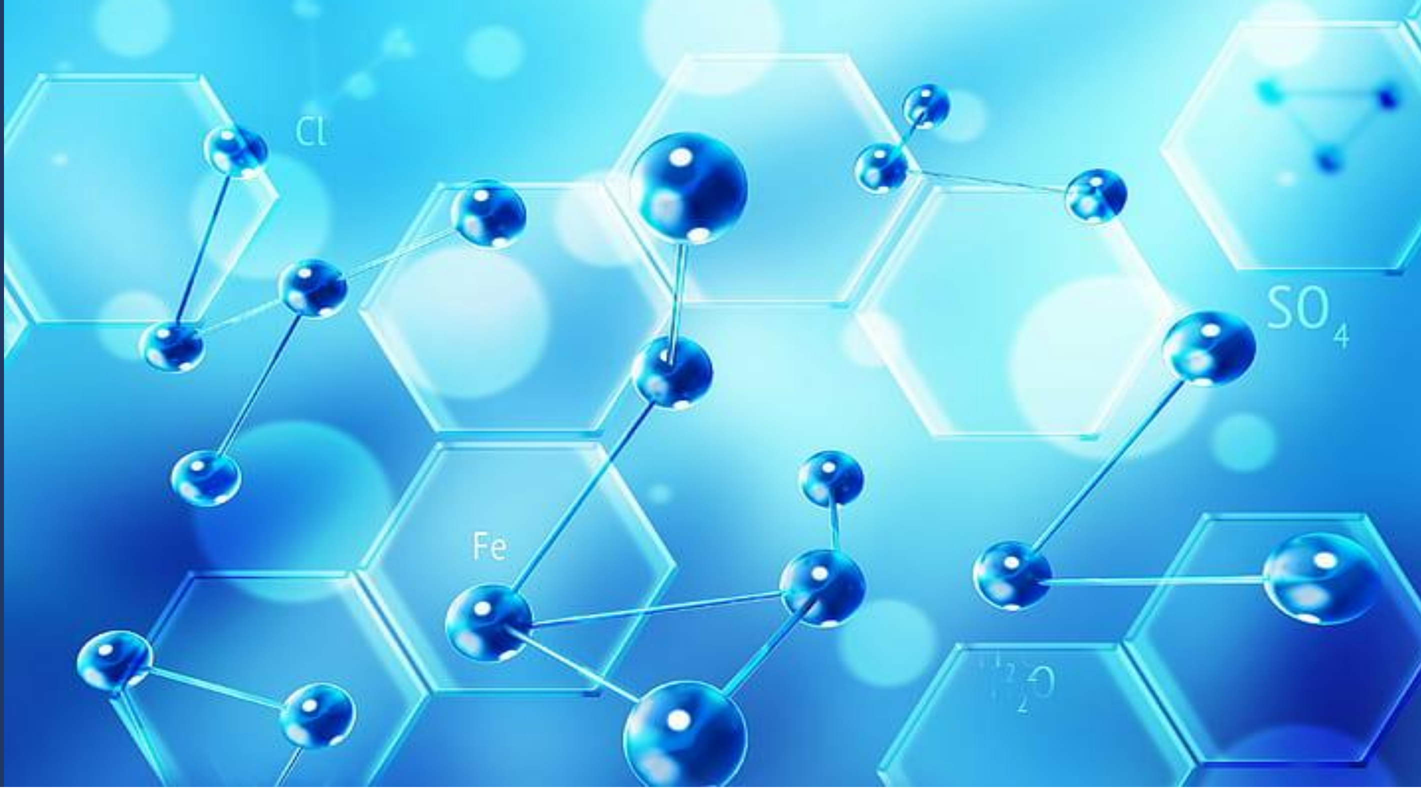
COORDINATION COMPOUNDS



CHAPTER – 9

COORDINATION COMPOUNDS

Introduction

The Coordination compounds are very important in day to day life, many compounds exist as coordination compounds as they have special type of linkage that is coordinate bond .It is formed between electron rich and electron deficient species.

Coordinate bond: It is a bond in which sharing of electrons occurs but not mutual sharing. In this the shared pair is donated by only one atom and the one that donates is donor and the other which accepts is acceptor.

Example

NH_3:   + BF_3-- {H_3N :-> BF3}In manufacture of ammonia, Fe with Mo is used as catalyst.

Nickel acts as a catalyst in hydrogenation of oils to fats.

Transition metals and their compounds exhibiting catalytic properties in various processes are given below.

In this NH_3 is donor atom as it has lone pair and BF_3 is acceptor as it is electron deficient compound.

Addition compounds: they are formed by the combination of two or more stable compounds in stoichiometric ratio.

Addition compounds are of two types:

Double salts

Coordination compounds

Double salts: compounds which lose their identity in solution are called double salts.

$K_2SO_4 + Al_2SO_4 + 24\ H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$ [Alum]

H_2O(aqueous) $2K^+ + 2Al^{+3} + 4SO_4^{2-}$

Coordination compounds:

Coordination compounds are chemical compounds that consist of an array of anions or neutral molecules that are bound to a central atom via coordinate covalent bonds. Coordination compounds are also referred to as coordination complexes. These molecules or ions that are bound to the central atom are referred to as ligands (also known as complexing agents).

Example

$[Co(NH_3)_6]Cl_3$ (hexaamminecobalt (III) chloride),

$K[AuCl_4]$ (Potassium tetrachloroaurate (III))

They do not break down into simple ions when they dissolve in water.

Coordinaton entity:

Coordination entity is a group of elements of a coordination compound that includes the central atom and the ligands around the central atom. The ligands are bound to the central atom by a covalent bond. The central atom is often a metal atom in d-block.

The electrical charge of a coordination compound is not mentioned in the coordination entity.

For example, $[CoCl_3(NH_3)_3]$ is a coordination compound in which cobalt ions are surrounded by three ammonia molecules and three chloride ions.

Coordination sphere

The coordination sphere is the collection of components of a coordination compound that includes the central atom and the ligands surrounding this central atom given along with the net electrical charge of the compound.

The electrical charge of a coordination compound is mentioned in coordination spheres.

Example

$[Fe(CN)_6]^{4-}$

Central atom or ion:

The atom/ion in a coordination entity that is bound to a fixed number of ions/groups in a definite geometrical arrangement is the central atom/ion. For example: In the coordination entities $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$, the central atoms/ions are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively. These central atoms/ ions are also Lewis acids.

Ligands:

Ligands are the ions or molecules bound to the central atom/ion in a coordination entity. These ions may be simple ions like Cl^- or small molecules such as NH_3 or H_2O. They may also be larger molecules like $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or macromolecules such as proteins.

Type of Ligand	Number of donor atoms	Examples
Monodentate	1	Water, ammonia
Bidentate	2	Ethylene diamine, DMG, Oxalic acid
Tridentate	3	Diethylenetriamine
Tetradentate	4	Triethylene tetramineEDTA
Hexadentate	6	

On the basis of Charge on Ligands

(i) Anionic ligands (negatively Charged) e.g., F^-, Cl^-, CN^-, S^{2-}, SO_4^{2-} etc.

(ii) Cationic ligands (positively charged) e.g., NO^+, NH_2-NH_3^+ etc.

(iii) Neutral ligands (uncharged and electron pair donor) e.g, CO, NH_3, H_2O etc.

Denticity: The denticity of the ligand is defined as the number of pairs of electrons shared with the metal atom or ion.

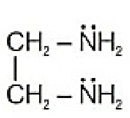
Ligands can be classified as monodentate and polydentate ligands depending upon the number of ligand donor atoms that attach to the metal atom or ion.

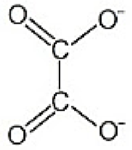
Unidentate ligands

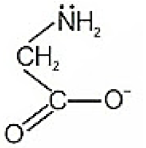
In a lot of cases, only one atom in the ligand is bound to the metal ion. In these cases, the ligand is unidentate. Examples of unidentate ligands are H_2O, NH_3 or Cl^-.

Bidentate Ligands

Ligands that bind to the metal ion through two donor atoms are bidentate or didentate ligands. Examples are $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) and $C_2O_4^{2-}$ (oxalate).

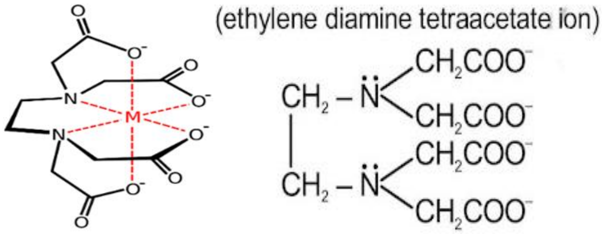

en (ethylene-1, 2-diamine)


ox (oxalate)


gly (glycinate)

Polydentate Ligands

Polydentate ligands are those that can bind to the metal ion through several donor atoms. Examples are $N(CH_2CH_2NH_2)_3$ and Ethylenediaminetetraacetate ion ($EDTA^{4-}$). EDTA is an important hexadentate ligand that can bind to a central metal ion through two nitrogen and four oxygen atoms.


(ethylene diamine tetraacetate ion)

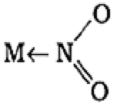
Ethylenediaminetetraacetic acid

A di or polydentate ligand that uses two or more of its donor atoms to bind to a single metal ion is a chelate ligand. The number of such donor groups is the denticity of the ligand. These complexes are chelate complexes and are more stable than other complexes containing unidentate ligands.

Ambidentate Ligands

Ambidentate ligands can ligate through two different atoms. Examples are NO_2^- and SCN^- ions where the NO_2^- ion can ligate with a central metal atom/ion through nitrogen or oxygen and SCN^- can ligate through sulphur or nitrogen.

Examples : (i)

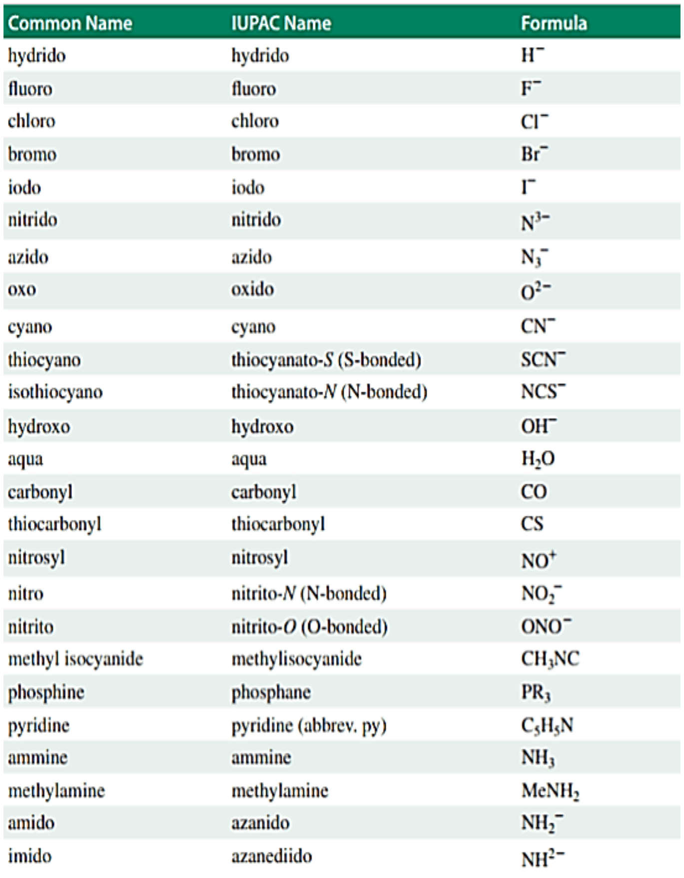

nitrito-N

M←O—N=O
nitrito — O

(ii) M←SCN
thiocyanato

M←NCS
isothiocyanato

List of ligands:



Common Name	IUPAC Name	Formula
hydrido	hydrido	H^-
fluoro	fluoro	F^-
chloro	chloro	Cl^-
bromo	bromo	Br^-
iodo	iodo	I^-
nitrido	nitrido	N^{3-}
azido	azido	N_3^-
oxo	oxido	O^{2-}
cyano	cyano	CN^-
thiocyano	thiocyanato-*S* (S-bonded)	SCN^-
isothiocyano	thiocyanato-*N* (N-bonded)	NCS^-
hydroxo	hydroxo	OH^-
aqua	aqua	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO^+
nitro	nitrito-*N* (N-bonded)	NO_2^-
nitrito	nitrito-*O* (O-bonded)	ONO^-
methyl isocyanide	methylisocyanide	CH_3NC
phosphine	phosphane	PR_3
pyridine	pyridine (abbrev. py)	C_5H_5N
ammine	ammine	NH_3
methylamine	methylamine	$MeNH_2$
amido	azanido	NH_2^-
imido	azanediido	NH^{2-}

Coordination number:

The number of ligand donor atoms to which the metal is directly bound is the coordination number (CN) of the metal ion in the complex. For example, the CN of Pt and Ni in the complex ions $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]_2^+$ are 6 and 4, respectively.
Likewise, the CN of Fe and Co in the complex ions $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$ is 6 because both $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are bidentate ligands.

Note

The CN of the central atom/ion is determined only by the number of sigma bonds between the central atom/ion and the ligand, not the Pi bonds.

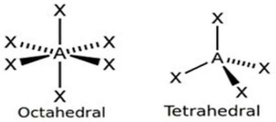
Counter ions:

Types in square brackets are composite associations or compounds and ions outside the square bracket are called count ions.

