or 6 electrons in d-



In above type ions, in ground state two 3-d orbitals are not vacant to partcipate thus 3d electrons are not disturbed and hence magnetc moment of free metal ions remains intact in outer orbital octahedral complex. Energy gap between 4s and 4d is large, the sp^3d^2 hybridisaton is not perfect hybridizaton and hence outer orbital complexes are comparatvely less stable. Moreover, 4d orbitals are more extended in space than 3dorbitals and hence sp^3d^2 hybrid orbitals are also more extended in space than d^2sp^3 hybrids. So bond length in outer orbital octahedral complexes is comparatvely longer and so they are less stable. Such complex is possible if ligand is weak

Aoother possibility



For strong ligand like CN^{-} maximizes pairing of 3d electrons, two 3d orbitals may be maid vacant for d^2sp^3 hybridisaton forming octahedral complex. As two d-orbitals of inner shell are involved in hybridisaton, complex are said to be inner orbital octahedral complex.

The energy of the orbitals involved in hybridisaton is in contnuaton. The d^2sp^3 hybridisaton is perfect and at the same tme due to less extension of 3d orbitals in space, bond length is also short. So, inner orbital octahedral complexs are more stable than outer orbital octahedral complex As the paring of 3d electrons is forced in d^2sp^3 hybridisaton in these systems, hence the magnetc moment of the free metal ion undergoes change on complexaton **Ooe more possibility**

In additon to inner orbital octahedral and outer octahedral complexes ions may

also form tetrahedral and square planner complex by sp³ and dsp² hybridizaton

 (3) Atom or ion of d-block element contain 7,8 or 9 electrons in dorbit (d⁷,d⁸,d⁹ system)
 Co(II), Ni(II, Cu(II)



Two vacant 3d orbitals cannot be made available for d²sp³ hybridizaton even afer maximum pairing. So, there is no chance of the formaton of inner orbital octahedral complex

Co²⁺ under the influence of HN₃ as ligand



In d^{7} , with promoton of one electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so, Co(II) will easily be oxidized to Co(III)

In d^8 , afer maximum pairing of 3d electrons, one 3d orbital may be vacated for dsp^2 hybridizaton and hence d^7 , d^8 systems favour the formaton of square planar complexs with changed magnetc nature

In d⁹, one d-orbital is not made available for dsp² hybridizaton. So there is no queston of the formaton of square planar complex by d⁹ **More possibility (weak ligaod)**

However they may undergo sp^3d^2 hybridizaton forming outer orbital octahedral complex with same magnetc propertes as in free metal. **Ooe more possibility**

Also sp³ hybridizatons can easily occur favouring the formaton of tetrahedral complexes with unchanged magnetc character

(4) In d¹⁰ Zn(II) , Cu(I)

In d¹⁰, 3d orbitals are completely flled up, so, it may form tetrahedral complex by sp³ hybridizaton or outer orbital octahedral complexes by sp³d² hybridizaton Magnetc propertes of the free metal ion remains unchaged in tetrahedral or outer orbital octahedral complexes

Defects of Valence bond theory

While the VB theory, to a larger extent, explains the formaton, structures and magnetc behaviour of coordinaton compounds, it sufers from the following shortcomings:

(i) It involves a number of assumptons.

(ii) It does not give quanttatve interpretaton of magnetc data.

(iii) It does not explain the colour exhibited by coordinaton compounds.

(iv) It does not give a quanttatve interpretaton of the thermodynamic or kinetc stabilites of coordinaton compounds.

(v) It does not make exact predictons regarding the tetrahedral and square planar structures of 4-coordinate complexes.

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

Crystal feld theory (CFT)

Main postulates of crystal feld theory are

- (i) In a coordinaton compound there are electrostatc interacton between metal atom/ion and ligands. Ligand assumed to be a point charge
- (ii) In an isolated metal atom or ion all fve d-orbitals have equal energy i.e. they are degenerate
- (iii) When metal atom/ion gets surrounded by ligands, there occur interacton between d-electron cloud of metal atom/ion and ligands
- (iv) If the feld due to ligan around metal atom is spherically symmetrical, dorbitals of metal remains degenerated
- If fled due to ligand surrounding metal is unsymmetrical (as in octahedral and tetra hedral complexes) the degeracy of d-orbitals is splited into two sets of orbitals
- (vi) Orbitals lying in the directon of ligands (point charges) are raised to higher energy state than those orbitals lying between theligands (point charges)
- (vii) The energy diference between two sets of orbitals is denoted by Δ_0 for octahedral and Δ_t for tetrahedral
- (viii) The magnitude of Δ_0 and Δ_t depends upon the feld strength of ligand around the metal
- (ix) Ligands which cause larger splitng (large Δ) are called strong feld ligands while those which causes small splitng (small Δ) are called weak fled ligands