Coordination Polyhedron:

It refers to the geometric pattern or spatial arrangement of the ligands directly attached to the central atom/ion.

The most common combinations of polyhedra are octahedral, square planar and tetrahedral. For example, $[Co\ (NH_3)\ _6]\ ^{3+}$ is octahedral, $[Ni\ (Co)\ _4]$ is tetrahedral and $[PtCl_4]\ ^{2-}$ is square planar.



Oxidation Number of Central Atom

It is the charge the central atom would carry if all the ligands are removed along with the electron pairs that are shared with it. It is represented as the name of the coordination entity followed by the oxidation number written in Roman numerals in parenthesis. For example, in $[Cu(CN)_4]^{3-}$, the oxidation number of copper is +1 and is Cu(I).

Homoleptic and Heteroleptic Complexes

Homoleptic complexes are complexes where a metal is bound to only one kind of donor group whereas in heteroleptic complexes the metal is bound to more than one kind of donor group. Examples – $[Co(NH_3)_6]^{3+}$ is homoleptic and $[Co(NH_3)_4Cl_2]^+$ is heteroleptic.

Nomenclature of coordination compounds

Naming for cationic species: in which coordination sphere is positively charged

Name of cation is written first

- Let's say the coordination sphere is cationic that is with positive charge for example $[Co\ (NH_3)_6]\ Cl_3$ for the naming of coordination entity is done first and later the counter ion .so in given complex the name of $[Co\ (NH_3)_6]$ is written first than the counter ion Cl
- In case of coordination entity: the name of ligands is written first and then the central metal atom. For example, in this $[Co\ (NH_3)_6]$the name of NH3 is written first than for Co.

If the ligands are homoleptic than you can write in any manner but if they are heterodetic than the alphabetical order is followed

Example

For example: in complex $[Co\ (NH_3)_5Cl]$ the name of ligands is written in alphabetical order that is for ammine first and then chloro.

Rules for writing the name of the ligand:

- If the ligand names end with 'ate' or 'its' than e is replaced by o
- Like for oxalate it is written as oxalate, sulphite as sulphito
- If ligand name end with' ide 'than ide is replaced by 'o '

Example

for chloride it becomes chlorido

- Neutral ligands are name as such like for water it is aqua, for ammonia it is ammine
- If more than one ligand is present than alphabetical order is followed and di,tri, tetra is prefixed before the name of ligand.

Example

in complex $[Co\,(NH_3)_6]$ ligand name will be hexamine that is hexa for 6

For polydentate ligands they include numerical prefix –like di is replaced by bi, tri is replaced by tris, tetra is replaced bytetra is so on

Example

$[CoCl_2(en)_2]$ Cl in this the ligands are dichlorobisethylenediamine

In case of Central metal atom:

Oxidation state of central metal atom is written in numeral after the name of central metal atom

Example

in complex $[Co\,(NH_3)_6]\,Cl_3$ it is hexamine cobalt (III) that is cobalt (III) is central metal atom with its Oxidation state in numeral

- if complex is cationic than normally the name is used: example is same as given above
- if complex is anionic than metal atom name ends with ate

Example

in complex $K_3[fe(CN)_6]$ in this the name is written as potassium hexacyanoferrate(III) that is in this example coordination entity is anionic complex and the name of central metal atom is written with ate followed by Oxidation state in numeral

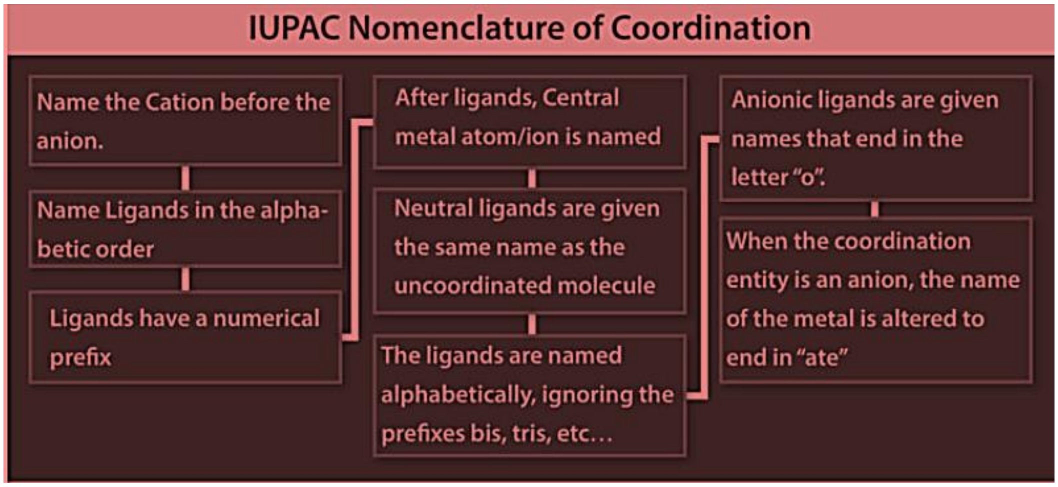
if complex is neutral than the normal central metal atom name is used

Some examples of iupac naming:

$[Cr\,(NH_3)(H_2O)_3]Cl_3$
Triaminetriaquachromium(III)chloride
$[Co(en)_3]_2(SO_4)_3$
Trisethylenediaminecobalt(III)sulphate
$[Ag(NH_3)_2][Ag(CN)_2]$
Diamine argentum(i)dicyanoargentate(i)
$[Pt\,(NH_3)_2Cl\,(NO_2)]$
Diaminechloronitroplatinum(III)
$K_4[Fe(CN)_6]$:
Potassium hexa cyanide ferrate (II)
$[Ni(CN)_4]^{-2}$:
Tetra cyanie Nickelate (II) ion.
$[Zn(OH)_4]^{-2}$:
Tetra hydroxide zincate (II) ion.
$[Ni(CO)_4]$:
Tetra carbonyl Nickel (O).

Q. **Write the IUPAC name of $[Fe(NH_3)_4O_2C_2O_4]Cl$.**

Sol. Ans: In this complex part has a charge of +1. The ligand oxalato has a charge of −2, so iron should be in +3 state meaning O_2 to be neutral. O_2 behaves as a neutral ligand and the IUPAC name is Tetraammineoxalatodioxygeniron (III) chloride.



IUPAC Nomenclature of Coordination

Name the Cation before the anion.

Name Ligands in the alphabetic order

Ligands have a numerical prefix

After ligands, Central metal atom/ion is named

Neutral ligands are given the same name as the uncoordinated molecule

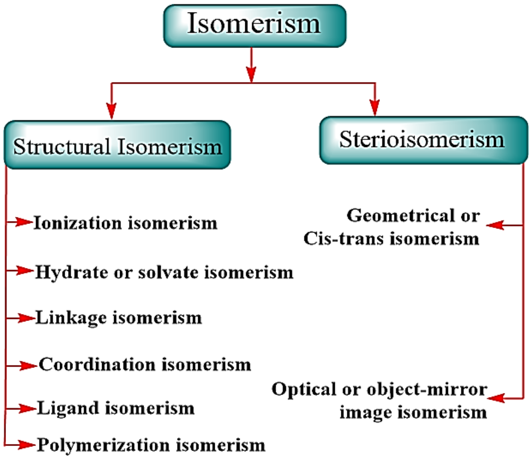
The ligands are named alphabetically, ignoring the prefixes bis, tris, etc…

Anionic ligands are given names that end in the letter "o".

When the coordination entity is an anion, the name of the metal is altered to end in "ate"

Isomerism:

Isomerism is the phenomenon in which compounds have same molecular formula but different structures and these different structures are called as isomers. Isomers are those that have different physical and chemical properties.



The types of isomerism represented by coordination compounds are:

Stereoisomerism

Coordination compounds which have the same chemical and chemical bonds but have different spatial arrangement are known as stereoisomers. These are further divided into optical isomerism and geometrical isomerism.

A. Geometrical isomerism: Geometrical isomerism is observed in heteroleptic complexes (complexes with more than one type of ligands) due to different possible geometric arrangements of the ligands.

This behaviour is mainly observed in coordination compounds having coordination numbers equal to 4 and 6.

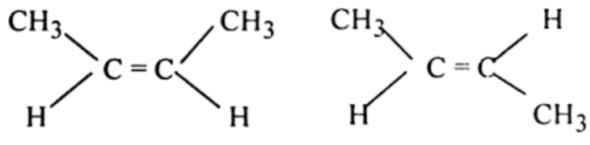
Geometrical isomerism of complexes with coordination number 4:

ML_4 tetrahedral complexes do not show cis-trans isomerism since ligands are in different directions.

MABCD has 3 geometrical isomers. 2-cis and 1-trans.

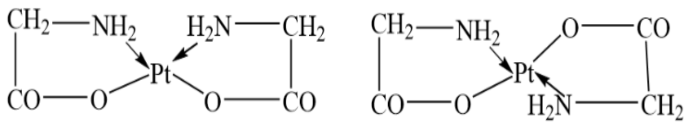
MA_2B_2 complex shows cis and trans isomers.

Example:



cis-But-2-ene trans-But-2-ene

Example:



Cis and trans glycine complexes

Another type of Geometrical isomerism that occurs in octahedral compounds in Ma3b3 like $[Co(NH_3)_3(NO_3)_3]$.

It can be of two types:

Facial

Meridional

Fac: In this three donor atoms of same ligands occupy adjacent positions at corners of an octahedral face

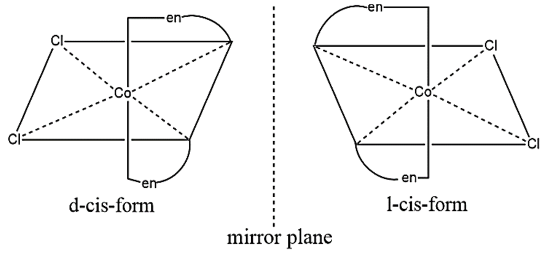
mer: In this three donor atoms of same ligands occupy positions around the meridian of an octahedron.

B. Optical isomerism: The isomer which forms non-super imposable mirror image is known as optical isomers or enantiomers. These are of two types

The isomer that rotates plane-polarized light towards clockwise direction is dextro or ‘d’ or ‘+’ isomer.

The isomer that rotates plane-polarized light to anti-clockwise direction is leavo isomer or ‘l’, ‘-‘ isomer.

The equimolar mixture of ‘d’ and ‘l’ isomer is known as the racemic mixture.

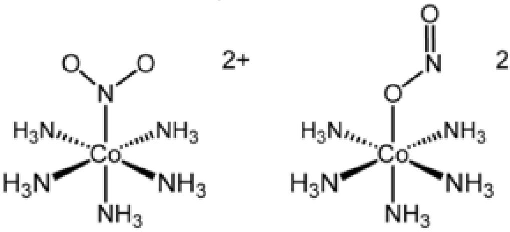


d-cis-form l-cis-form

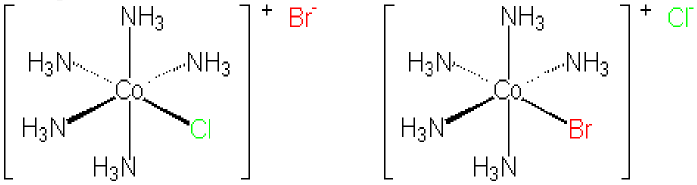
mirror plane

Structural isomerism: The compounds have same molecular phenomenon but different structures

Linking isomerism: Two or more coordination compounds in which at least one of the ligands has a different donor atom are called linkage isomers (i.e., the connectivity between atoms is different). This type of isomerism can only exist with ambidentate or ambident ligand.



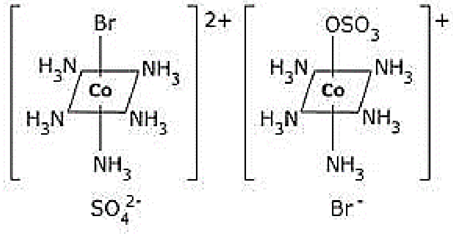
Coordination isomerism: Incoordination isomerism, the interchange of ligands between cationic and anionic entities of different metal ions present in coordination compounds takes place.



$[Co(NH_3)_5Cl]Br$ $[Co(NH_3)_5Br]Cl$

Ionization isomerism: Ionization isomers are coordination compounds with the same molecular formula but different ions in solution. This property is known as ionization isomerism.

Example: $[Co\ (NH_3)\ 5Br]\ SO_4$.



$[CO(NH_3)_5Br]SO_4$ $[CO(NH_3)_5SO_4]Br$

Solvate or hydrate isomerism:

Solvate isomers are a special case of ionisation isomerism in which compounds differ depending on the number of the solvent molecule directly bonded to the metal ion.

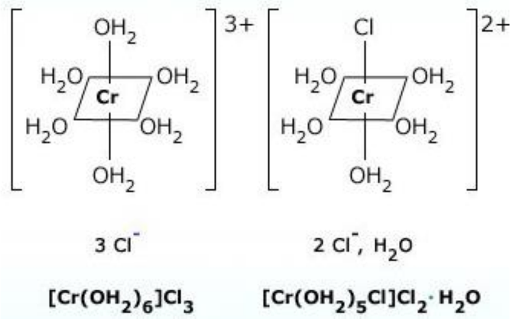
Example

$[Co(H_2O)_6]Cl_3$

$[Co(H_2O)_5Cl]Cl_2.H_2O$

$[Co(H_2O)_4Cl_2]Cl.2H_2O$

$[Co(H_2O)_3Cl_3].3H_2O$



Ligand isomerism

Certain ligands can exist in isomeric forms. They can incorporated into complexes to give rise to isomers called ligand isomers.

example: $[Co(pn)_2Cl_2]Cl$ and $[Co(tn)_2Cl_2]Cl$

Polymerization isomerism

This is not true isomerism because it occurs between compounds having the same empirical formula but different molecular weights.

$[Pt(NH_3)_2Cl_2)$, $[Pt(NH_3)_4][PtCl_4]$, $[Pt\ (NH_3)_4]\ [Pt(NH_3)\ Cl_3]_2$ and $[Pt(NH_3)_3Cl_2[PtCl_4]$

Chelate:

coordination or complex compounds consisting of a central metal atom attached to a large molecule, called a ligand, in a cyclic or ring structure.

Example

$[Cu\ (NH_2CH_2NH_2)\ _2]\ ^{2+}$

Bonding in Coordination compound

- Werner's Theory
- Valence bond theory
- Crystal field theory

Bonding in coordination compounds

The first theory in order to explain it was given by Alfred Werner in 1892.

He performed various experiments to show that the surrounding atoms exist around central atom. He actually conducted ppt. studies

$CoCl_2+NH_3 \rightarrow CoCl_3.6NH_3$

When CoCl3.6NH3 was precipitated with $AgNO_3$ it gave 3 moles of AgCl this shows that 3 Chloride ions are not directly bonded with cobalt that is why it was precipitated with silver nitrate which gave him the idea about primary and secondary valances' and accordingly he postulated his theory.

Werner's theory of Coordination compounds

In 1893 Werner produced a theory to explain the structures, formation and nature of bonding in the coordination compounds. This theory is known as Werner's theory of coordination compounds.

Werner's theory postulates of Coordination compounds:

(a) The central metal atom\ ion in a coordination compound exhibits two types of valencies - primary and secondary

(b) Primary valencies are ionisable and correspond to the numbSer of charges on the complex ion. Primary valencies apply equally well to simple salts and to complexes and are satisfied by negative ions.

(c) Secondary valencies correspond to the valencies that a metal atom (or) ion exercises towards neutral molecules (or) negative ions in the formation of its complex ions.

(d) Secondary valencies are directional and so a complex has a particular shape. The number and arrangement of ligands in space determines the stereochemistry of a complex.

Primary and secondary valencies

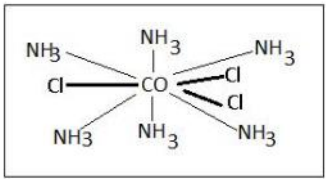
Primary valency are those which a metal exhibits in the formation of its simple salts.

Secondary valencies are those which a metal atom or cation exercises towards neutral molecules or negative groups in the formation of its complex ions.

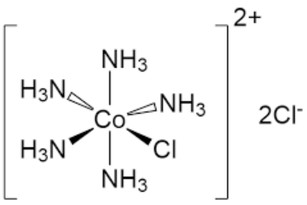
For example, in $[Pt(NH\ _3)_6]Cl_4$ primary valency is 4 and secondary valency is 6.

Depending upon this theory various structures of coordination compound was explained:

In $CoCl_3.\ (NH_3)_6$ → In this NH3 is secondary valency and Cl is primary valency



In $CoCl_3.(NH_3)_5$ the ionizable chlorides are only 2



Structure of $CoCl_3.5NH_3$

Note

in modern formulation: Primary valency corresponds to oxidation state of metals

Secondary valency corresponds to the coordination number of metals

Spatial arrangements are called coordination polyhedral.

Limitations of Werner's theory

- It failed to explain why all elements don't form coordination compounds.
- It failed to explain the directional properties of bonds in coordination compounds.
- It does not explain the colour, and the magnetic and optical properties shown by coordination compounds.

You must have studied that Werner's theory for coordination compounds failed to explain many critical aspects of valence electrons and directions in the coordination compounds. Now we use the Valence bond theory which came on to replace the Werner's theory.

One of the major drawbacks of Werner's theory is its failure to explain the coordination compounds' directional properties. Valence bond theory became successful in explaining the structure and bond linkages in these coordination compounds.

Valence bond theory:

Valence bond theory (VBT) was developed by Linus Pauling. The main assumption made by him was that the metal-ligand bonds are formed by the donating of an electron pair by the ligand to the metal and thus form a coordinate bond between the metal and ligand.

Postulates of VBT:

1. The central metal cation or atom makes available a number of vacant s, p and or d-orbitals equal to its coordination number to form coordinate covalent bonds with ligands.

2. These vacant atomic orbitals of metal are hybridised to form a new set of equivalent bonding orbitals, called hybrid orbitals. These orbitals have the same geometry, the same energy and definite directional properties.

3. The bonding in metal complexes arises when a filled ligand orbital containing a lone pair of electrons overlaps a vacant hybrid orbital on the metal cation or atom to form a coordinate covalent bond.

4. Each ligand has at least one orbital containing a lone pair of electrons. Pauling classified the ligands into two categories (i) Strong ligands like CN^-, CO^- etc. (ii) weak ligands like F^-, Cl^- etc.

5. Strong ligands have a tendency to pair up the d-electrons of a metal cation or atom to provide the necessary orbitals for hybridization. On the other hand, weak ligands do not have a tendency to pair up the d-electrons.

6. The d orbital used in hybridization may be either inner (n-1) d-orbitals or outer n d-orbitals. The complex formed by inner (n-1) d-orbitals, is called inner orbital complex whereas the complex formed by outer d-orbital is called outer orbital complex.

7. If unpaired electrons are present within the complex, then complex is paramagnetic in nature while if all the electrons are paired then complex is diamagnetic in nature.

Examples of Octahedral complexes

(a) Inner Orbital Complexes:

$[Co(CN)_6]^{3-}$ ion:

In this complex, the oxidation state of cobalt is +3.

The valence shell electronic configuration of Co^{3+} is $3d^6$.

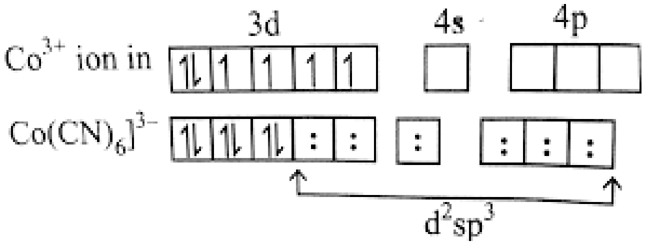
The CN^- ligands are strong and therefore cause pairing of 3d-electrons.

All six 3d-electrons are therefore paired and occupy three of the five 3d orbitals.

The vacant 3d- orbitals combine with the vacant 4s and 4p orbitals to form six d^2sp^3-hybrid orbitals.

These six hybrid orbitals overlap with six filled orbitals of ligands to form six-coordinate covalent bonds.

In $[Co(CN)_6]^{3-}$, Co is present as Co^{3+}



(b) Outer Orbital Complexes:

$[Fe(F)_6]^{3-}$ ion:

In this complex, the oxidation state of Iron(Fe) is +3.

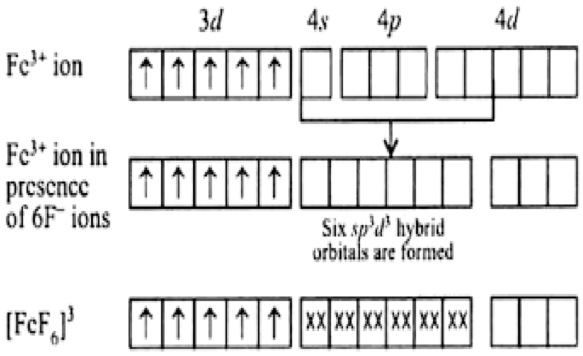
The valence shell electronic configuration of Fe^{3+} is $3d^5$.

The F- ligands are weak and therefore cause no pairing of 3d-electrons.

All five 3d-electrons are therefore occupied on five 3d orbitals.

The vacant 4s- orbitals combine with the vacant 4p and two vacant 5d orbitals mixed with each other to form six sp3d2-hybrid orbitals.

These six hybrid orbitals overlap with six filled orbitals of ligands to form six-coordinate covalent bonds.



Examples of tetrahedral complexes

$[NiCl_4]^{2-}$ ion:

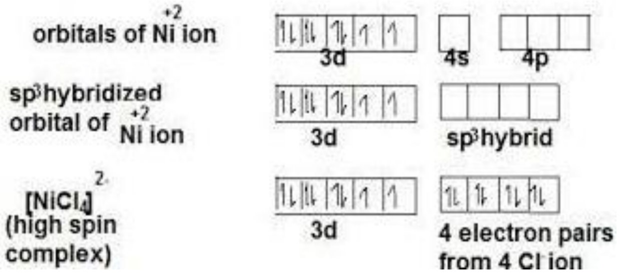
In this complex ion, the oxidation state of Ni is +2.
The valence shell electronic configuration is 3d8.

Since Cl^- is a weak ligand, therefore no pairing of electrons will occur in 3d-orbitals.

None of the five 3d- orbitals is vacant.

Vacant 4s and 4p orbitals combine to give four sp^3 hybrid orbitals.

These four hybrid orbitals form bonds with four ligands by sharing four pairs of electrons.



$[Ni(CN)_4]^{2-}$ ion:

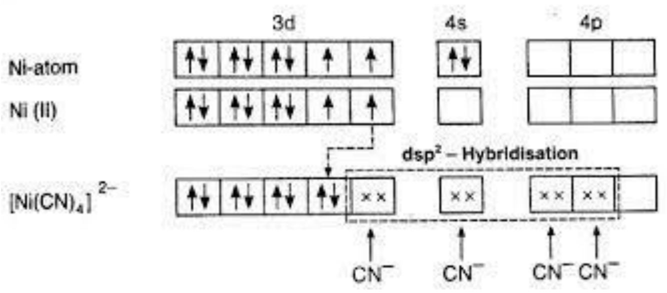
In this complex ion, the oxidation state of Ni is +2.

The valence shell electronic configuration is 3d8.

Since CN^- is a strong ligand, therefore these ligands cause to pair up the two unpaired electrons in one d-orbital resulting in a vacant 3d-orbital.

This vacant 3d-orbital gets hybridised with the vacant 4s and two 4p orbitals to give four dsp^2 hybrid orbitals.

These four hybrid orbitals form bonds with four ligands by sharing four pairs of electrons.



VBT Limitation:

- It could not explain the nature of ligands.
- It could not explain why the pairing of electrons occurs in the presence of strong ligands.
- It could not explain the colour and electronic spectra of complexes.
- It could not explain reaction rates and the mechanism of reactions of complexes.
- This theory does not provide any quantitative interpretation data about the thermodynamic and kinetic stability of coordination complexes.

Coordination number	Type of hybridisation	Shape of hybrid
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2 (nd orbitals are involved – outer orbital complex or high spin or spin free complex)	Octahedral
6	d^2sp^3 (n-1) d orbitals are involved –inner orbital or low spin or spin paired complex.	Octahedral

Magnetic properties of coordination compounds:

The complex in which central transition metal ion has unpaired electrons is Paramagnetic.
The complex in which central transition metal ion has no unpaired electrons is diamagnetic.
The magnetic moment of a complex is calculated by the spin only formula

Magnetic moment - $\mu = \sqrt{n(n+2)}$ BM

BM – Bohr magneton
When n the number of unpaired electrons.

The magnetic moment of complex compounds depends upon:

- Type of hybridization.
- The oxidation state of central transition metal ion.
- The number of unpaired electrons.

Crystal field theory:

Crystal Field Theory (CFT) is a model of binding interactions between transition metals and ligands. Explains the effect of attraction between the positive charge of the metal cation and the negative charge on the unified electrons of the ligand. The nature of the lines around the metal ion.

Crystal field stabilization energy

A consequence of Crystal Field Theory is that the distribution of electrons in the orbitals can lead to stabilisation for some electron configurations. It is a simple matter to calculate the stabilization since all that is needed is the electron configuration. For an octahedral complex, an electron in the more stable t2(g) subset is treated as contributing $-2/5\Delta$

whereas an electron in the higher energy eg subset contributes to a destabilisation of 3/5Δ

The final answer is then expressed as a multiple of the crystal field splitting parameter Δ(Delta)

Based on this, the crystal field stabilisation energies for d0 to d10 configurations can then be used to calculate the Octahedral Site Preference Energies which is defined as OSPE = CFSE (oct) - CFSE (tet)

Note

The conversion between Δoct and Δtet used for these calculations is $\Delta_{tet} = \Delta_{oct} \times 4/9$
CFSE = ΔE = $E_{\text{ligand Field}} - E_{\text{isotropic Field}}$

Spectrochemical series:

The series of increasing order of field strength of ligands is known as Spectrochemical series.

Spectrochemical Series

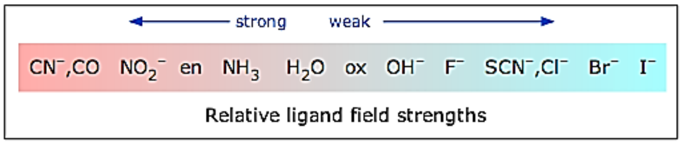
$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- <$ urea, $OH^- <$ ox, $O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en < bpy, phen $< NO_2^- < CH_3^-, C_6H_5^- < CN^- < CO.$

Weak field ligands:

These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ0 is less than pairing energy (p) in a single orbital.
Contains X, O and S as donor atoms

Strong field ligands:

These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ_0 is greater than pairing energy (p).
Contains C, N and P as donor sites.