Spectrochemical series

Arrangement of ligands in order of their ability to cause splitng (Δ) is called spectrochemical series

 $I^{\circ} < Br^{\circ} < S^{2^{\circ}} < SCN^{\circ} < CI^{\circ} < F^{\circ} < OH^{\circ} < C_2O_4^{2^{\circ}} < O^{2^{\circ}} < H_2O < NCS^{\circ} < NH_3 < en < NO_2^{\circ} < CN^{\circ} < CO$ The spectrochemical series is an experimentally determined series. It is difcult to explain the order as it incorporates both the effect of σ and π bonding. A patern of increasing σ donaton is as follows

Halides donors < O donors < N donors < C donors

Crystal feld splitng in octahedral complexes

The octahedral arrangement of six ligands surrounding the central metal ion can be shown as follows



It is obvious from the fgure, that ligands approaching the x, y, and z axis. The two d orbitals namely $d(x^2 - y^2)$ and $d(z^2)$ will sufer more electrostatc repulsion and hence their energy will be grater than other three orbitals d(xy), d(yx) and d(xz) which will have their lobes lying between the axis Thus degenerate set of d-orbitals split into two sets: e_g orbitals of higher energy including $d(x^2 - y^2)$ and $d(z^2)$ and t_{2g} orbitals of lower energy including d(xy), d(yx), d(yx) and d(xz)

The crystal feld splitng is measured in terms of energy diference between t_{2g} and e_g orbital and is denoted by a symbol Δ_0 . It is generally measured in terms of D_q . It is called as crystal feld splitng energy or crystal feld stabilizaton energy E_g orbitals are 6Dq above the average energy level and t_{2g} orbitals are 4Dq below the average energy level



Signifcance of Δ_0

A strong feld ligand approaches the central metal atom/ion strongly and thus the magnitude of Δ_0 is high. Hence in the case of strong feld ligand, the magnitude of Δ_0 is grater than, the pairing energy (the energy required to pair up two negatvely charged electrons having opposite spin in an orbital). However, under the infuence of weak feld ligand, Δ_0 is smaller than pairing energy (P) Now, let us consider the d⁴ confguraton of the central atom/ion. The frst three electrons will go into t₂₉ orbitals using Hund'd rule of maximum multplicity. The fourth electron will go in the eg orbital when the ligands are weak as, $\Delta_0 < P$ giving the confguraton t₂₉³eg¹. But if the ligands are strong, then the fourth electron will pair up when any of the singly occupied t₂₉ orbitals (as $\Delta_0 > P$) to give the confguraton t₂₉⁴eg⁰

Crystal feld splitng in tetrahedral complexes



The tetrahedral arrangement of four ligands surrounding the metal ions can be shown as shown in fgure.

It is obvious from the fgure that none of the dornital point exactly towards the ligands. However, three d-orbitals d(xy), d(yz) and d(zx) are pointng close towards ligands As a result of this, the energy of these three orbitals increases much more than the other two d-orbitals $d(x^2 - y^2)$ and $d(z^2)$. The d- orbitals thus split in two sets of orbitals: t₂₉ orbitals of higher energy including d(xy), d(yz), d(xz) and e₉ orbitals of lower

energy including $d(x^2 - y^2)$ and $d(z^2)$

Energy diference between two sets of orbitals is represented by Δ_f . However splitng is much smaller than that in octahedral complexes

Negatve sign denotes that order of splitng in tetrahedral complexes is reverse of that in octahedral complexes.

Because of the small value of Δt , electrons generally do not pair and results in formaton of high-spin complex.