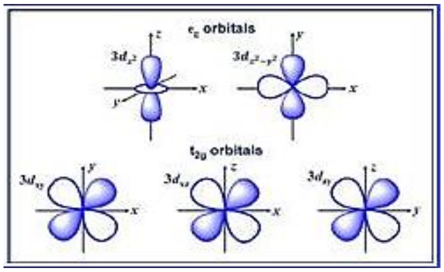
Crystal field splitting theory

It was given by Hans Bethe and John van vleck

Postulates

- It assumes the central metal atom and ligands as point charges
- When a complex is formed: central metal atom positive charge
  Ligands –have negative charge
- This theory considers the interaction between central metal atom and ligand is purely electrostatic
- When a complex is formed the central metal atom is surrounded by oppositely charged ligands
- No hybridization takes place
- To form a bond the ligand molecule must approach towards central metal atom
- In absence of external magnetic field, the d orbital of central metal atom is degenerate but this degeneracy breaks when ligand approaches.

The d orbital splits into two sets:	
Axial set	non-axial set
dxy, dyz, dzx	d_{x2-y2}, d_{z2}

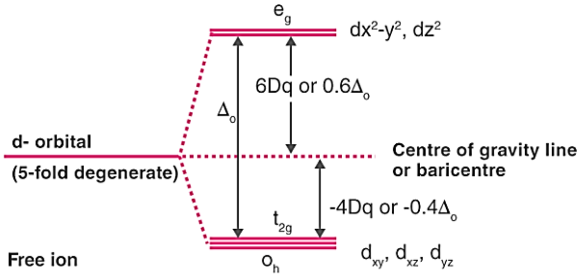


This is crystal field splitting.

- Repulsive forces occur between electrons of metal and with lone pair ligands due to which energy of electron fluctuate or changes.

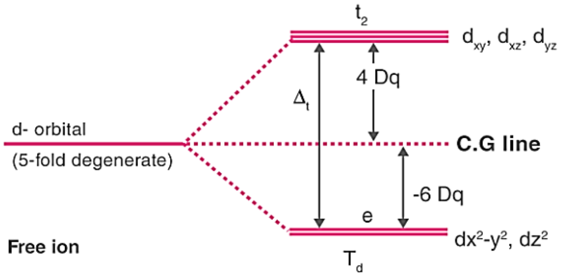
Crystal field splitting into octahedral coordination complexes:

To form octahedral complex the ligands, have to approach central metal atom along the coordination axis. During the approach the d orbitals whose lobes lie along the axis will experience more repulsion due to this their energy will increase and the other non-axial set will suffer less repulsion. As a result, the non-axial will have less energy as compare to axial set (eg. greater than t_{2g})



Crystal field splitting into tetrahedral coordination complexes:

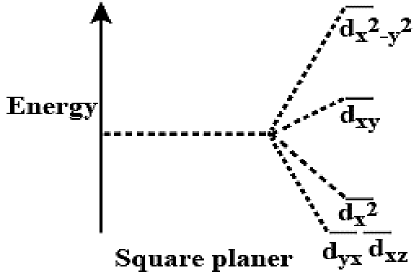
The ligands have to approach central metal atom in between the coordination axis. During the approach the d orbital's whose lobes lie along the axis will experience less repulsion due to this their energy will increase and the other non-axial set will suffer more repulsion. as a result, the non-axial will have more energy as compared to axial set (t_{2g} greater than e_g)



Crystal Field Splitting in Tetrahedral Complex

Square planar complex:

In the different order is seen i.e
dx^2-y^2,dxy,dz^2,dyz,dzx



Note

for strong ligands: the CFSE is more therefore pairing will occur
for weak ligands: the CFSE Is less

Why is the crystal field splitting of d-orbitals in tetrahedral less than octahedral complexes?

In the tetrahedral complex none of the d-orbitals point directly at the ligands lowering the electron-electron repulsion so the energy separation is small as compared to the octahedral field and a small number of ligands produces a small crystal field separation.

Limitations of crystal field theory

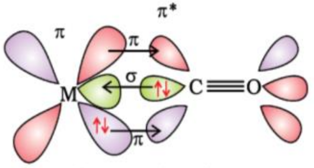
- The assumption that the interaction between metal-ligand is purely electrostatic cannot be said to be very realistic.
- This theory takes only d-orbitals of a central atom into account. The s and p orbits are not considered for the study.
- The theory fails to explain the behaviour of certain metals which cause large splitting while others show small splitting. For example, the theory has no explanation as to why H_2O is a stronger ligand as compared to OH^-.
- The theory rules out the possibility of having p bonding. This is a serious drawback because is found in many complexes.
- The theory gives no significance to the orbits of the ligands. Therefore, it cannot explain any properties related to ligand orbitals and their interaction with metal orbitals.

Bonding in metal carbonyls:

Metal carbonyls:

Metal carbonyls are coordination complexes of transition metals with carbon mono-oxide ligands. Metal carbonyls are useful in organic synthesis and as catalysts or catalyst precursors in homogeneous catalysis, such as hydroformylation, e.g., $[Fe(CO)_5]$, $[V(CO)_6]$.

Structure of metal carbonyls:



Synergic bonding

Due to donation of electrons by the carbonyl molecules to the vacant orbitals of the metal, a metal-carbon σ bond is formed.

Due to the donation of a pair of electrons from a filled d orbital metal into the vacant anti-bonding π* orbital of carbonyl ligand, a metal-carbon π bond is formed.

Bonding in metal carbonyls

Carbon monoxide bonds to transition metals using "synergistic pi star back-bonding." The bonding has three components, giving rise to a partial triple bond. A sigma bond arises from overlap of the nonbonding (or weakly anti-bonding) sp-hybridized electron pair on carbon with a blend of d-, s-, and p-orbitals on the metal. A pair of bonds arises from overlap of filled d-orbitals on the metal with a pair of -antibonding orbitals projecting from the carbon atom of the CO. The latter kind of binding requires that the metal have d-electrons, and that the metal is in a relatively low oxidation state (<+2) which makes the back donation process favourable. As electrons from the metal fill the -antibonding orbital of CO, they weaken the carbon-oxygen bond compared with free carbon monoxide, while the metal-carbon bond is strengthened. Because of the multiple bond character of the M-CO linkage, the distance between the metal and carbon atom is relatively short, often < 1.8 , about 0.2 shorter than a metal-alkyl bond. Several canonical forms can be drawn to describe the approximate metal carbonyl bonding modes.

Uses of metal carbonyls

- Metal carbonyls are useful in organic synthesis and as catalysts or catalyst precursors in homogeneous catalysis, such as hydroformylation, In the Mond process, nickel carbonyl is used to produce pure nickel.

Properties of carbonyl metal

- Most of the metal carbonyls are solids at room temperature and atmospheric pressure.
- They are soluble in nonpolar and polar organic solvents.
- Their reactivity is partly due to the central metal atom and partly due to the CO ligands.

Stability of Coordination Compounds:

Coordination compounds are found to dissociate in various solutions. The stability of a coordination compound in a solution mainly depends on the degree of association between the two species involved in the state of equilibrium. Quantitatively the stability of any complex is given by the magnitude of the equilibrium constant for the formation of the compound. A general example is given below:

$A + 4B \rightarrow AB_4$

Thus, the amount of AB_4 molecule in the solution depends upon the value of the equilibrium constant, k. This is also known as the stability constant. On the other hand, the instability constant or the dissociation constant of complexes is given by the reciprocal of the equilibrium constant of the formation reaction.

Organo-metallic compounds

They are those compounds in which metal or metalloid or a non-metal is directly linked to carbon atom of a hydrocarbon.

Example

$(C_2H_5)_2Zn$ etc $[Co(H_2O)_3Cl_3].3H_2O$

Note

Metal cyanides and metal carbides are not organometallic compounds as in them carbon atom is not directly joined to metal.

Types of organometallic compounds:

Sigma organometallic compounds

Pi organometallic compounds

Sigma organo-metallic compounds: these are the compounds obtained by bonding of non-metal with metalloid elements with carbon. forexample: RMgX, $(CH_3)Al$ etc.

Pi organo- metalliccompound: these compounds are formed mainly by transition elements. Normal sigma bond is formed through the pi electron cloud of organic molecule. Forexample: ferrocene ,zeisse's salt etc

Sigma and pi organo-metaliccompound: these compounds are formed by transition metal carbonyls.

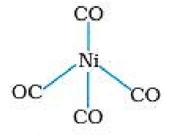
Example

$Ni(CO)_4$,$Fe(CO)_5$ etc

Shapes of these structures are shown below:

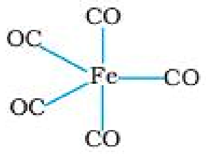
For example:

Shape of $[Ni(Co)_4]$



$Ni(CO)_4$
Tetrahedral

Shape of $[Fe(Co)_5]$



$Fe(CO)_5$
Trigonal bipyramidal

The importance and application of coordination compound

- They are used in estimation of hardness of water as calcium and, magnesium ions form complexes with EDTA.
- It is used in estimation and detection of metal ions. for example: Ni^{2+}ions is estimated using dimethyl glyoxime
- It is used in Extraction of metals
- It is used in medicines like cis platin is used in treatment of cancer
- It is used in animal and in plant world like hemoglobin is a complex of iron, chlorophyll is a complex of magnesium and so on

SUMMARY

The chemistry of coordination compounds is an important and stimulating chapter of modern inorganic chemistry. During last fifty years, advances in this area have provided development of new concepts and models of bonding and molecular structure, novel breakthrough in chemical industries and huge insights into functioning of critical component of biological systems.

The first trial in explaining the formation, reactions, structure and bonding of a coordination compound was done by **Werner**. His theory postulated the use of two types of linkage by a metal ion/ atom in a coordination compound. In the modern language of chemistry these are known as ionisable and non-ionisable bonds respectively. Using the isomerism property, Werner predicted the geometrical shape of a large number of coordination entities.

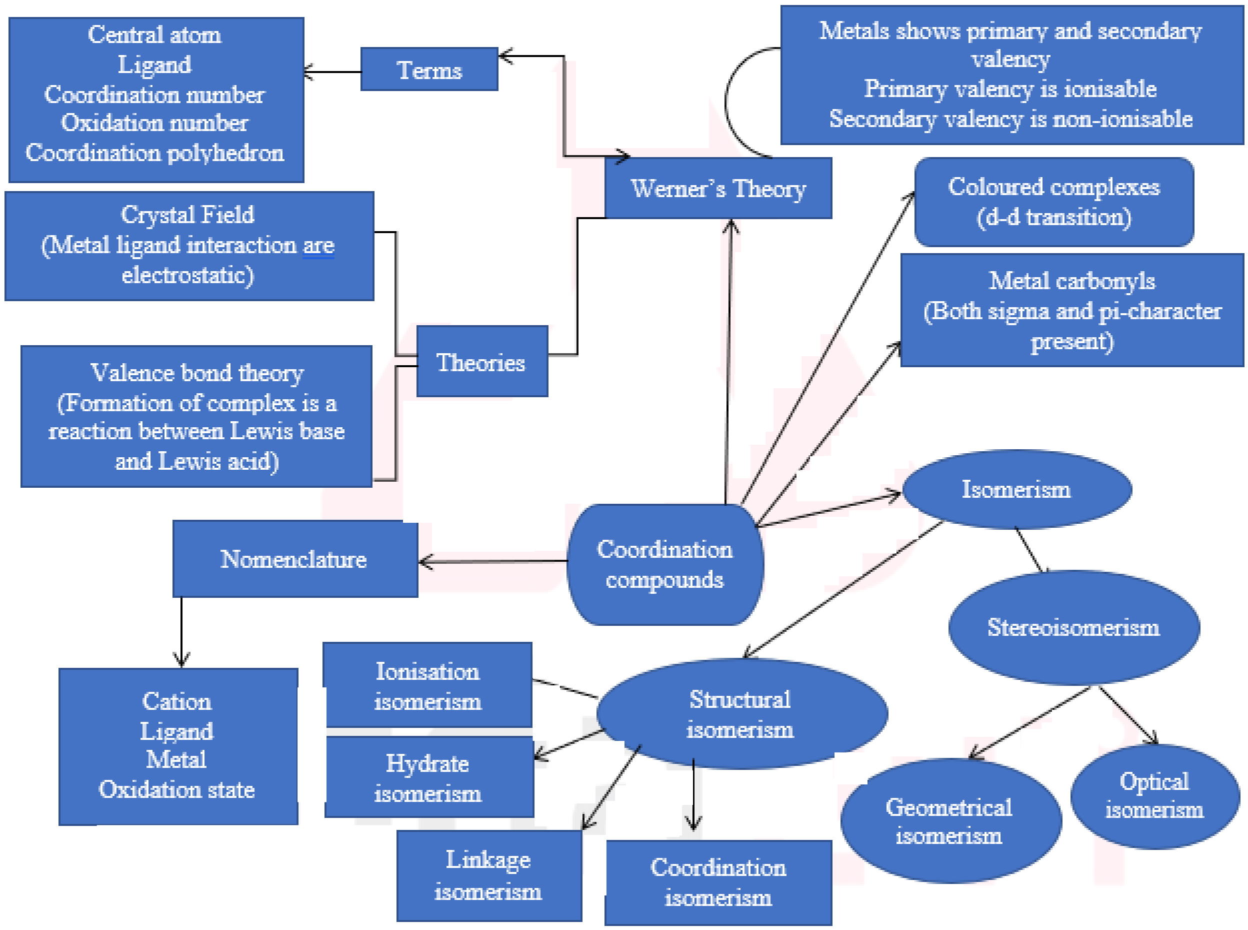
VBT explains with responsible success, the formation, magnetic behaviour and geometrical shapes of coordination compounds. It was not able to give the quantitative interpretation of magnetic behaviour and not able to tell about the optical properties of these compounds.

CFT of coordination compounds is based on the effect of different crystal fields on the degeneracy of d orbital energies of the central metal atom/ion. The splitting of d orbitals provides different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimation of orbital separation energies, magnetic moment and spectral and stability parameters. However, the assumption that ligands constitute point charges creates many theoretical difficulties.

The metal-carbon bond in metal carbonyl possesses both Sigma and pi character. The ligand to metal is Sigma bond and metal to ligand is pi bond. This unique synergic bonding provides stability to metal carbonyl s.

Coordination compounds have extensive applications in metallurgical processes, analytical and medicinal chemistry.

MIND MAP



Central atom
Ligand
Coordination number
Oxidation number
Coordination polyhedron

Terms

Metals shows primary and secondary valency
Primary valency is ionisable
Secondary valency is non-ionisable

Werner's Theory

Crystal Field
(Metal ligand interaction are electrostatic)

Coloured complexes
(d-d transition)

Theories

Metal carbonyls
(Both sigma and pi-character present)

Valence bond theory
(Formation of complex is a reaction between Lewis base and Lewis acid)

Isomerism

Nomenclature

Coordination compounds

Stereoisomerism

Cation
Ligand
Metal
Oxidation state

Ionisation isomerism

Structural isomerism

Hydrate isomerism

Geometrical isomerism

Optical isomerism

Linkage isomerism

Coordination isomerism

QUESTIONS FOR PRACTICE

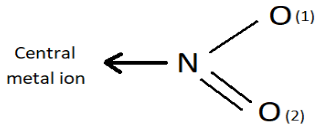
Q1. Which of the following is the coordination entity in $K_2[Zn(OH)_4]$?
(a) K^+
(b) Zn^{2+}
(c) OH–
(d) $[Zn(OH)_4]^{2-}$

Q2. The central atom/ion of a coordination complex is also referred to as
(a) Lewis acid
(b) Lewis base
(c) Bronsted-Lowry acid
(d) Bronsted-Lowry base

Q3. Which of the following cannot be a ligand?
(a) Ni^{2+}
(b) Cl^-
(c) H_2O
(d) NH_3

Q4. How many donor atoms can $EDTA^{4-}$ ligand bind through?
(a) 2
(b) 4
(c) 6
(d) 8

Q5. Which is the donor atom in the coordinate bond shown below?



(a) N
(b) O1
(c) O2
(d) Both N and O

Q6. Coordination number is a characteristic of which of the following?
(a) Central atom
(b) Ligand
(c) Coordination entity
(d) Coordination compound

Q7. Identify the coordination sphere in the compound $K_4[Fe(CN)_6]$.
(a) K^+
(b) Fe_{2+}
(c) $[Fe(CN)_6]^{4-}$
(d) CN^-

Q8. Select the correct IUPAC name for: $[Co(NH_3)_6]^{2+}$
(a) hexammoniacobaltate(II) ion
(b) hexaamminecobaltate(II) ion
(c) hexammoniacobalt(II) ion
(d) hexaamminecobalt(II) ion
(e) hexammoniacobalt ion

Q9. Strong field ligands such as CN^-:
(a) usually produce high spin complexes and small crystal field splittings.
(b) usually produce low spin complexes and small crystal field splittings.
(c) usually produce low spin complexes and high crystal field splittings.
(d) usually produce high spin complexes and high crystal field splittings.
(e) cannot form low spin complexes.

Q10. Consider the complex ion $[Mn(OH_2)_6]^{2+}$ with 5 unpaired electrons. Which response includes all the following statements that are true, and no false statements?
I. It is diamagnetic.
II. It is a low spin complex.
III. The metal ion is a d^5 ion.
IV. The ligands are weak field ligands.
V. It is octahedral.
(a) I, II
(b) III, IV, V
(c) I, IV
(d) II, V
(e) III, IV

Q11. When the valence d orbitals of the central metal ion are split in energy in an octahedral ligand field, which orbitals are raised least in energy?
(a) dxy and dx^2-y^2
(b) dxy, dxz and dyz
(c) dxz and dyz
(d) dxz, dyz and dz^2
(e) dx^2-y^2 and dz^2

Q12. How many unpaired electrons are there in a strong field iron(II) octahedral complex?
(a) 0
(b) 1
(c) 2
(d) 4
(e) 6

Q13. The coordination complex, $[Cu(OH_2)_6]^{2+}$ has one unpaired electron. Which of the following statements are true?
(1) The complex is octahedral.
(2) The complex is an outer orbital complex.
(3) The complex is d^2sp^3 hybridized.
(4) The complex is diamagnetic.
(5) The coordination number is 6.
(a) 1, 4
(b) 1, 2, 5
(c) 2, 3, 5
(d) 2, 3
(e) 4, 5

Q14. A molecule that cannot be superimposed on its mirror image is said to exhibit which of the following?
(a) geometrical isomerism
(b) optical isomerism
(c) linkage isomerism
(d) reactive isomerism
(e) coordination isomerism

Q15. Which one of the following complexes can exhibit geometrical isomerism?

(a) $[Pt(NH_3)_2Cl_2]$	(square planar)
(b) $[Zn(NH_3)_2Cl_2]$	(tetrahedral)
(c) $[Cu(NH_3)_4]^{2+}$	(square planar)
(d) $[Co(NH_3)_5Cl]^{2+}$	(octahedral)
(e) $[Cu(CN)_2]^-$	(linear)

Q16. Which name-formula combination is NOT correct?

FORMULA	**NAME**
(a) $[Co(NH_3)_4(OH_2)I]SO_4$	tetraammineaquaiodocobalt(III) sulfate
(b) $K[Cr(NH_3)_2Cl_4]$	potassium diamminetetrachlorochromate(III)
(c) $[Mn(CN)_5]_{2-}$	pentacyanomanganate(II) ion
(d) $[Ni(CO)_4]$	tetracarbonylnickel(0)
(e) $Ca[PtCl_4]$	calcium tetrachloroplatinate(II)

Q17. Given the list of ligands and their corresponding names, choose the pair that disagree.

LIGAND	NAME
(a) OH^-	hydroxo
(b) CN^-	cyanide
(c) Cl^-	chloro
(d) H_2O	aqua
(e) NH_3	ammine

Q18. In coordination chemistry, the donor atom of a ligand is

(a) a Lewis acid.

(b) the counter ion

(c) the central metal atom.

(d) the atom in the ligand that shares an electron pair with the metal.

(e) the atom in the ligand that accepts a share in an electron pair from the metal.

Q19. The ______ sphere is enclosed in brackets in formulas for complex species, and it includes the central metal ion plus the coordinated groups.

(a) ligand (b) donor

(c) oxidation (d) coordination

(e) chelating

Q20. Consider the coordination compound, $Na_2[Pt(CN)_4]$. The Lewis acid is

(a) $[Pt(CN)_4]^{2-}$ (b) Na^+

(c) Pt (d) Pt^{2+}

(e) CN^-

Q21. The formula of potassium dicyanobis (oxalato) nickelate (II) is

(a) $K4[Ni(CN)(Ox)_2]$

(b) $K_3[Ni_2 (CN)_2 (Ox)_2]$

(c) $K_4[Ni(CN)_2(Ox)_2]$

(d) $K_2[Ni(CN)_2(Ox)_2]$

Q22. The name of $[Co(NH_3)_3 (NO_2)_3]$ is

(a) Triammine trinitro-N-cobalt(III)

(b) Trinitrotriamminecobalt(II)

(c) Trinititrotriamjninecobalt (III) ion

(d) Trinitrotnamminecobatate (III).

Q23. The co-ordination number of cobalt in the complex $[Co(en)_2Br_2]Cl_2$ is

(a) 4

(b) 6

(c) 5

(d) 2.

Q24. $K_3[Al(C_2O_4)_3]$ is called

(a) Potassium alumino oxalate

(b) Potassium aluminium (III) trioxalate

(c) Potassium trioxalato aluminate (III)

(d) Potassium tris (oxalato) aluminium.

Q25. The cation that does not form an ammine complex with excess of ammonia is

(a) Ag^+ (b) Al^{3+}

(c) Cu^{2+} (d) Cd^{2+}

Q26. One among the following is an example of hexadentate ligands

(a) 2, 2-bipyridyl

(b) ethylenediammine tetra acetate ion

(c) dimethyl glyoxime

(d) Tetracarbonyl nickel.

Q27. One among the following is not an organometallic compound

(a) Trimethylboron

(b) Trimethyl aluminium

(c) Trimethoxy titanium chloride

(d) Tetracarbonyl nickel.

Q28. The correct structural formulae of Zeise's salt is

(a) $K^+ [PtCl_3(C_2H_4)]^-$

(b) $K^+ [PtCl_2\text{-}\eta^2\text{-}(C_2H_4)]Cl^-$

(c) $K_2 [PtCl_3\text{-}\eta^2\text{-}C_2H_4)]$

(d) $K^+ [PtCl_3\text{-}\eta^2\text{-}(C_2H_4)]^-$.

Q29. Amongst Ni $(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$

(a) Ni(CO)4 and NiCl42- are diamagnetic and [Ni(CN)4]2- is paramagnetic

(b) NiCl42- arrd [Ni(CN)4]2- are diamagnetic and Ni(CO)4 is paramagnetic.

(c) Ni(CO)4 and [Ni(CN)4]2- are diamagnetic and [NiCl4]2- is paramagnetic.

(d) Ni(CO)4 is diamagnetic and [NiCl4]2- and [Ni(CN)4]2- are paramagnetic.

Q30. Which of the following compounds can exhibit linkage isomerism?
(a) $[Co(en)_3]Cl_3$
(b) $[Co(en)_2Cl_2]Cl$
(c) $[Co(en)_2NO_2Cl]Br$
(d) $[Co(NH_3)_5Cl]Br_2$.

Q31. Which of the following ligands is a tridentate ligand?
(a) DMG (b) Bipy
(c) acac (d) dien.

Q32. In Ni $(CO)_4$, the nickel atom is ……… hybridised
(a) sp^2 (b) sp^3
(c) dsp^2 (d) sp^3d.

Q33. Ziegler-Natta catalyst is $TiCl_3$ dissolved in
(a) Triethylaluminium (b) Ether
(c). Water (d) Ammonia.

Q34. $[Fe(NO_2)_3\ Cl_3)$ and $[Fe\ (O\text{-}NO)_3\ Cl_3]$ show
(a) linkage isomerism
(b) geometrical isomerism
(c) optical isomerism
(d) none of these.

Q35. Which one of the following is expected to exihibit optical isomerism (en = ethylene diammine).
(a) cis-$[Pt\ (NH_3)_2Cl_2)$
(b) cis-$[Co(en)_2Cl_2]$
(c) trans-$[Co(en)_2\ Cl_2]$
(d) trans-$[Pt\ (NH_3)_2Cl_2]$

Q36. Which of the following compounds has tetrahedral geometry?
(a) $[Ni(CN)_4]^{2-}$ (b) $[Pd(CN)_4]^{2-}$
(c) $[PdCl_4]^{2-}$ (d) $[NiCl_4]^{2-}$

Q37. According to Werner's theory of coordination compounds
(a) Primary valency is ionisable
(b) Secondary valency is ionisable
(c) Primary and secondary valencies are lonisable
(d) Neither primary nor secondary valency is ionisable

Q38. The ligand $N(CH_2CH_2NH)_3$ is
(a) bidentate (b) tridentate
(c) tetradentate (d) pentadentate

Q39. Among the following which arc ambidentate ligands?
(i) SCN– (ii) NO_3^-
(iii) NO_2^- (iv) $C_2O_4^{2-}$
(a) (i) and (iii) (b) (i) and (iv)
(c) (ii) and (iii) (d) (ii) and (iv)

Q40. Which of the following is not a neutral ligand?
(a) H_2O (b) NH_3
(c) ONO (d) CO_2

Q41. Which of the following ligands will not show chelation?
(a) EDTA (b) DMG
(c) Ethene-1, 2-diamine (d) SCN^-

Q42. The correct IUPAC name of the following compound is $|Cr(NH_3)_5(NCS)||ZnCl_4|$
(a) Penta amine isothiocyanato chromium (III) tetrachlorozincate (II)
(b) Penta amine isothicocyanatezinc chloridechromate (III)
(c) Penta amine isothicoyanato chromate (II)
(d) isothiocyanatopenta amine chromium (II) zinc chloride (IV)

Q43. Which of the following isomers will give white precipitate with BaCl2 solution?
(a) $[CO(NH_3)_5SO_4]Br$
(b) $[CO(NH_3)_5Br]SO_4$
(c) $[CO(NH_3)_4(SO_4)_2]Br$
(d) $[CO(NH_3)_4(SO_4)]$

Q44. $|Pt(NH_3)_4|\ |CuCl_4|$ and $|Cu(NH_3)_4||PtCl_4|$ are known as
(a) ionisation isomers.
(b) coordination isomers
(c) linkage isomers
(d) polymerisation isomers

Q45. Which of the following will not show geometrical isomerism?
(a) $[Cr(NH_3)_4Cl_2]Cl$ (b) $[Co(en)_2Cl_2]Cl$
(c) $[(Co(NH_3)_5NO_2]Cl_2$ (d) $[Pt(NH_3)_2Cl_2]$

Q46. The oxidation number of Cr in a $[Cr(NH_3)_2F_4]^-$ complex is
(a) II (b) III
(c) IV (d) VI.