Limitaton of Crystal feld theory

The crystal feld model is successful in explaining the formaton, structures, colour and magnetc propertes of coordinaton compounds to a large extent. However, from the assumptons that the ligands are point charges, it follows that anionic ligands should exert the greatest splitng 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 feld theory (LFT) and molecular orbital theory

Factors afectng the stability of complexes

 A coordinate compound is formed in soluton by the stepwise additon of ligands to metal ion. The overall stability constant is given by M + nL ⇒ MLn

$$\beta_f = \frac{[MLn]}{[M][L]^n}$$

Higher the value of β_f more stable is the complex or more the quantity of ML_n be exists in soluton.

Free metal ions rarely exist in the soluton so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them.

For simplicity, we generally ignore these solvent molecules and write stability constants as follows in the formaton of MLn are

 $M + L \hookrightarrow ML \quad K_1 = [ML]/[M][L]$

 $ML + L \Leftrightarrow ML_2 \quad K_2 = [ML_2] / [ML][L]$ $ML_2 + L \Leftrightarrow ML_3 \quad K_3 = [ML_3] / [ML_2][L]$

 $ML_{n-1} + L \rightleftharpoons [ML_n] / [ML_{n-1}][L]$

where K1, K2, etc., are referred to as stepwise stability coostacts. Alternatively, we can write the **oierall stability coostact** thus: M + nL \Rightarrow ML4

 $\beta = [ML_n]/[M][L]^n$

The stepwise and overall stability constant are therefore related as follows: $\beta 4 = K_1 \times K_2 \times \dots \times K_n$

- 2) Higher is the charge density on the central metal ion, grater is the stability of the complexes. For example $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)]^{4-}$
- 3) More is the basic character of ligand, more stable is the complex
- 4) Chelatng ligands form more stable complexes than the monodentated ligands

ISOMERISM

Compounds having the same chemical formula but diferent physical and chemical propertes due to the diferent structural arrangements are called isomers. This phenomenon is known as isomerism.

Coordinaton compounds exhibit two major types of isomerism, namely

(A) structural isomerism and (B) stereoisomerism (space

isomerism). Each of these is further classifed as shown below.

A)Structural isomerism

a) Coordinaton isomerism b) Ionisaton isomerism

c) Hydrate or Solvate isomerism d) Linkage isomerism

e)Ligand Isomerism

B) Stereoisomerism

a) Geometrical isomerism b) Optcal isomerism

A) Structural isomerism

a) Coordioatoo isomerism

In a bimetallic complex, both complex caton and complex anion may be present. In such a case the distributon of ligands between the two coordinaton spheres can vary, giving rise to isomers called the coordinaton isomers. This phenomenon is called coordinaton isomerism. This isomerism is illustrated by the following pairs of complexes where the complex caton and anion contain different metal centres.

1. [Co(NH ₃) ₆]	[Cr(CN)6]	and [Cr(NH ₃) ₆]	[Co(CN)6]
Hexammine	hexacyano	Hexamine	hexacyano
cobalt(III)	chromate(III) chromium (III)	cobaltate (III)

2. [PtII(NH3)4]	[CuCl4]	and [Cu(NH3)4]	[PtCl4]
Tetraammine	Tetrachloro	Tetraammine	Tetrachloro
platnum (II)	cuparate (II)	copper (II)	platnate (II)

b) looisatoo isomerism

Coordinaton compounds having the same molecular formula but forming diferent ions in soluton are called ionisaton isomers. This property is known as ionisaton isomerism. An example of this type of isomerism is furnished by the red-violet, $[Co(NH_3)_5Br]SO_4$ $[Co(NH_3)_5SO_4]Br$ pentaamminebromocobalt(III) sulphate pentaamminesulphatocobalt (III) bromide

The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in soluton.

[Co(NH ₃) ₄ Cl ₂]NO ₂	and	[Co(NH ₃) ₄ NO ₂ Cl]Cl
Tetraamminedichlorocobalt(III)		nitrite Tetraamminechloronitrocobalt(III) chloride
	ζ, γ	
[Co(NH₃)₅NO₃]SO₄	and	[Co(NH₃)₅ SO₄]NO₃

pentaamminenitratocobalt(III) sulphate pentaamminesulphatocobalt(III) nitrate

c) Hydrate isomerism or Soliate isomerism

The best known examples of this type of isomerism occurs for chromium chloride "CrCl₃.6H₂O" which may contain 4, 5, (or) 6 coordinated water molecules. 1. [Cr(H₂O)₄Cl₂]Cl.2H₂O - Bright green Tetraaquadichlorochromium(III) chloride dihydrate 2. [Cr(H₂O)₅Cl]Cl₂.H₂O - grey-green Pentaaquachlorochromium(III) chloride monohydrate 3. [Cr(H₂O)₆]Cl₃ - Violet Hexaaquachromium(III) chloride These isomers have very diferent chemical propertes and on reacton with AqNO₃ to test for Cl⁻ ions, would fnd 1,2, and 3 Cl⁻ ions in soluton respectively.