Q47. The number of halide ions in $[Pt(NH_3)_3Cl_3Br]Cl$ will be
(a) 4 (b) 3
(c) 2 (d) 1.

Q48. On adding $AgNO_3$ solution to 1 mole of $PdCl_2.4NH_3$ two moles of AgCl are formed. The secondary valency of Pd in the complex will be
(a) 0 (b) 2
(c) 4 (d) 1

Q49. What kind of isomerism exists between $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$?
(a) Linkage isomerism
(b) Solvated isomerism
(c) Ionisation isomerism
(d) Coordination isomerism

Q50. In the following chelating ligand is

(a) OH^- (b) $H_2NCH_2CH_2NH_2$

(c) Cl^- (d) CN^-

ASSERTION AND REASONING

Q1. **Assertion:** NF_3 is a weaker ligand than $N(CH_3)_3$.

Reason: NF_3 ionizes to give F^- ions in aqueous solution.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

Q2. **Assertion:** $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

Reason: $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

Q3. **Assertion:** $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Reason: d-d transition is not possible in $[Sc(H_2O)_6]^{3+}$.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

Q4. **Assertion:** Toxic metal ions are removed by the chelating ligands.

Reason: Chelate complexes tend to be more stable.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

Q5. **Assertion:** Geometrical isomerism is also called cis-trans isomerism.

Reason: Tetrahedral complexes show geometrical isomerism.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

TRUE/FALSE

Q1. The coordination number of an atom in hexagonal close packed structure is 12.

(a) True (b) False

Q2. The coordination number of a face-centred atom in a unit cell is equal to 12.

(a) True (b) False

Q3. Face-centred cubic structure possesses the most closed packing of atoms in it.

(a) True (b) False

QUESTIONS FOR PRACTICE

Q1. A coordination complex's core atom/ion is also known as _______

(a) Bronsted-Lowry acid

(b) Lewis base

(c) Lewis acid

(d) Bronsted-Lowry base

Q2. Which of the following has a coordination number as a feature?

(a) Coordination entity

(b) Ligand

(c) Central atom

(d) Coordination compound

Q3. Which of the following statements about coordination compounds' bonding is incorrect?

(a) Crystal Field Theory

(b) VSEPR Theory

(c) Valence Bond Theory

(d) Molecular Orbital Theory

Q4. More than one sort of hybridization can occur in a complex with geometry.

(a) tetrahedral

(b) octahedral

(c) trigonal bipyamidal

(d) square planar

Q5. Determine which of the following statements about VBT is inaccurate.

(a) It does not explain the colour of coordination compounds
(b) It can distinguish between strong and weak ligands
(c) It does not explain the kinetic stabilities of coordination compounds
(d) It is unreliable in the prediction of geometries of 4-coordinate complexes

Q6. Which of the following determines the position of ligands in a mononuclear coordination entity's formula?

(a) Atomicity of the ligand
(b) Charge on the ligand
(c) The first letter in the name of the ligand
(d) Denticity of the ligand

Q7. Which of the following statements about a charged coordinating entity is correct?

(a) The sign of the charge is written after the number
(b) The charge of the complex ion is written in parenthesis while naming the entity
(c) The charge is indicated as a subscript outside the square bracket on the right
(d) The charge on the complex ion is depicted along with the counter ion

Q8. Determine the proper name for $K_2[PdCl_4]$.

(a) Potassium tetrachlorinepalladium(II)
(b) Potassium tetrachloridopalladate(II)Potassium
(c) Potassium tetrachloridopalladium(II)
(d) tetrachlorinepalladate(II)

Q9. Which substance is used to determine the hardness of water using a simple titration?

(a) Mg(EDTA) (b) Fe(EDTA)
(c) Na_2(EDTA) (d) Co(EDTA)

Q10. The core atom of which of the following biologically significant coordination molecules is magnesium?

(a) Vitamin B_{12}
(b) Haemoglobin
(c) Chlorophyll
(d) Carboxypeptidase-A

Q11. According to Werner's theory of coordination compounds,

(a) Primary valency is ionisable
(b) Secondary valency is ionisable
(c) Primary and secondary valencies are ionisable
(d) Neither primary nor secondary valency is ionisable

Q12. A coordination compound $CrCl_3.4H_2O$ gives a white precipitate of AgCl with $AgNO_3$. The molar conductance of the compound corresponds to two ions. The structural formula of the compound is

(a) $[Cr(H_2O)_4Cl_3]$ (b) $[Cr(H_2O)_3Cl_3]$ H_2O
(c) $[Cr(H_2O)_4Cl_2]Cl$ (d) $[Cr(H_2O)_4Cl]$ Cl_2

Q13. Identify the statement which is not correct.

(a) Coordination compounds are mainly known for transition metals.
(b) Coordination number and oxidation state of metal are the same.
(c) A ligand donates at least one electron pair to the metal atom to form a bond.
(d) $[Co(NH_3)_4Cl_2]^+$ is a heteroleptic complex.

Q14. The coordination number and the oxidation state of the element E in the complex $[E(en)_2(C_2O_4)]NO_2$ (where (en) is ethylenediamine) are, respectively

(a) 6 and 3 (b) 6 and 2
(c) 4 and 2 (d) 4 and 3

Q15. The charges x and y on the following ions are,

I. $[Co(NH_3)_2Cl_4]X$
II. $[Fe(CN)_6]Y$
(Oxidation state of Co is +3 and Fe is +2 in their respective complexes.)

(a) x = +1, y = -1 (b) x = -1, y = +3
(c) x = -1, y = -4 (d) x = -2, y = -3

Q16. Among the following compounds which are both paramagnetic and coloured?

(a) $K_2Cr_2O_7$
(b) $[Co(SO)_4]$
(c) $(NH_4)_2[TiCl_6]$
(d) $K_3[Cu(CN)_4]$

Q17. $CuSO_4.5H_2O$ is blue in colour while $CuSO_4$ is colourless due to

(a) Presence of strong field ligand in CuSO4.5H2O.
(b) Absence of water (ligand), d – d transitions are not possible in CuSO4.
(c) Anhydrous CuSO4 undergoes d – d transitions due to crystal field splitting.
(d) Colour is lost due to the loss of unpaired electrons.

Q18. A coordination complex $[MX_2L_2]$, has a CN=4 and two unidentate ligands X and L. When the two L ligands are arranged opposite to each other in their geometry, it is called _______ isomer.

(a) Cis (b) Trans
(c) Fac (d) Mer

Q19. Which of the following compounds does not have a coordination isomer?

(a) $[Ag(NH_3)_2][Ag(CN)_2]$
(b) $[Cr(NH_3)_6][Co(CN)_6]$
(c) $[Zn(NH_3)_4][PtCl_4]$
(d) $[Cu(NH_3)_4][FeCl_4]$

Q20. (a)Which of the following compounds has a meridional isomer?

(a) $[Fe(NO)_5Br]^+$
(b) $[Al(CO)_3(NO_2)_3]$
(c) $[K(NH)_3)_4(NO)_2]^+$
(d) $[Fe(H_2O)_2(CO)_2(NO)_2]^{3+}$

Q21. The coordination complex chloridotris (triphenylphosphine) rhodium(I) is used in the hydrogenation of alkenes. It is also known as _________ catalyst.
(a) Ziegler-Natta (b) Grubb
(c) Pearlman (d) Wilkinson

Q22. The complex ion $[Ag(S_2O_3)_2]^{3-}$ is associated with which field?
(a) Photography (b) Electroplating
(c) Medicine (d) Water treatment

Q23. How are the stepwise stability constants (K) related to the overall stability constant (β)?
(a) $\beta_n = K_1 + K_2 + ... + K_n$
(b) $\beta_n = K_1 \text{ x } K_2 \text{ x } ... \text{ x } K_n$
(c) $\beta_n = \log K_1 + \log K_2 + ... + \log K_n$
(d) $\beta_n = 1/(K_1 + K_2 + ... + K_n)$

Q24. If β is the formation constant, then the instability constant =
(a) log(β) (b) 1 – β
(c) β – 1 (d) (1/β)

Q25. Two complexes A and B have dissociation constants $1.0 \text{ x } 10^{-12}$ and $4.7 \text{ x } 10^{-14}$ respectively. Which complex will be more stable?
(a) A
(b) B
(c) Both are equally stable
(d) Neither A nor B

Q26. What is the geometry of pentacarbonyliron(0)?
(a) Square planar
(b) Tetrahedral
(c) Trigonal bipyramidal
(d) Octahedral

Q27. How is the M-C pi bond formed?
(a) Donation of electron pair of half-filled metal d orbital to empty antibonding pi orbital of CO
(b) Donation of electron pair of half-filled metal d orbital to empty bonding pi orbital of CO
(c) Donation of electron pair of filled metal d orbital to empty bonding pi orbital of CO
(d) Donation of electron pair of filled metal d orbital to empty antibonding pi orbital of CO

Q28. The donation of lone pair of electrons of CO carbon into the vacant orbital of metal atom results in _____ bond.
(a) Synergic (b) Sigma
(c) Pi (d) Back

Q29. Which type of isomerism exhibits compounds with same chemical formula and bonds but different spatial arrangement?
(a) Solvate isomerism
(b) Optical isomerism
(c) Linkage isomerism
(d) Structural isomerism

Q30. Which of the following is not a subdivision of structural isomerism?
(a) Ionisation isomerism
(b) Geometrical isomerism
(c) Linkage isomerism
(d) Coordination isomerism

ASSERTION AND REASONING

Q1. **Assertion:** Linkage isomerism arises in coordination compounds containing ambidentate ligand. Reason: Ambidentate ligand has two different donor atoms.
(a) Assertion and reason both are correct and the reason is the correct explanation of assertion.
(b) Both assertion and reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is correct but Reason is incorrect
(d) Assertion is a wrong statement but the reason is a correct statement
(e) Both Assertion and Reason are incorrect

Q2. **Assertion:** Complexes of MX_6, MX_5L type (X and L are unidentate) do not show geometrical isomerism.
Reason: Geometrical isomerism is not shown by complexes of coordination number 6.
(a) Assertion and reason both are correct and the reason is the correct explanation of assertion.
(b) Both assertion and reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is correct but Reason is incorrect
(d) Assertion is a wrong statement but the reason is a correct statement
(e) Both Assertion and Reason are incorrect

Q3. **Assertion:** $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
Reason: Because it has d^2sp^3 type hybridization.
(a) Assertion and reason both are correct and the reason is the correct explanation of assertion.
(b) Both assertion and reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is correct but Reason is incorrect
(d) Assertion is a wrong statement but the reason is a correct statement
(e) Both Assertion and Reason are incorrect

Q4. **Assertion:** Potassium ferrocyanide and potassium ferricyanite both are diamagnetic.
Reason: Both have unpaired electrons.
(a) Assertion and reason both are correct and the reason is the correct explanation of assertion.
(b) Both assertion and reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is correct but Reason is incorrect
(d) Assertion is a wrong statement but the reason is a correct statement
(e) Both Assertion and Reason are incorrect

Q5. **Assertion:** The $[Ni(en)_3]Cl_2$ (en = ethylene diamine) has lower stability than $[Ni(NH_3)_6]Cl_2$

Reason: In $[Ni(en)_3]Cl_2$ the geometry of Ni is trigonal bipyramidal.

(a) Assertion and reason both are correct and the reason is the correct explanation of assertion.
(b) Both assertion and reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is correct but Reason is incorrect
(d) Assertion is a wrong statement but the reason is a correct statement
(e) Both Assertion and Reason are incorrect

TRUE/FALSE

Q1. There are four formula units in fluorite and antifluorite structure.

(a) True (b) False

Q2. A cubic crystal possess all 23 elements of symmetry.

(a) True (b) False

Q3. $K_2[CuCl_4]$ is an anionic complex.

(a) True (b) False

Q4. Oxidation number of Ni in $[Ni(CO)_4]$ is zero.

(a) True (b) False

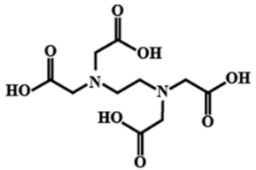
SOLUTIONS

S1. **(d)** $[Zn(OH)_4]^{2-}$ A coordination entity consists of a central metal atom bonded to a fixed number of atoms/molecules. Here, K^+ is the counter ion, OH is the molecule bonded to the central atom which is Zn.

S2. **(a)** Lewis acid A Lewis acid is a species that can accept an electron pair. All cations are Lewis acids. Since the central atom of a coordination complex is metal and always accept electrons, it is a Lewis acid.

S3. **(a)** Ni^{2+} The ions/molecules bound to the central atom/ion is called a ligand. Ni^{2+} is a metal ion, and according to Werner the secondary valences can be satisfied only by neutral molecules or negative ions. Cl^-, H_2O and NH_3 are all possible ligands.

S4. **(c)** Six donor atoms are present in EDTA.
EDTA is ethylene diamine tetraactic acid also called 2,2',2'',2'''-(ethane-1,2 diylbis (azanetriyl)) tetraacetic acid. It has 2 N and 4 O donor atoms. Thus, EDTA is a hexadentate ligand.



2,2′,2″,2‴–(ethane-1,2-diylbis(azanetriyl)tetraacetic acid
EDTA

S5. **(a)** N This is nitrito-N, formed by ambidentate ligand NO_2^- ion when it bonds through its N atom to the central metal ion. The other form is nitrito-O, which is formed when NO_2^- coordinates through the O1 atom.

S6. **(a)** Central atom Coordination number is also known as the secondary valence of a central metal ion in a complex and is defined as the number of donor atoms it is directly bonded to. Hence, coordination number is a quantity associated with the metal ion.

S7. **(c)** $[Fe(CN)_6]^{4-}$ The coordination sphere refers to the square bracket within which the central atom/ion and the groups attached to it are enclosed. This is a non-ionisable group as compared to the entity outside the bracket, which is ionisable and is known as the counter ion.

S8. **(d)** In $[CO(NH_3)_6]^{2+}$the oxidation state of CO is 2. So the correct IUPAC name is hexaamminecobalt(II) ion.

S9. **(c)** Strong field ligands, such as CN^-, usually produce low spin complexes and large crystal field splitting.

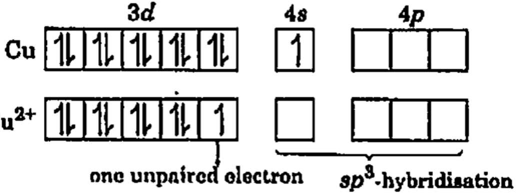
The spectrochemical series is an empirically derived list of ligands ordered by the size of the splitting Δ that they produce. It can be seen that the low-field ligands are all π-donors (such as I^-), the high field ligands are π-acceptors (such as CN^- and CO) and ligands such as H_2O and NH3, which are neither are in the middle.

S10. **(b)**

S11. **(b)** When the *d* orbital of central metal atom is split in an octahedral ligand field, it will produce t_{2g} and e_g orbitals. The t_{2g} orbitals are lower in energy while the e_g orbitals are higher in energy. The t_{2g} orbitals are made up of dxy, dxz and dyz orbitals while e_g orbitals are made up of $dx^2{-}y^2$ and dz^2. Therefore, the orbitals which are raised least in energy are dxy, dxz and dyz orbitals.

S12. **(a)** To find the number of unpaired electrons: The electron configuration of iron(II) is $[Ar]3d^6$. When a strong-field ligand is in the complex, the pairing of electrons will take place, and the electron configuration of the valence subshell becomes $t^6{}_{2g}e^0{}_g$ $t_{2g}{}^6$ $e_g{}^0$. Thus, there will be no unpaired electrons.

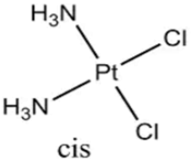
S13. **(b)** $[Cu(OH_2)_6]^{2+}$ The coordination number of metal ion Cu^{2+} is 6. Cu (Atomic no. 29) $3d^{10}\ 4s^1$



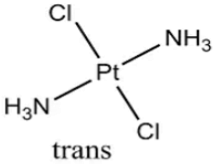
So, complex is paramagnetic hybridisation is sp and the complex is octahedral. It is an outer-orbital complex

S14. **(b)**

S15. **(a)** Square planar-$[Pt(NH_3)_2Cl_2]$ can exhibit geometrical isomerism (cis trans isomerism).
Tetrahedral- $[Zn(NH_3)_2Cl_2]$, octahedral-$[Co(NH_3)_5Cl]^{+2}$ and linear-$[Cu(CN)_2]^{-1}$ do not exhibit geometrical isomerism.



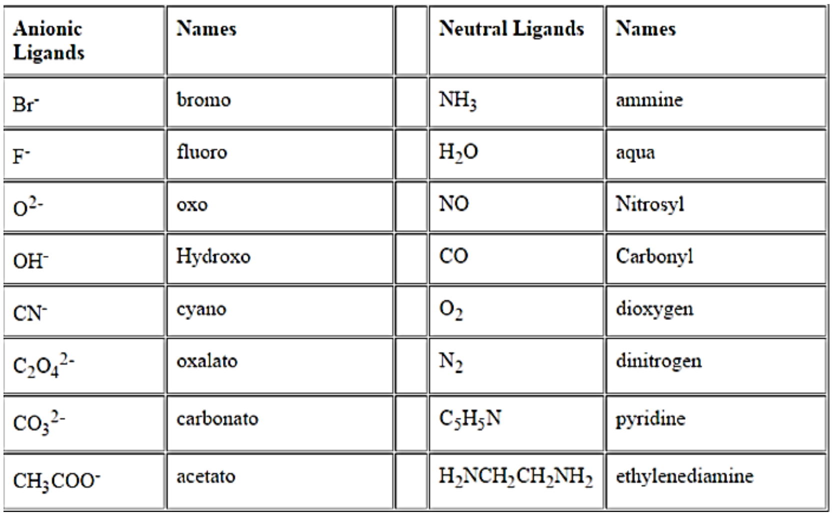
cis



trans

S16. **(c)** The IUPAC name of the compound $[Mn(CN)_5]^{2-}$ is Pentacyanomanganate(III)ion as the oxidation number of manganese is +3.

S17. **(b)** CN^-, it is cyano.



Anionic Ligands	Names		Neutral Ligands	Names
Br^-	bromo		NH_3	ammine
F^-	fluoro		H_2O	aqua
O^{2-}	oxo		NO	Nitrosyl
OH^-	Hydroxo		CO	Carbonyl
CN^-	cyano		O_2	dioxygen
$C_2O_4^{2-}$	oxalato		N_2	dinitrogen
CO_3^{2-}	carbonato		C_5H_5N	pyridine
CH_3COO^-	acetato		$H_2NCH_2CH_2NH_2$	ethylenediamine

S18. **(d)** Within a ligand, the atom that is directly bonded to the metal atom/ion is called the donor atom. A coordinate covalent bond is a covalent bond in which one atom (i.e., the donor atom) supplies both electrons. This type of bonding is different from a normal covalent bond in which each atom supplies one electron.

S19. **(d)** The initial coordination sphere in coordination chemistry refers to the collection of molecules and ions (ligands) that are immediately connected to the centre metal atom. The second coordination sphere is made up of molecules and ions that are attached to the first coordination sphere in various ways.

For example, in the complex $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ is the coordination sphere and K+ is the counter ion.

S20. **(d)** Lewis acids have the tendency to accept electron pairs from lewis bases.
Ligands are lewis bases because they have one or more additional pairs of electrons to donate to a metal ion.
Here, the oxidation state of Pt is 2+ and it will accept electrons from CN^-, thus it is a lewis acid.

S21. **(c)** The formula of potassium dicyano–bis–(oxalato) nickelate(II) is $K_4[Ni(CN)_2(ox)_2]$.
Nickelate (II) implies anion forms the complex part with Ni as the central atom and in +2 oxidation state.
bis-oxalato implies there are 2 oxalato ligands.

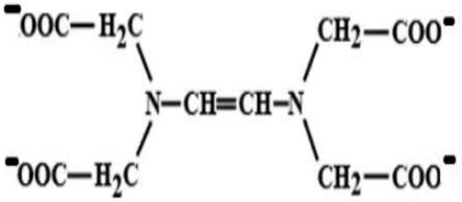
S22. **(a)** The correct IUPAC name is Triammine trinitro-N-cobalt(III). In this case, the alphabetical order of the groups is followed i.e. ammine group followed by the nitro- group. Co is in +3 oxidation state.

S23. **(b)** The coordination number of cobalt in the complex $[Co(en)_2Br_2]Cl_2$ is 6.

S24. **(c)** The name of the counter ion is potassium.
The complex ion has aluminium(III), so it will be called as aluminate(III). Note that we can determine the oxidation number of aluminium by the charge balance. Also, it contains 3 $[C_2O_4]^{-2}$ groups, so it will be called as trisoxalato. Combining all, we get that the name of the negative ion is trisoxalatoaluminate(III). So, the name of the compound becomes potassium trisoxalatoaluminate(III).

S25. **(b)** Aluminium is a p–blocks element and does not from complex compounds.

S26. **(b)** Ethylene diammine tetra acetate ion [EDTA] is the example of the hexadentate ligand.



S27. **(c)** No metal carbon bond is present in trimethoxy titanium chloride.

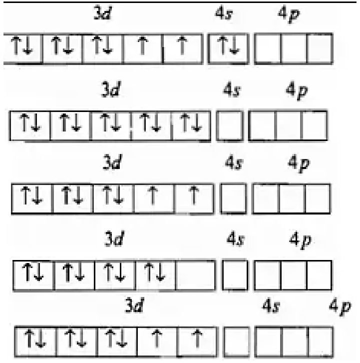
S28. **(d)**

S29. **(c)** $[Ni(CO)_4]$
The oxidation number of Ni is 0.
Atomic number = 28
Ni = $[Ar]3d^84s^2$
sp^3-Hybridization (tetrahedral)
There are no unpaired electrons, so the complex is diamagnetic.
Spin magnetic moment = zero
$[Ni(CN)_4]^{2-}$
The oxidation number of Ni is +2.
Atomic number = 28
Ni = $[Ar]3d^84s^2$
Ni2+ = $[Ar]3d^8$

dsp^2-Hybridization (square planar)
There are no unpaired electrons so, the complex is diamagnetic.
Spin magnetic moment = zero
$[NiCl_4]^{2-}$
The oxidation number of Ni is +2 .
Atomic number = 28
Ni = $[Ar]3d^84s^2$
Ni^{2+} = $[Ar]3d^8$
Chlorido is a weak field ligand, no pairing
sp3-Hybridization (tetrahedral)
There are two unpaired electrons, so the complex is paramagnetic.
Spin magnetic moment

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

$$= \sqrt{2(2+2)}\ \text{BM} = \sqrt{8}\ \text{BM}$$



S30. **(c)** $[Co(en)_2(NO_2)Cl]Br$ and $[Co(en)_2(ONO)Cl]Br$ are linkage isomers.

S31. **(d)** Dien (Diethylenetriamine) has following structure
$H_2N^{\cdot\cdot}–CH_2–CH_2–N^{\cdot\cdot}H–CH_2–CH_2–N^{\cdot\cdot}H_2$.
The number of donor atoms is three hence it is a tridentate ligand. Each nitrogen atom is a donor atom.
$EDTA^{4-}$ is a hexadentate ligand. $(COO)_2^{2-}$ is a bidentate ligand. NO^{2-} is a monodentate ligand.

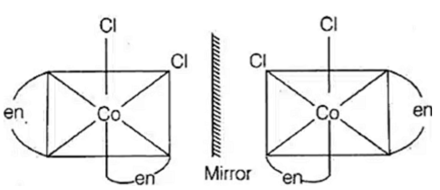
S32. **(b)** Ni is in zero oxidation state in $Ni(CO)_4$ so the electronic configuration of Ni is $3d^8\,4s^2$. As CO is a strong ligand, it pushes all the electrons in the 3d orbital, therefore the hybridisation of $Ni(CO)_4$ is sp^3 and it has tetrahedral geometry.

S33. **(a)**

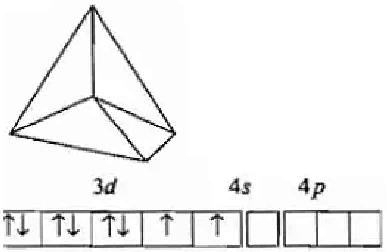
S34. **(a)** $[Fe(NO_2)_3Cl_3]$ and $[Fe(O–NO)_3Cl_3]$ contain an ambidentate ligand. Hence, the compound exhibits linkage isomerism.

S35. **(b)**

cis- $[Co(en)_2Cl_2]$

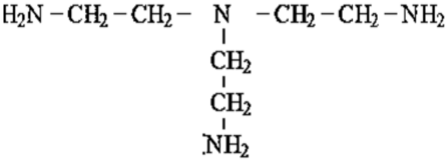


S36. **(d)** $[Ni(Cl)_4]^{2-}$
The oxidation state of Ni is +2.
The atomic number of Nickel is 28.
Ni = $[Ar]3d^84s^2$
Ni2+=$[Ar]3d^8$



S37. **(a)** The molecules or ions that satisfy the secondary valency are called ligands and they can be either negatively charged or neutral.

S38. **(c)**



$H_2\ddot{N}-CH_2-CH_2-\underset{\underset{\underset{\underset{\ddot{N}H_2}{|}}{CH_2}}{|}}{\overset{\cdot\cdot}{N}}-CH_2-CH_2-\ddot{N}H_2$ (N–CH_2–CH_2–NH_2 branch)

Number of donor atoms in $N(CH_2CH_2NH_2)_3$ is four hence it is a tetradentate ligand. Each nitrogen atom is a donor atom.