d) Liokage isomerism

Linkage isomerism occurs with ambidentate ligands. These ligands are capable of coordinatng in more than one way. The best known cases involve the monodentate ligands SCN⁻/NCS⁻ and NO₂ -/ONO Forexample [Co(NH₃)₅ONO]Cl₂ the nitrito isomer - red colour pentaamminenitritocobalt(III) chloride - O atached

[Co(NH₃)₅ NO₂]Cl₂ the nitro isomer - yellow colour pentaamminenitrocobalt(III) chloride - N atached

e) Ligaod isomerism

Ligand isomerism arises from the presence of ligands which can adopt diferent isomeric forms. An example is provided by diaminopropane, which may have the amine groups in the terminal (1,3-) positons or in the 1,2-positons.

 $H_2N - CH_2 - CH_2 - CH_2 - NH_2$ or $H_2N - CH_2 - CH - CH_3$

NH₂

B)Stereoisomerism (space isomerism)

Consider two compounds containing the same ligands atached to the same central metal ion, but the arrangement of ligands in space about the central metal ion are diferent, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoisomerism. There are two diferent types of stereoisomerism. a) Geometrical isomerism or b) Optcal isomerism.

a) Geometrical (or) cis-traos isomerism

Geometrical isomerism is due to ligands occupying diferent positon around the central ion. The ligands occupy positon either adjacent to one another or opposite

to one another. These are referred to as cis-form respectvely. This type of isomerism is, therefore, also referred to as cis-trans isomerism. Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral Geometrial isomerism io 4- coordioate complex .

(1) [Ma₂b₂] type complexes Square planar



In a cis- isomer two identcal (or) similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other.

Square planar complexes of the type $[Ma_2b_2]^{n+}$ where a and b

are monodentate ligands, exist as cis and trans-isomers as





Example of this type of complexes are [Pt (NH₃)₂ Cl₂] and $[Pd(NH_3)_2 (NO_2)_2]$. The cis trans isomers of these compounds are represented as Cisdiamine dichloroplatnum(II) and

trans- diammine dichloroplatnum(II)

(2) [Mabcd] type complexs

Square planar complex of this type exist in three isomeric forms for example [Pt(NH₃)(Py)(Cl)(Br)] exist in the following structures



(3) [Ma₂bc] type complexes

Square planar complexes of this type also shows cis-trans isomerism. For example [Pd (Cl)₂Br I]²⁻ exists in the following cis-trans



 $(4)[M(AB)_2]^{n\pm}$ type complex

Here m is the central metal ion and (AB) represents an unsymmetrical bidentate ligand(A) and (B) arethe two ends (i.e. coordinating atoms) of the bidentates ligands such type of complexes also show trans and cis isomerism



For example [Pt(gly)₂]; here gly represents the glycinato ligands, NH₂CH₂COO⁻ which has N (A)and O (B)atoms as its donar

Geometrial isomerism io 6-coordioate complex, octahedral complex



A complex compound having the central metal ion with coordinaton number equal to 6 has octahedral shape. The system used for numbering diferent positons of ligands in an generally it is assumed that the 1,2 positons are cis-positons. Normally it is taken that 1,6 positons are trans-positons

n±

(1)An octahedral complex of the type [Ma₄b₂] where a and b are monodentate

ligands, exists as two geometrical lsomers:



(2) [Ma₃b₃] type complexes



When each trio of donor atoms(viz ligands (a, a and a) occupy adjacent positon at the corners of an octahedral face, we have facial isomers When the positons are around the meridian of octahedron, Owe get Meridional (mer) isomer

b) Optcal Isomerism

This is a phenomenon in which certain organic or inorganic compounds have the property of rotating plane polarized light. The compounds which exhibit this property are called optcal isomers. The optcal isomers of a compound have identcal physical and chemical propertes. The only distinguishing property is that the isomers rotate the plane of polarized light either to the lef or right. If the rotaton is on the lefside, then that isomer is levo and if on right side, then isomer is dextro. The equal proporton of levo and dextro mixture is called racemic mixture It is generally found octahedral chelate ions. The two isomers of this type of complex are mirror image of each other and cannot super impose on each other, hence they possess



chirality character.

coordinaton compound of type [PtCl₂(en)₂]²⁺ two geometrical isomers are possible. They are cis and trans. Among these two isomers, cis isomer shows optcal activty because the whole molecule is asymmetric.

The optcal isomers of $[CoCl_2(en)(NH_3)_2]^+$ are as follows



Optcal isomeric structure of $[Cr(ox)_3]^{3-}$ or $[Cr(C_2O_4)_3]^{3-}$ as follows



Bonding in Metal Carbonyls

The homoleptc carbonyls (compounds containing carbonyl ligands only) are formed by most of the transiton metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral,

NI(CO)₄ Tetrahedral Pentacarbonyliron(0) is trigonalbipyramidal



Fe(CO)₅ Trigonal bipyramidal

Hexacarbonyl chromium(0) is octahedral.



Cr(CO)₆ Octahedral

Decacarbonyldimanganese(0) is made up of two square pyramidal Mn(CO)₅ units joined by a Mn – Mn bond.



 $[Mn_2(CO)_{10}]$ Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups



[Co₂(CO)₈] Colour of coordinaton complexes

(i)Colour of a complex is not because of the light absorbed but is due to the light refected (complementary colour) e.g. If radiaton corresponding to red light are absorbed from visible region, the compound appears to have blue colour (ii0 In coordinaton complexes energy diference (Δ) between two d-sets of d-orbitals is small. Radiatons of appropriate frequency absorbed from visible region can cause excitaton of d-electron from lower energy orbital to higher energy orbital. Remaining light is transmited and compound appears coloured (iii)IF there are no d-electrons present or completely flled d-orbitals are present then there is no d-d transiton possible and complex appears colourless

Importance and applicatons of Coordinaton Compounds

Coordinaton compounds are widely present in the mineral, plant and animal worlds and are known to play many important functons in the area of analytcal chemistry, metallurgy, biological systems, industry and medicine. These are described below:

• Coordinaton compounds fnd use in many qualitatve and quanttatve chemical analysis. The familiar colour reactons given by metal ions with a number of ligands (especially chelatng ligands), as a result of formaton of coordinaton enttes, form the basis for their detecton and estmaton by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α – nitroso– β –naphthol, cupron, etc.

• Hardness of water is estimated by simple thraton with Na₂EDTA. The Ca²⁺ and Mg²⁺ ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.

 Some important extracton processes of metals, like those of silver and gold, make use of complex formaton. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordinaton entty [Au(CN)₂]⁻ in aqueous soluton. Gold can be separated in metallic form from this soluton by the additon of zinc

 Similarly, purifcaton of metals can be achieved through formaton and subsequent decompositon of their coordinaton compounds.
 For example, impure nickel is converted to [Ni(CO)₄], which is decomposed to

yield pure nickel.

Coordinaton compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordinaton compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordinaton compound of iron. Vitamin B₁₂, cyanocobalamine, the ant–pernicious anaemia factor, is a coordinaton compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptdase A and carbonic anhydrase (catalysts of biological systems).
Coordinaton compounds are used as catalysts for many industrial processes. Examples include rhodium complex, [(Ph₃P)₃RhCl], a Wilkinson catalyst, is used for the hydrogenaton of alkenes.

• Artcles can be electroplated with silver and gold much more smoothly and evenly from solutons of the complexes, [Ag(CN)₂]⁻ and [Au(CN)₂]⁻ than from a soluton of simple metal ions.

• In black and white photography, the developed flm is fxed by washing with hypo soluton which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

• 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 proportons in plant/animal systems. Thus, excess of copper and iron are removed by the chelatng ligands D-penicillamine and desferrioxime B via the formaton of coordinaton compounds. EDTA is used in the treatment of lead poisoning. Some coordinaton compounds of platnum effectively inhibit the growth of tumours. Examples are: *cis*-platn and related compounds.