S39. **(a)** Ambidentate ligand has two or more donor atoms, but during complex formation, only one donor atom is attached to central metal. SCN– ion has donor atoms N and S. It links to metal as either M–SCN or M–NCS. NO_2^- group has donor atoms N and O. It links to metal as either M–ONO or M–NO_2 .

S40. **(c)** ONO is an anionic ligand (ONO^-).

S41. **(d)** SCN^- is a monodendate ligand. Hence, it does not chelate.

S42. **(a)** $[Cr[NH_3]_5(NCS)][ZnCl_4]$
$[ZnCl_4]^{2-}$ ⇒ Tetrachlorozincate
$[NH_3]_5$ = Pentaammine
(NCS) = Isothiocyanato
IUPAC name is:
Pentaammine isothiocyanato chromium (III) tetrachloro zincate.

S43. **(b)** The complex $[Co(NH_3)_5Br]SO_4$ dissociates to give $[Co(NH_3)_5Br]^{2+}$ and SO_4^{2-} ions. SO_4^{2-} ions reacts with barium chloride($BaCl_2$) to give white precipitate ($BaSO_4$).
$[Co(NH_3)_5Br]SO_4 \rightleftharpoons [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$
$SO_4^{2-} + BaCl_2 \rightarrow BaSO_4\downarrow + 2Cl^-$
SO_4^{2-} ions will give a precipitate with barium chloride only if the sulphate ion is not present in the coordination sphere. Only then it will be able to dissociate as an anion in aqueous solution.

S44. **(b)** Different complex ions have the same molecular formula. Ligands are interchanged between the complex cation and complex anion. These type of complexes are called coordination isomers.
In $[Pt(NH_3)_4][CuCl_4]$, ammonia ligands are attached to Pt metal and chloride ligands are attached to Cu metal.
In $[Cu(NH_3)_4][PtCl_4]$, ammonia ligands are attached to Cu metal and chloride ligands are attached to Pt metal.

S45. **(c)**

S46. **(b)**

S47. **(d)** $[Pt(NH_3)Cl_2Br]Cl \rightleftharpoons [Pt(NH_3)Cl_2Br]^+ + Cl^-$
The number of precipitable halide ions in the sample $[Pt(NH_3)Cl_2Br]Cl$ will be 1 since only 1 free chloride or halide ion is formed when dissolved in the solvent.

S48. **(c)** Moles of AgCl precipitated per mole of the compound is equal to the primary valences of the metal.
So, $PdCl_2.4NH_3$ with 2 moles of AgCl precipitated means secondary valence of Pd is 4⇒$[Pd(NH_3)_4]Cl_2$

S49. **(b)** 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.

S50. **(b)** Ethylenediamine $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ is s bidentate ligand can form a five membered ring with metal ions,via lone pairs of electrons of the two nitrogen atoms, it is chelating ligand.

ASSERTION AND REASONING

S1. **(c)** It is correct statement that NF_3 is a weaker ligand than $N(CH_3)_3$, the reason is that fluorine is highly electronegative therefore, it withdraws electrons from the nitrogen atom. Hence, the lone pair of nitrogen atom cannot be ligated. While $N(CH_3)_3$ is a strong ligand because CH_3 has an electron releasing group.

S2. **(b)** Both assertion and reason are true but reason is not the correct explanation of assertion.
$[Fe(CN)_6]^{3-}$ has EAN equal to 35 and thus possesses unpaired electron to show paramagnetic nature while $[Fe(CN)_6]^{4-}$ possesses no unpaired electron and thus shows diamagnetic nature.

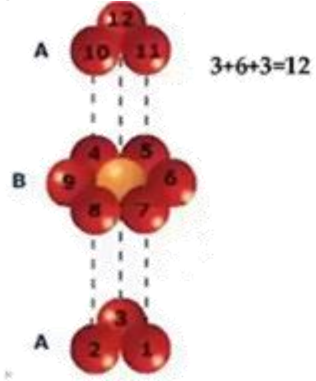
S3. **(a)** Both assertion and reason are true and reason is the correct explanation of assertion.
$[Sc(H_2O)_6]^{3+}$ has no unpaired electron in its d subshell and thus d–d transition is not possible whereas $[Ti(H_2O)_6]^{3+}$ has one unpaired electron in its d subshell which gives rise to d–d transition to impart colour.

S4. **(a)** Toxic metal ions are removed by chelating ligands. When a solution of the chelating ligand is added to a solution containing toxic metals ligands chelates the metal ions by the formation of a stable complex.

S5. **(c)** Tetrahedral complexes do not show geometrical isomerism because the relative position of the atoms with respect to each other will be the same.

TRUE/FALSE

S1. **(a)** The coordination number of an atom in hexagonal close-packed structure is 12.
It can be seen easily from the image that the coordination number of a metal crystallizing in a hexagonal close-packed structure is 12.



S2. **(a)** In face centred structure, the coordination number of an atom is 12.
Each atom is surrounded by 4 atoms in its own plane, 4 above the plane and 4 below the plane.

S3. **(a)**

QUESTIONS FOR PRACTICE

S1. **(c)** A Lewis acid is a species that has the ability to receive an electron pair. Lewis acids are all cations. It is a Lewis acid because the core atom of a coordination complex is metal and always accepts electrons.

S2. **(c)** The coordination number of a central metal ion in a complex, also known as the secondary valency, is defined as the number of donor atoms it is directly bound to. As a result, the coordination number is a quantity related to the metal ion.

S3. **(b)** The VSEPR Theory uses electron pairs in atoms to explain the structure of particular molecules. The theories VBT, CFT, LFT, and MOT explain the nature of bonding in coordination compounds.

S4. **(b)** Depending on whether the outer or inner d orbitals are engaged in hybridisation, complexes with octahedral geometry can have either sp^3d^2 or d^2sp^3 hybridisation.

S5. **(b)** One of VBT's flaws is that it can't tell the difference between weak and powerful ligands. Other s have their own set of drawbacks.

S6. **(c)** The alphabetical order of the ligands in the formula of mononuclear coordination entities, including shortened ligands, is used. It is independent of the ligand's atomicity, denticity, or charge.

S7. **(a)** The charge of a coordination entity is written outside the square brackets on the right side as a superscript with the number before the sign of charge, without the existence of the counter ion.

S8. **(b)** Because Cl is an anionic ligand, it has the suffix -o, therefore chlorido. Furthermore, because the complex ion is anionic, the metal must end in -ate, so palladate.

S9. **(c)** With EDTA, the ions Ca^{2+} and Mg^{2+} form stable complexes, and the difference in the stability constants of the Ca and Mg complexes aids in the assessment of water hardness.

S10. **(c)** Chlorophyll is a coordination molecule of magnesium that is found in plants and is important for photosynthesis.

S11. **(a)** According to Werner's theory of coordination compounds primary valency is ionizable and non-directional which is equivalent to the oxidation state of the central atom and it is satisfied by the negative charge. For example, primary valencies of Co and Pt in $CoCl_3$ and $PtCl_4$ respectively.

S12. **(c)** Here in this question, it is given that the molar conductance of the compound corresponds to two ions and it gives white precipitate so, it is sure that one ion will be Cl^- because it gives white precipitate on reaction with Ag. Hence the structure of the reaction will be,
$[CrH_2O)_4Cl_2Cl \rightarrow [CrH_2O)_4Cl_2^+ + Cl^-$

S13. **(b)** B is an incorrect statement because it is not necessary that the oxidation number and coordination number of metal are the same. Because coordination number refers to the number of ligands that are bound to the central atom by coordination bond whereas oxidation state refers to a process where electrons are either gained or lost.

S14. **(a)** Both the ligands present in the above complex $[E(en)_2(C_2O_4)]NO_2$ are bidentate ligands and hence coordination number of the above complex is 6 which means it is octahedral in nature. Therefore, using the formula oxidation state of E will be 3.

S15. **(c)** In $[Co(NH_3)_2Cl_4]X$ it is given that oxidation state of Co is +3. Therefore, $x=3+2\times0+4\times-1=-1$. This implies that the charge of x is -1. Similarly, the oxidation state of Fe is given as +2, therefore, the value of y for the compound $[Fe(CN)_6]Y$ will be $y=2+6\times-1=-4$.

S16. **(b)** In $[Co(SO)_4]$ Co has +2 oxidation state and there are unpaired electrons present in 3d- orbital, therefore, it shows paramagnetic nature. And due to the partially filled d-orbital, it is coloured.

S17. **(b)** Due to the absence of ligand in anhydrous $CuSO_4$ crystal field splitting does not take place and hence it is colourless. Whereas in $CuSO_4.5H_2O$, water act as a ligand and hence crystal field splitting takes place and results in d – d transition. Therefore, it is coloured.

S18. **(a)** There are four CN, hence square planar will be the shape of complex and in tetrahedral shape isomerism cannot be observed.

S19. **(a)** Coordination symmetry occurs when there is a ligand exchange between cation and ionic complex ions containing different metal ions. In the compound $[Ag(NH_3)_2][Ag(CN)_2]$, both complexes contain the same metal ion Ag^+, and are therefore not a coordination isomer.

S20. **(b)** Fac-mer isomerism is only exhibited in octahedral coordination entities of the type $[MA_3B_3]$ depending on the positions of the similar ligands.

S21. **(d)** Coordination compounds may be used as homogeneous or heterogeneous catalysts for many reactions. Wilkinson catalyst is used as a homogeneous catalyst in hydrogenation of alkenes, whereas Ziegler¬-Natta catalyst is used as a heterogeneous catalyst for the polymerisation of olefins.

S22. **(a)** In black and white photography, the film is fixed by washing with hypo solution which dissolves the undecomposed silver bromide to form $[Ag(S_2O_3)_2]^{3-.}$

S23. **(b)** The overall stability constant is the product of all the stepwise stability constants of each individual reaction.

S24. **(d)** The instability constant is also known as the dissociation constant. It is defined as the reciprocal of the formation or stability constant.

S25. **(b)** The smaller the value of dissociation constant, more stable the complex will be in solution. Since $4.7 \times 10^{-14} < 1.0 \times 10^{-12}$, complex B is more stable.

S26. **(c)** The coordination number of pentacarbonyliron(0) is 5 as CO is a unidentate ligand and hence its geometry id trigonal bipyramidal.

S27. **(d)** The pi bond involves donation of electrons from filled metal d orbitals into empty antibonding pi orbitals of CO. This is also called a back bond.

S28. **(b)** Synergic bonding is the overall effect of the sigma and pi interactions in metal carbonyl bonds. M-C pi bonds are also known as back bonding.

S29. **(b)** Stereoisomers have the same chemical formula and binds but have different spatial arrangement. Optical isomerism is a type of stereoisomerism.

S30. **(b)** Geometrical isomerism is a type of stereoisomerism. Linkage, coordination and ionisation isomers show structural isomerism with different bonds.

ASSERTION AND REASONING

S1. **(a)** Assertion and reason both are correct and the reason is the correct explanation of assertion. Linkage isomerism arises in coordination compounds containing ambidentate ligands because ambidentate ligand has two different donor atoms. e.g. CN, SCN, NCS

S2. **(c)** In MX_6 & MX_5L, their shape is Square Bipyramidal. In a plane, there are four atoms, all are the same, linked to the metal atom, so they don't show geometrical isomerism.
If the ligands present in complexes are Bidentate. Then they will show optical isomerism.

S3. **(e)** The assertion "$[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons is false as it contains only one unpaired electron only d^2sp^3 hybridization, which cannot be regarded as a true reason for its weak paramagnetic behaviour.

S4. **(e)** Potassium ferrocyanide and potassium ferricyanide both are not diamagnetic because both do not have paired electrons. Assertion and reason both are false.

S5. **(e)** $[Ni(en)_3]Cl_2$ is a chelating compound and chelated complexes are more stable than similar complexes involve the breaking of two bonds rather than one. In $[Ni(en)_3]Cl_2$, Ni with d^8 configuration shows octahedral geometry. Six electrons will occupy the t_{2g} orbitals and two electrons will occupy the e_g orbitals.

TRUE/FALSE

S1. **(a)** There are four formula units in fluorite and antifluorite structure.
In fluorite structure, Ca^{2+} ions form fcc unit cell.
F^- ions occupy all the tetrahedral holes.
An fcc arrangement has 4 particles per unit cell. Thus the number of Ca^{2+} ions is 4. The number of tetrahedral voids is equal to the number of particles per unit cell. Hence, the number of F^- ions is also 4.
In antifluorite structure, the arrangement of cations and anions is opposite to the fluorite structure.

S2. **(a)** A cubic crystal possesses a total of 23 elements of symmetry.
Plane of symmetry =(3+6)=9
Axes of symmetry =(3+4+6)=13
Centre of symmetry =1

S3. **(a)** $K_2[CuCl_4]$ dissociates to form the following ions-
$K_2[CuCl_4] \rightarrow 2K^+ + [CuCl_4]^{2-}$
Thus $[CuCl_4]^{2-}$ is formed which is an anionic complex because this ion is negatively charged and it is a complex compound.
Hence, $K_2[CuCl_4]$bis an anionic complex.

S4. **(a)** Let x be the oxidation number of Ni in $[Ni(CO)_4]$. Since the overall charge on the complex is 0, and the individual charge of the ligand is also 0 therefore,
$x+4\times(0)=0$
$\Rightarrow x=0$
Thus, the oxidation number of Ni in $[Ni(CO)_4]$ is 0.
Therefore the statement is correct..